

Electrochemical power generation from geothermal brines

Joost Helsen¹

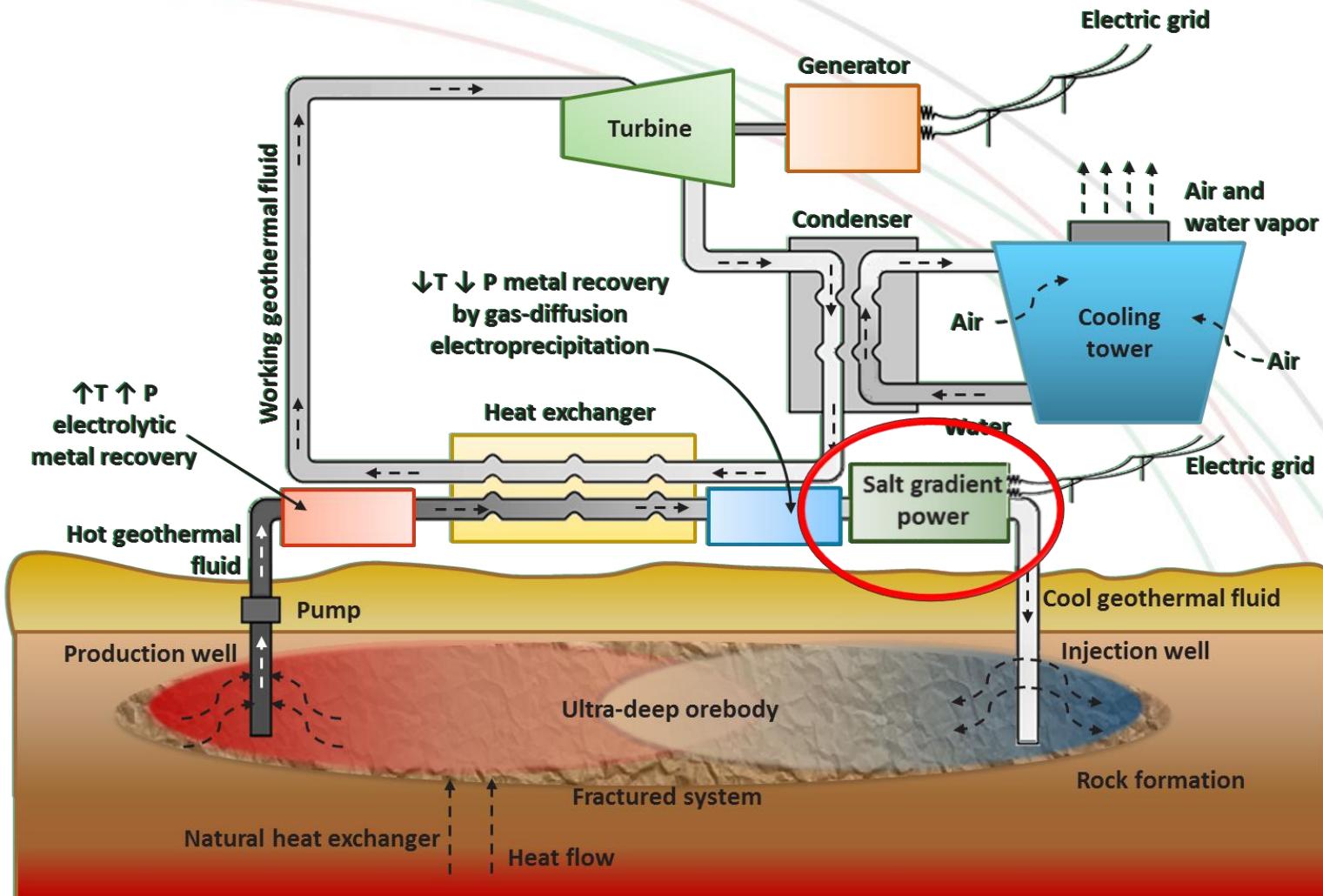
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<http://www.powermag.com>

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research (Belgium)

Energy Recovery from Geothermal Fluids by RED



Early days of salinity gradient energy

R. E. PATTLE

N A T U R E

October 2, 1954

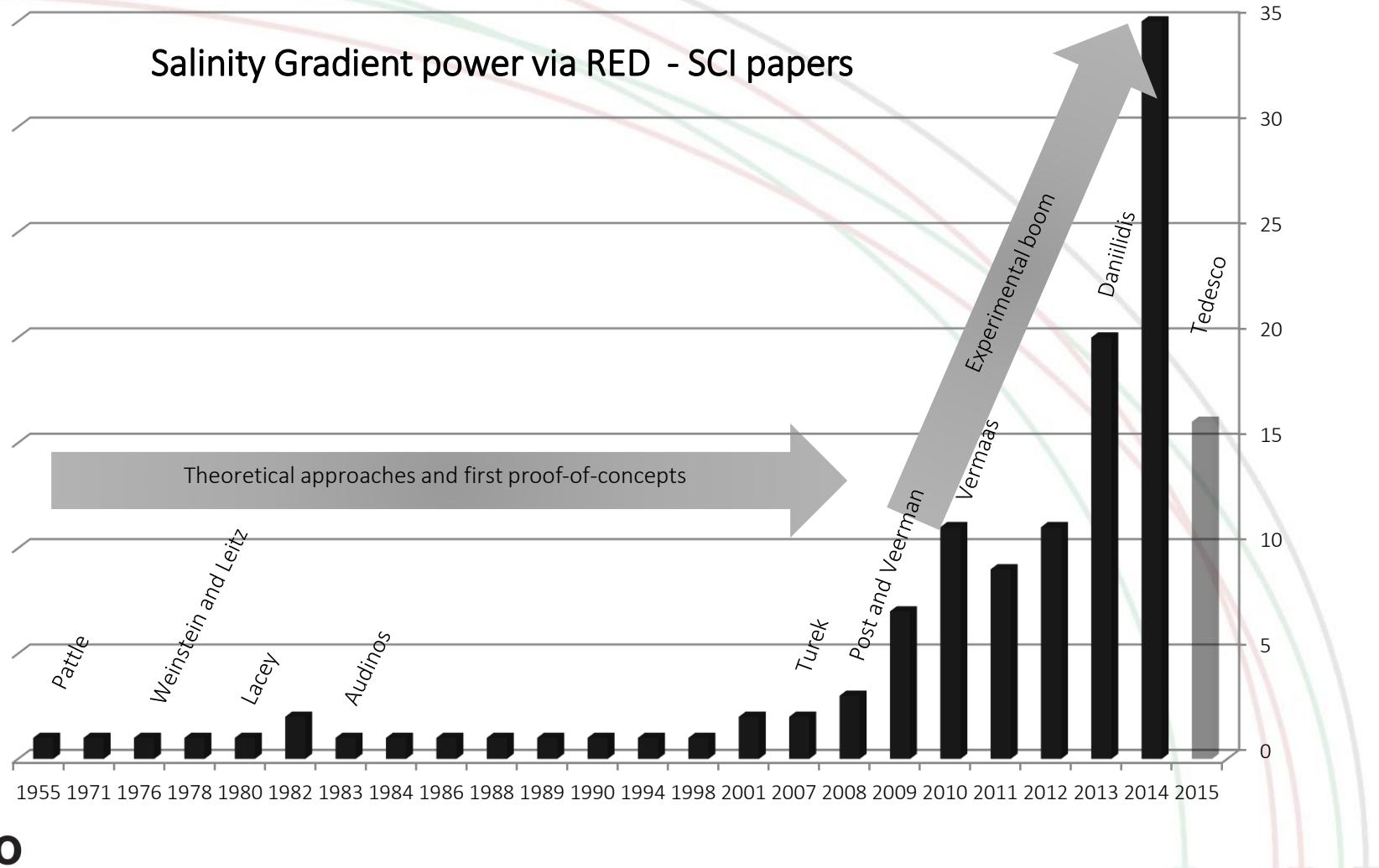
VOL. 174

Production of Electric Power by mixing Fresh and Salt Water in the Hydro-electric Pile

WHEN a volume V of a pure solvent mixes irreversibly with a much larger volume of a solution the osmotic pressure of which is P , the free energy lost is equal to PV . The osmotic pressure of sea-water is about 20 atmospheres¹, so that when a river mixes with the sea, free energy equal to that obtainable from a waterfall 680 ft. high is lost. There thus exists an untapped source of power which has (so far as I know) been unmentioned in the literature.

Until the mid '70s where a practical method of exploiting it using selectively permeable membranes by Loeb was outlined, scientific developments remained virtually non-existent...

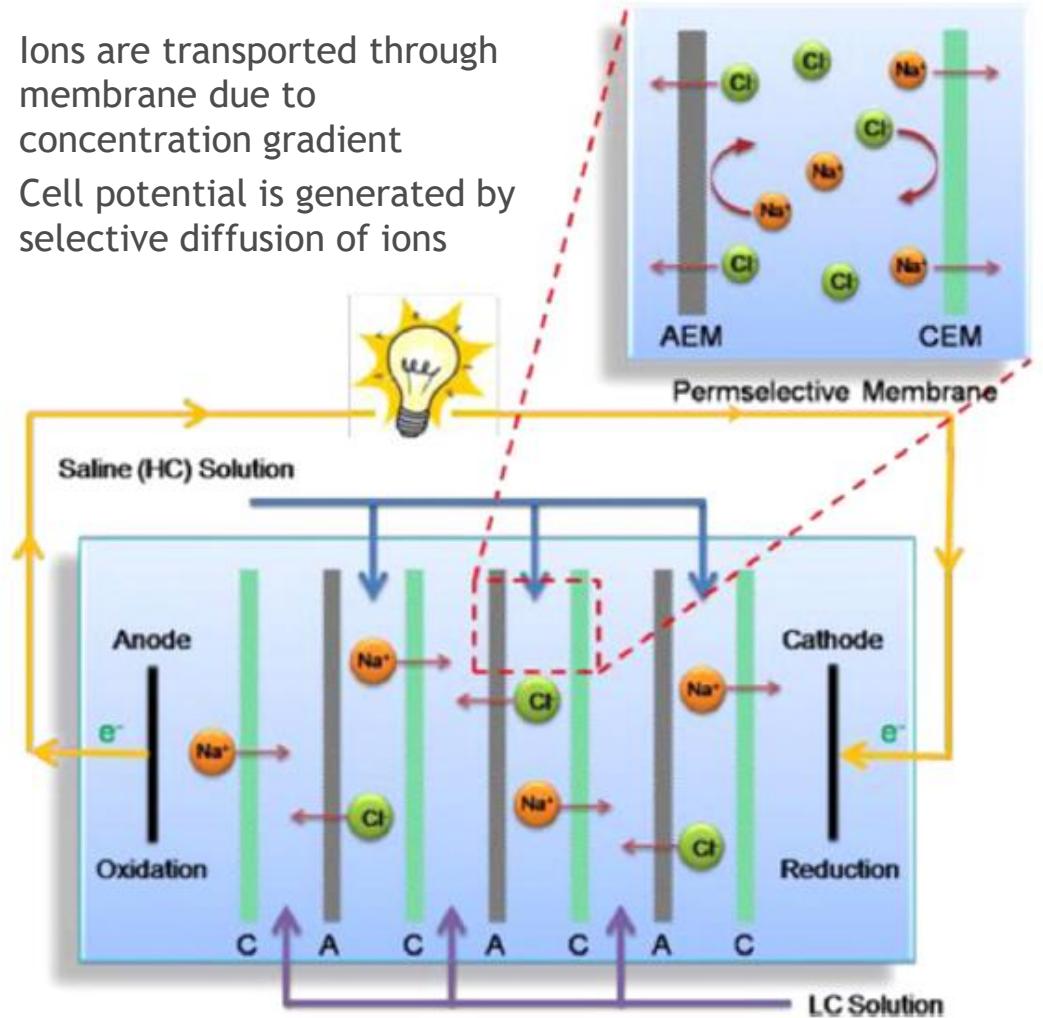
Scientific milestones over the years



Energy Recovery from Geothermal Fluids by RED

RED directly converts the difference in chemical potential to electrical energy

- Ions are transported through membrane due to concentration gradient
- Cell potential is generated by selective diffusion of ions



- Electrode reactions induce electric current
- Applicable at different salinity gradients
 - Seawater – Fresh water (Blue energy)
 - Brine – seawater (REAPower)
 - Brine – brackish water (REAPower)

Energy Recovery from Geothermal Fluids by RED

$1m^3 \text{ seawater} + 1m^3 \text{ brine} = \text{max } 17 \text{ MJ}$

Brine source	Brine concentration	Flow rate	Theoretical potential
Great Salt Lake (Ohio, US)	100-300g/l	125m ³ /s	15,8 TWh/yr
Dead Sea and Red Sea	340g/l	25m ³ /s	2,6 TWh/yr
Garabogazköl Aylagy	350g/l	25m ³ /s	2,7 TWh/yr
RO SWDU	40-100g/l		
Chlor-alkali	210-250g/l		
Salt ponds	250-300g/l		
Geothermal brine	1-300g/l		

Potential = very diffuse and site-specific

EIA, *International energy outlook 2011*. U.S. Department of Energy: Washington D.C., 2011; 301 p.
 Wick, G. L., Power from salinity gradients. *Energy* 1978, 3, (1), 95-100.



Reverse electrodialysis – stack performance

Gross power density

$$P_d = \frac{P}{NA}$$

Net power density

$$P_{d,net} = \frac{P - \Delta p_{HIGH} Q_{HIGH}^{tot} - \Delta p_{LOW} Q_{LOW}^{tot}}{NA}$$

Corrected power density

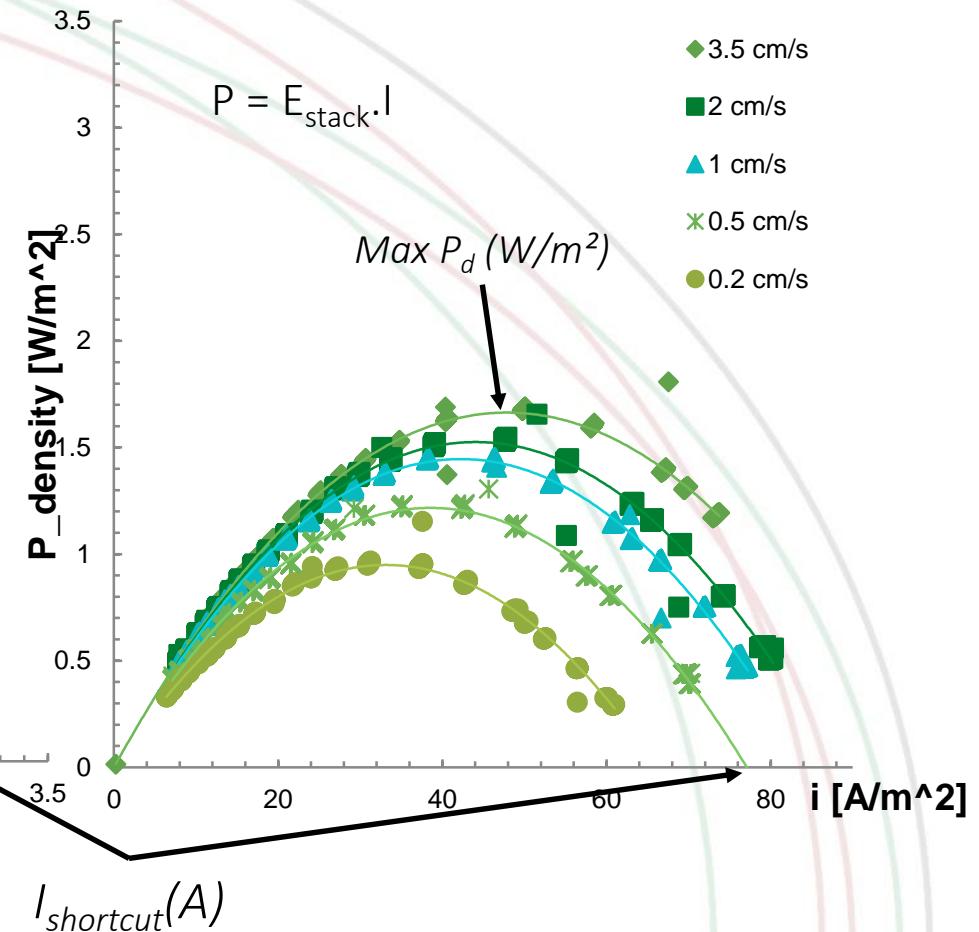
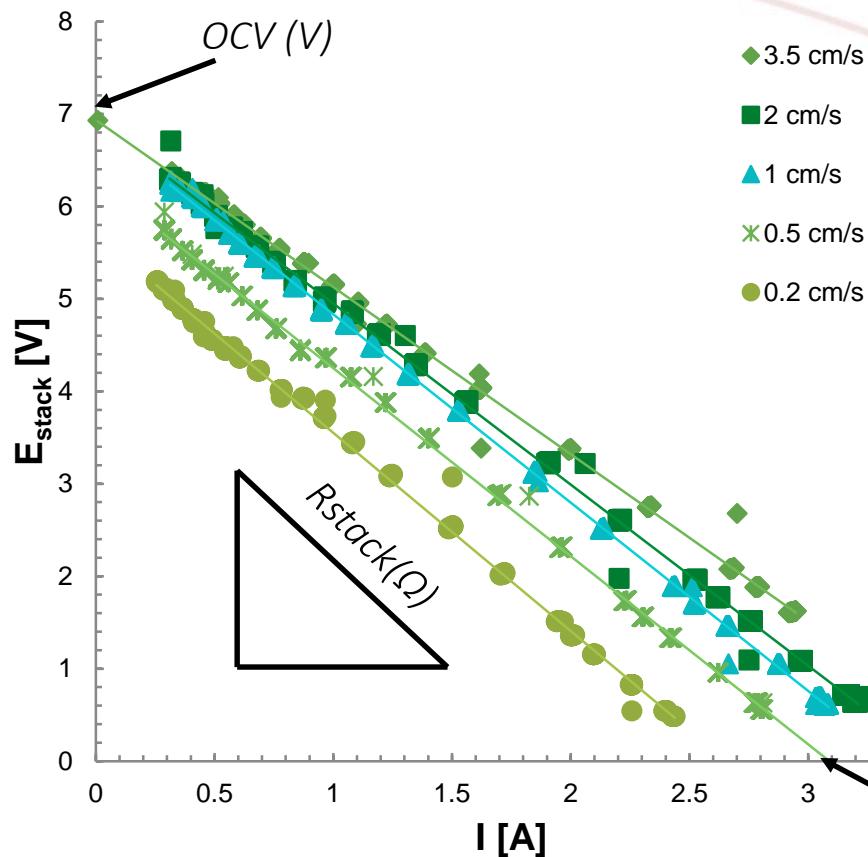
$$P_{d,corr} = \frac{OCV^2}{AR_u (1 + (R_{cells}/R_u))^2}$$

Efficiency

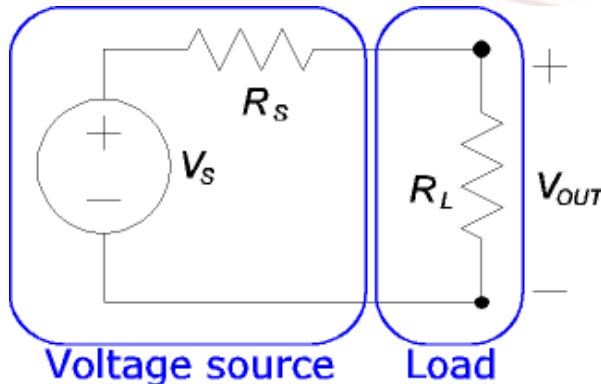
$$\eta = \frac{P}{P_{ideal}}$$

$$P_{ideal} = 2RTQ^{tot} \left(C_{LOW} \ln \frac{\gamma_{LOW} C_{LOW}}{\gamma_{eq} C_{eq}} + C_{HIGH} \ln \frac{\gamma_{HIGH} C_{HIGH}}{\gamma_{eq} C_{eq}} \right)$$

Reverse electrodialysis – stack performance

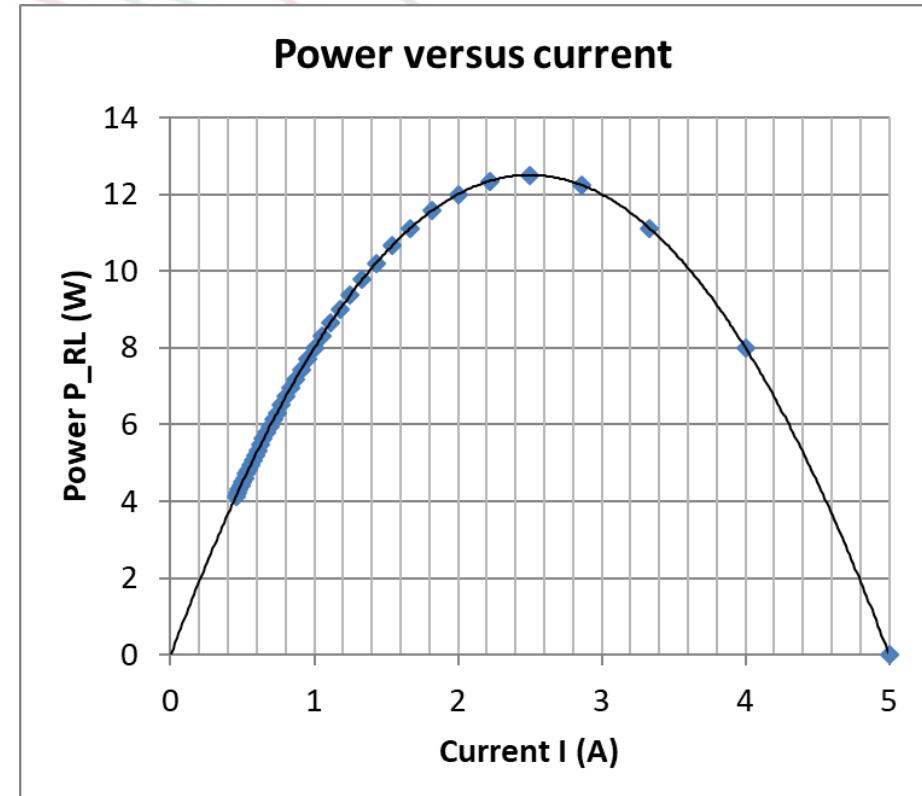


Equivalent electrical circuit – importance of internal resistance

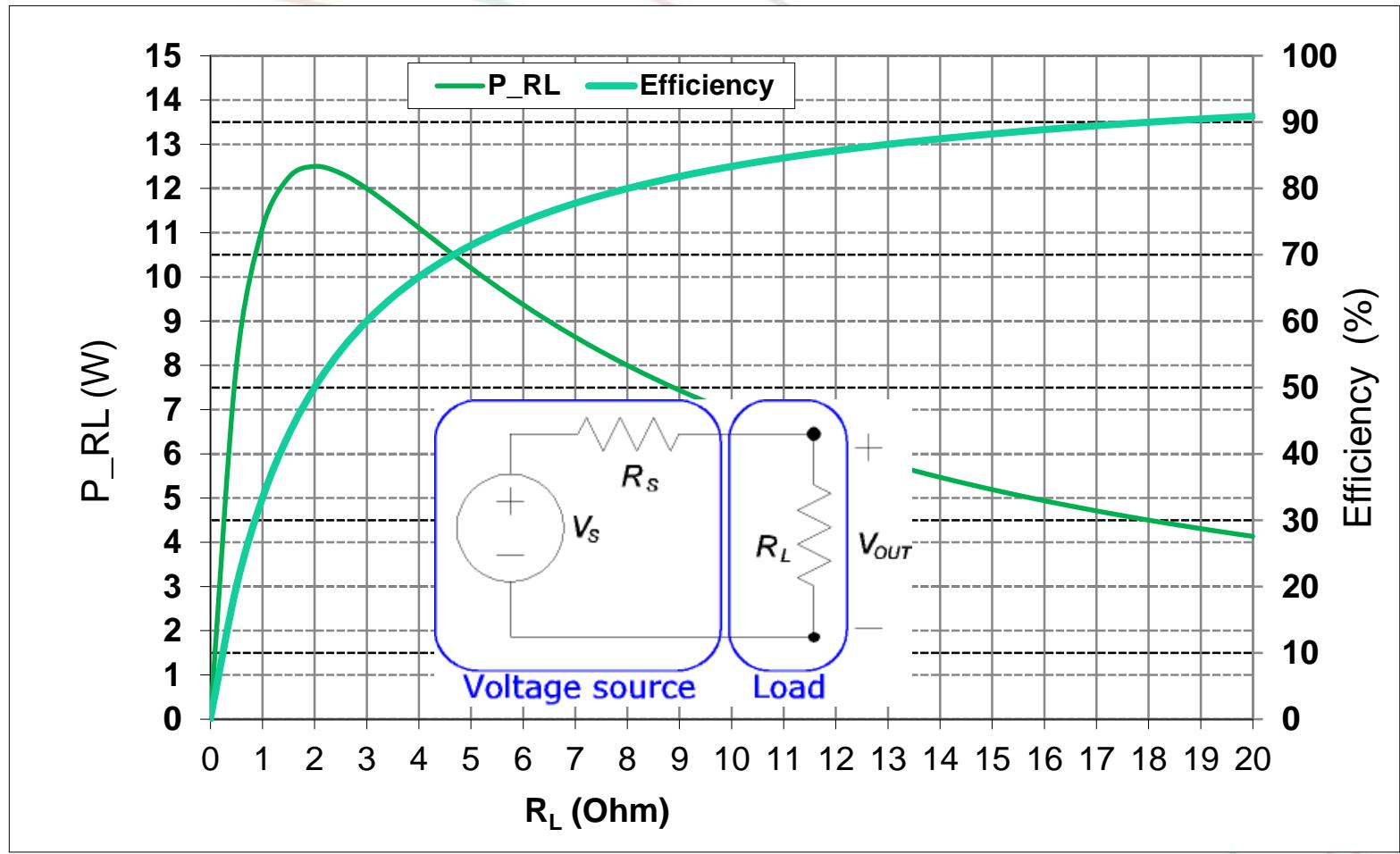


$$V_{OUT} = V_s \cdot \frac{R_L}{R_L + R_s}$$

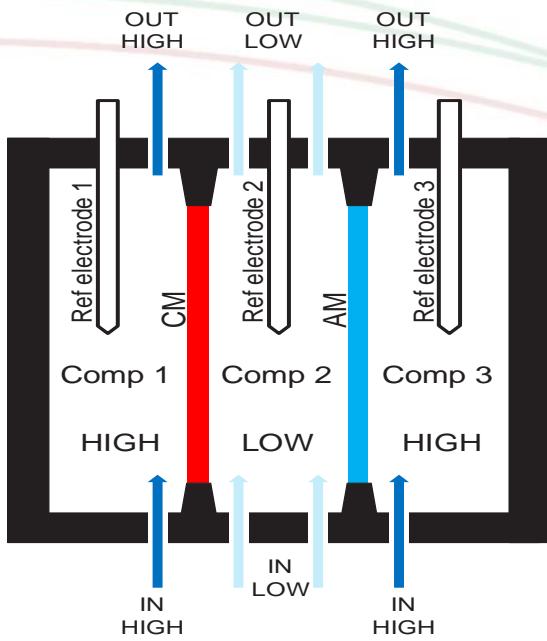
- Membrane
- Spacer channel
- Boundary layers
- Electrical contacts
- ...



Equivalent electrical circuit – importance of internal resistance



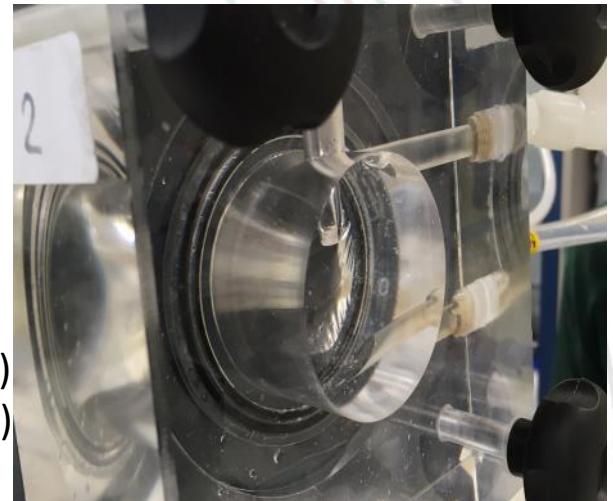
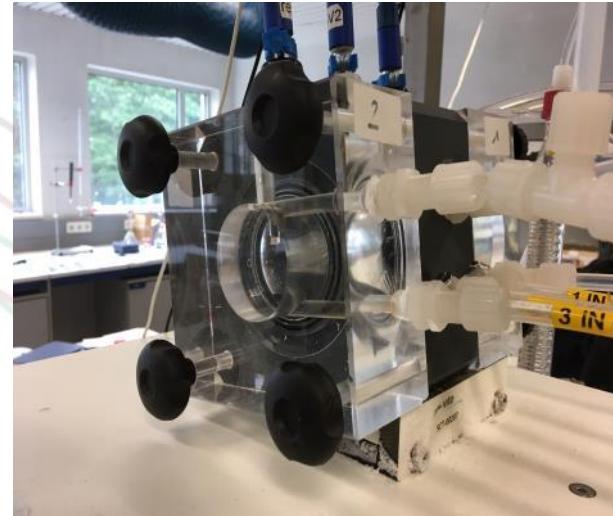
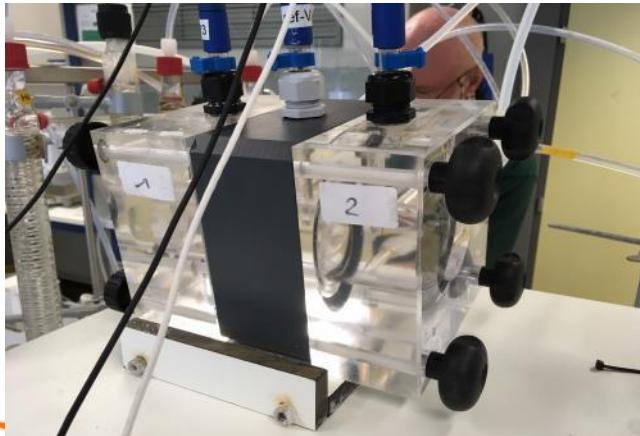
Single cell pair experiments



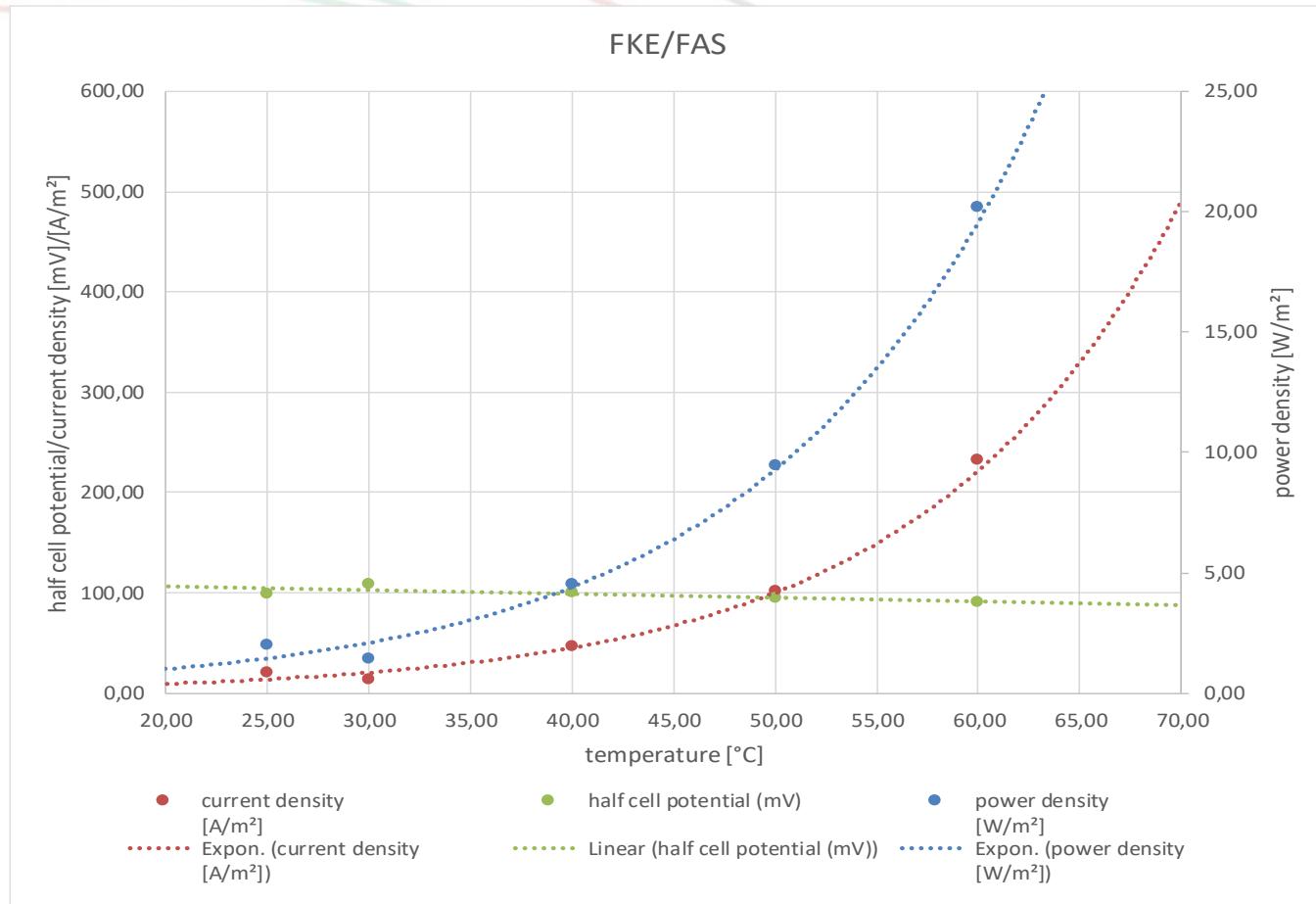
- Three separate compartments
- Outside: HIGH
- Inside: LOW
- Membrane potentials measured as bulk potential
- [HIGH]: constant
- [LOW]: measured continuously
- Temperature controlled

Membranes tested:

- FUJI RP1 (160 μ m)
- Fumasep FAS/FKS (20 μ m)
- Fumasep FAS/FKE (20 μ m)

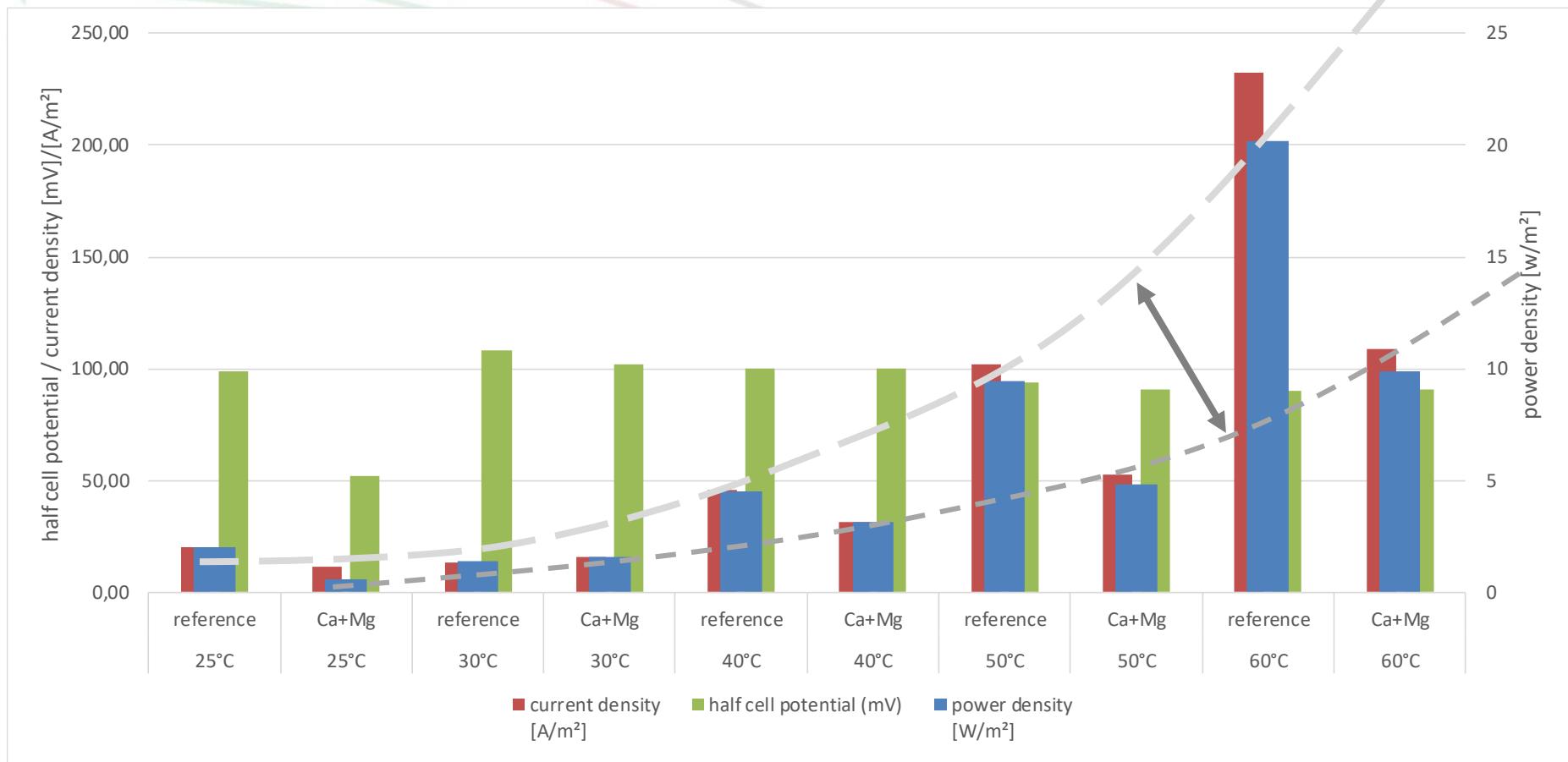


Single cell pair experiments – high T°



FKE/FAS @ increased temperature: power and current density results

Single cell pair experiments – $\text{Ca}^{2+}/\text{Mg}^{2+}$ (20-60°C)



Cell potential

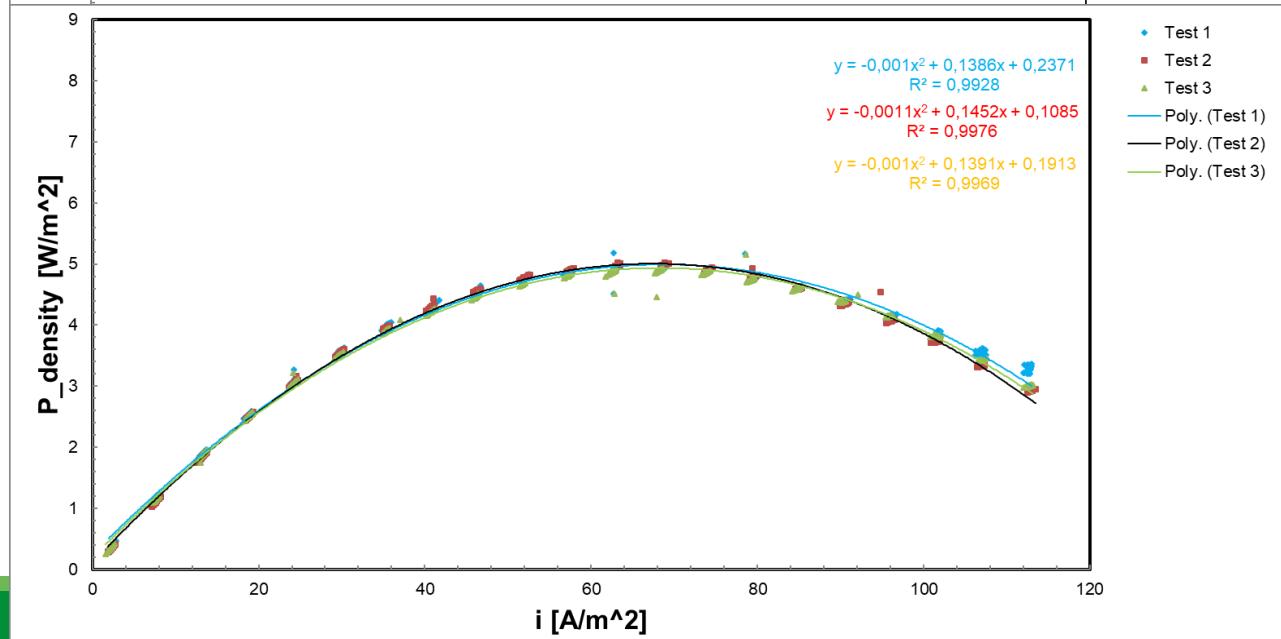
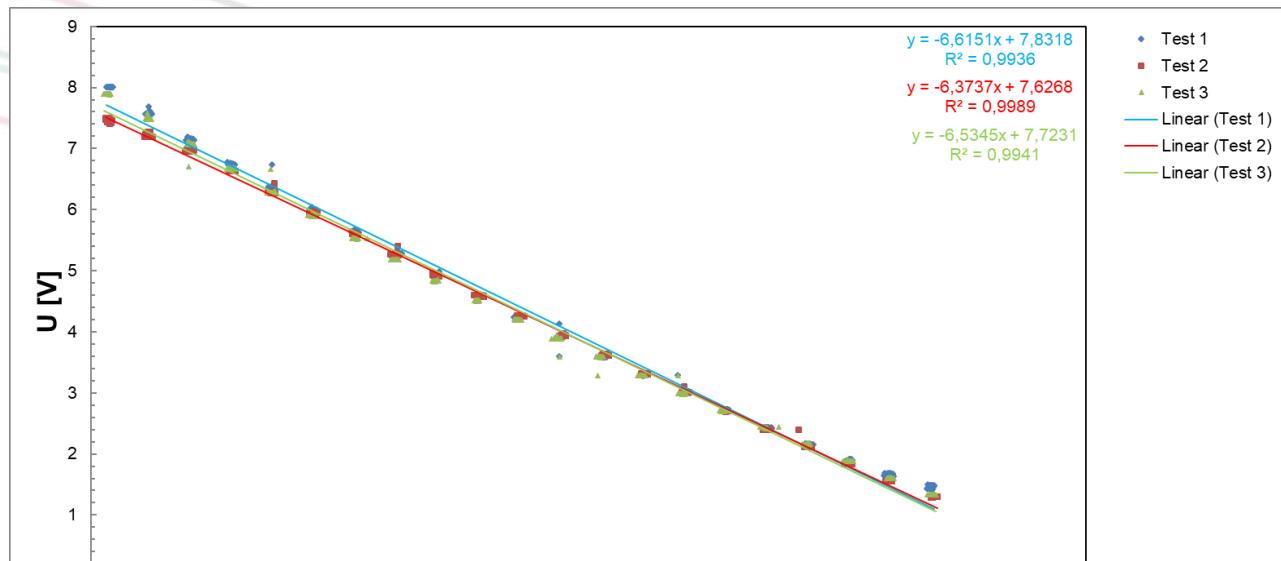
SGP-RE pilot experiments: 50 CP



SGP-RE pilot experiments: 50 CP @25°C

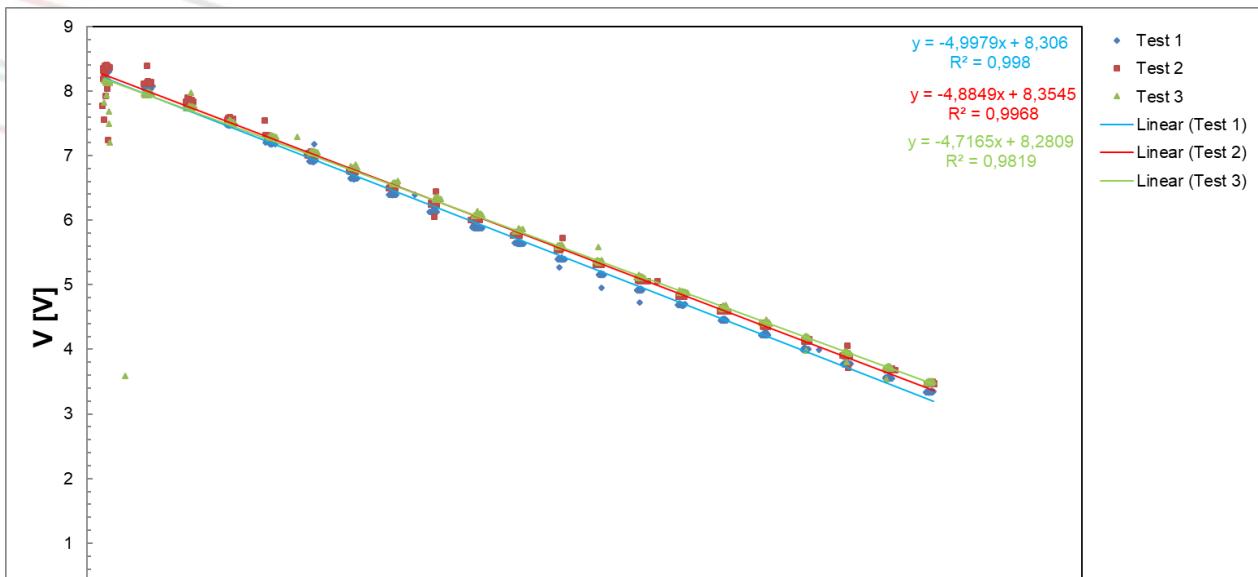
membranes	FAS/FKS
Active cell area	100cm ²
Total cell pair area	0,5m ²
Linear flow velocity	1 cm/s
Temperature	25°C
ERS	0,3M Fe(CN) ₆ ³⁺ 0,3M Fe(CN) ₆ ⁴⁺
HIGH	2M NaCl
LOW	0,01M NaCl

	OCV [V]	R_stack [Ω]	I_shortcut [A]	PMax [A/m ²]	V_PMax [V]	P density_max [W/m ²]
test 1	7,832	6,62	1,18	69,30	6,93	4,80
test 2	7,627	6,37	1,20	72,60	7,26	5,27
test 3	7,723	6,53	1,18	69,55	6,96	4,84
average	7,727	6,51	1,19	70,48	7,05	4,97

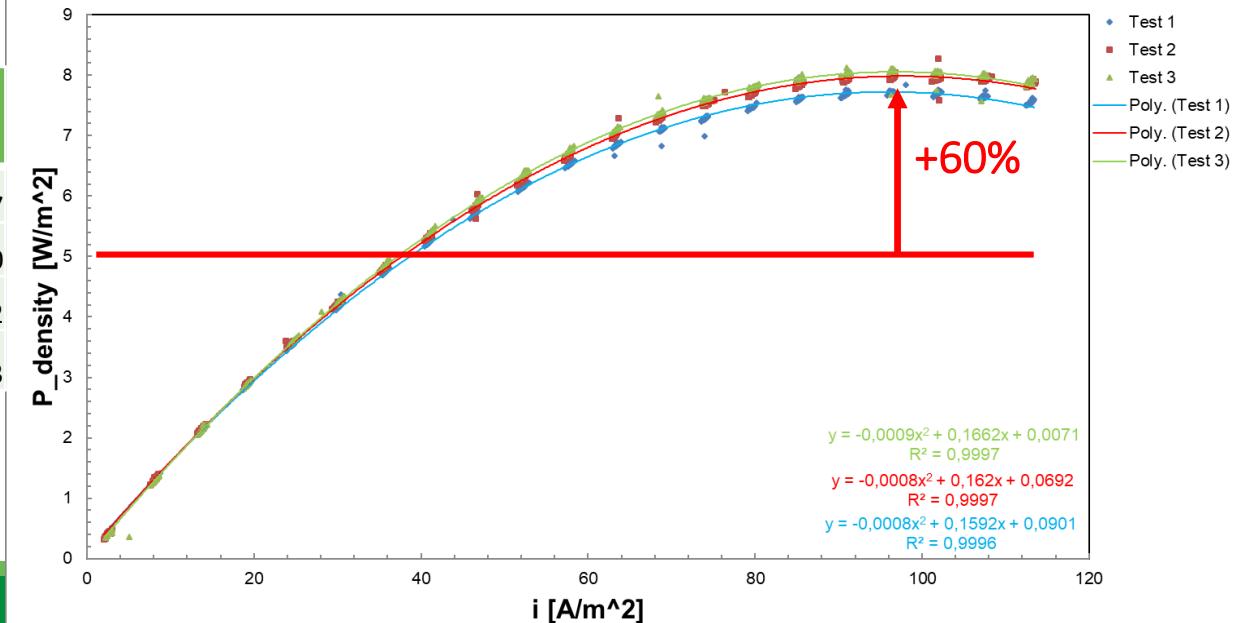


SGP-RE pilot experiments: 50 CP @25°C

membranes	FAS/FKS
Active cell area	100cm ²
Total cell pair area	0,5m ²
Linear flow velocity	1 cm/s
Temperature	50°C
EES	0,3M Fe(CN) ₆ ³⁺ 0,3M Fe(CN) ₆ ⁴⁺
HIGH	2M NaCl
LOW	0,01M NaCl



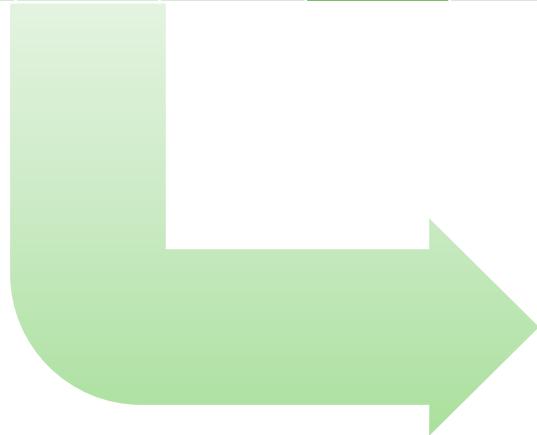
	OCV [V]	R _{stack} [Ω]	I _{shortcut} [A]	I _{PMax} [A/m ²]	V _{PMax} [V]	P _{density_max} [W/m ²]
test 1	11,34	1,27	8,94	92,33	8,31	7,67
test 2	11,41	1,31	8,69	101,25	8,10	8,20
test 3	10,82	1,45	7,49	99,50	7,96	7,92
average	11,19	1,34	8,37	97,69	8,12	7,93



SGP-RE pilot experiments: artificial brine

Composition of an artificial brine, based on data from Belgium and France

	mg	mM	mEq		mg	mM	mEq
HCO ₃	1000	16	16	Ca	10000	250	500
Cl	100000	2817	2817	Fe	500	9	18
SO ₄	2000	21	42	K	3000	77	77
				Mg	1000	42	83
				Na	55000	2391	2391
				Sr	400	5	9
	TOTAL -	2874,962			TOTAL +		3078,417

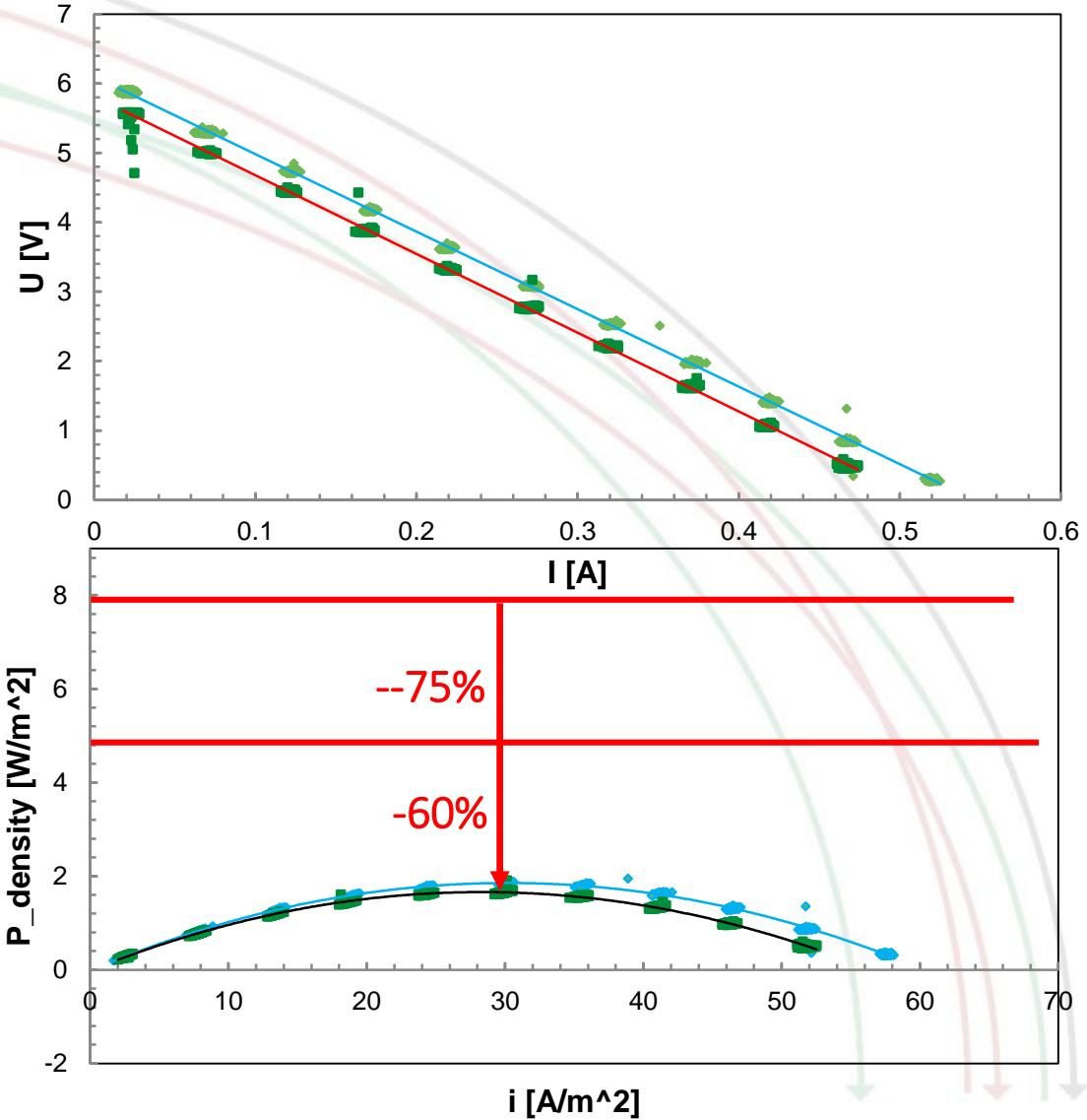


mM	
CaCl ₂	250
FeCl ₂	9
MgCl ₂	42
SrCl ₂	5
NaHCO ₃	16
Na ₂ SO ₄	21
NaCl	2333

SGP-RE pilot experiments: artificial brine

membranes	FAS/FKS
Active cell area	100cm ²
Total cell pair area	0,5m ²
Linear flow velocity	1 cm/s
Temperature	50°C
EBS	0,3M Fe(CN) ₆ ³⁺ 0,3M Fe(CN) ₆ ⁴⁺
HIGH	Artificial brine
LOW	0,01M NaCl

	I _{OCV} [A]	R _{stack} [Ω]	I _{shortcut} [A]	I _{PMax} [A/m ²]	V _{PMax} [V]	P _{density_max} [W/m ²]
test 1	6.100	11.17	0.55	30.70	3.07	1.88
test 2	5.814	11.35	0.51	27.90	2.93	1.64
average	5.957	11.26	0.53	29.30	3.00	1.76



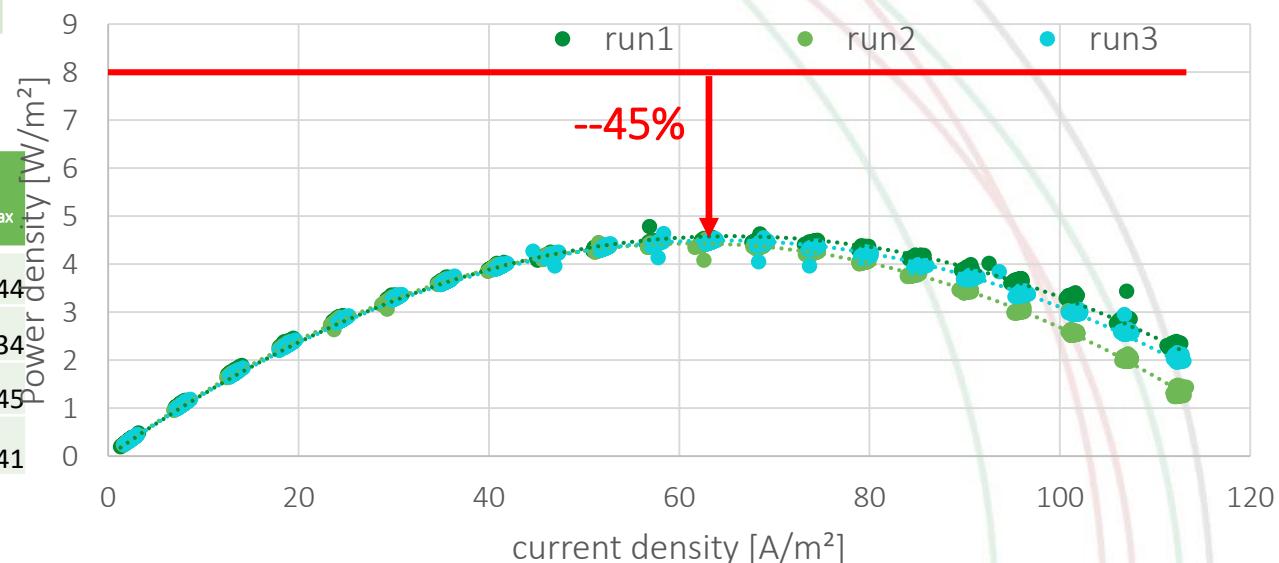
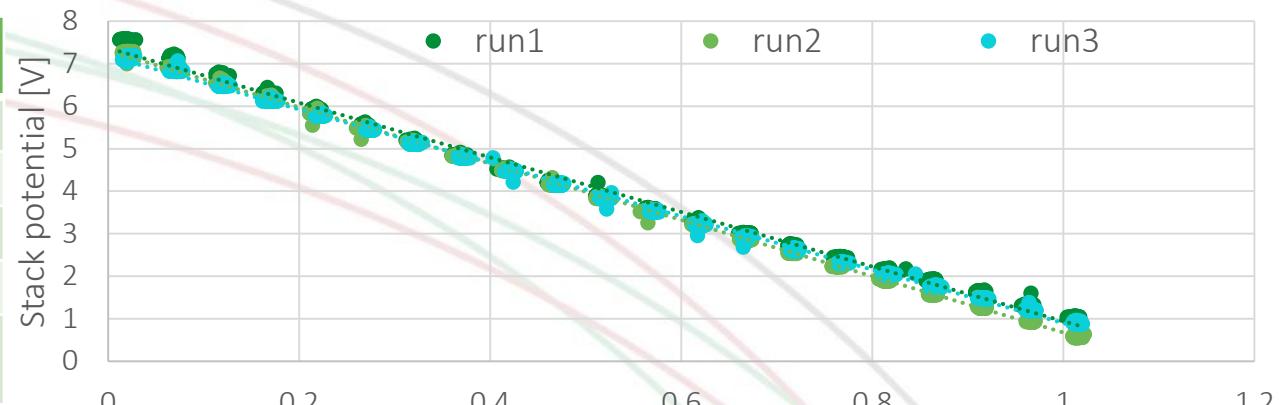
SGP-RE pilot experiments: real brine

TYPE		Deep geothermal Brine
EC (ms/cm)		149,6
pH		3,44
TAM (M getal) (titrimetrisch)	meq/l	< 0.50
TAP (P getal) (titrimetrisch)	meq/l	< 0.50
buffercapaciteit 4.5 (titrimetrisch)	meq/l	< 0.50
carbonaat (titrimetrisch)	meq/l	< 0.50
hydroxide (titrimetrisch)	meq/l	< 0.50
bicarbonaat (titrimetrisch)	meq/l	< 0.50
bromide	mg/l	188
chloride	mg/l	75000
sulfaat	mg/l	130
calcium opgelost	mg/l	8230
kalium opgelost	mg/l	4340
magnesium opgelost	mg/l	112
natrium opgelost	mg/l	34200
ijzer opgelost	µg/l	4250
strontium opgelost	µg/l	459000
Lithium opgelost	µg/l	197000

SGP-RE pilot experiments: real brine

membranes	FAS/FKS
Active cell area	100cm ²
Total cell pair area	0,5m ²
Linear flow velocity	1 cm/s
Temperature	50°C
ERS	0,3M Fe(CN) ₆ ³⁺ 0,3M Fe(CN) ₆ ⁴⁺
HIGH	Real brine
LOW	River water

	OCV [V]	R _{stack} [Ω]	I _{shortcut} [A]	I _{PMax} [A/m ²]	V _{PMax} [V]	P _{density_max} [W/m ²]
test 1	7.302	6.630	1.101	63.5	3.50	4.44
	7.367	6.430	1.146	60.1	3.61	4.34
test 2	7.183	6.288	1.142	63.6	3.50	4.45
average	7.284	6.449	1.130	62.4	3.53	4.41



Steady state SGP-RE model

Black box

Steady state

Assuming pure NaCl solutions

Activities, temperature, viscosity

Post-correction for multivalent ions

Input variables	
$Q_{H, \text{in}}$	$C_{H,\text{in}}$
$Q_{L, \text{in}}$	$C_{L,\text{in}}$
$T_{H, \text{in}}$	$T_{L,\text{in}}$

SGP-Re modelparameters
n
$\delta_{\text{HIGH}} / \delta_{\text{LOW}}$
b
$L_{\text{HIGH}} / L_{\text{LOW}}$
$R_{\text{AEM}} / R_{\text{CEM}}$
$\alpha_{\text{AEM}} / \alpha_{\text{CEM}}$

Output variables
$P [\text{Watt}] / P_d [\text{Watt/m}^2]$
$U_{\text{stack}} = f(I_{\text{stack}})$
$P_d = f(i_{\text{stack}})$
n

Steady state SGP-RE model

M. Tedesco et al. / Desalination and Water Treatment 49 (2012)

$$E_{\text{cell}}(x) = \alpha_{\text{CEM}} \frac{RT}{F} \ln \frac{\gamma_b^{\text{Na}}(x) C_b(x)}{\gamma_s^{\text{Na}}(x) C_s(x)} + \alpha_{\text{AEM}} \frac{RT}{F} \times \ln \frac{\gamma_b^{\text{Cl}}(x) C_b(x)}{\gamma_s^{\text{Cl}}(x) C_s(x)}$$

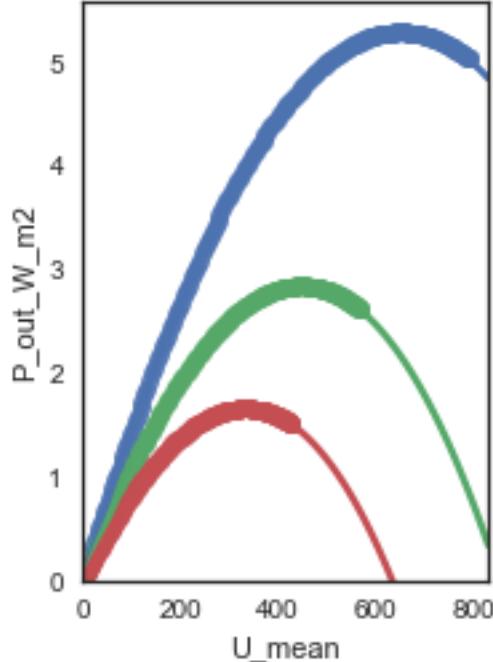
Cell potential (Nernst)

$$\frac{dC_s(x)}{dx} = \frac{b}{Q_s} J_{\text{tot}}(x)$$

Mass balance equations

$$\frac{dC_b(x)}{dx} = - \frac{b}{Q_b} J_{\text{tot}}(x)$$

Steady state SGP-RE model

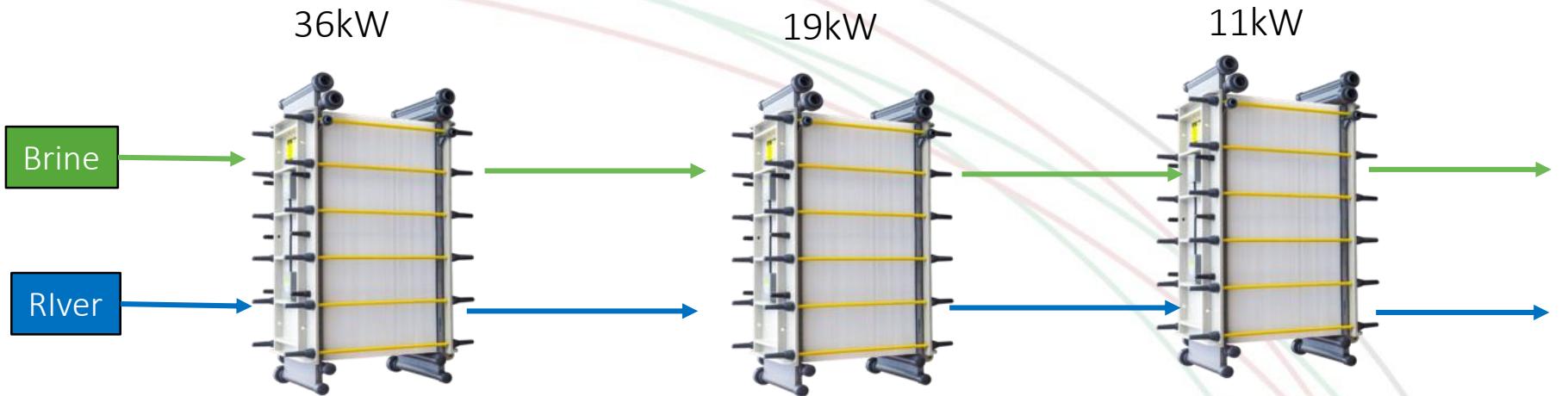


$l = 0.5$ # length of stack [m]
 $b = 1$ # width of stack [m]
 $\text{Raem} = 0.00005$ # AEM membrane resistance [ohm.m^2]
 $\text{Rcem} = 0.00017$ # CEM memrbane resistance [ohm.m^2]
 $tk = 0.995$ # transport number CEM [-]
 $ta = 0.95$ # transport number AEM [-]
 $v_b = 0.01$ # brine flow velocity [m s^{-1}]
 $f = 1/0.8$ # obstruction factor (1/spacer shadow) [-]
 $\eta_P = 0.85$ # pump power efficiency

2000mM Brine concentration
200mM river water concentration
323K (Brine and River)
30% desalination

M. Tedesco et al. / Desalination and Water Treatment 49 (2012)

Steady state SGP-RE model



stack_nr	1
P_W_m2	5.3 W/m ²
P_net	36508 W
OCV_mean	1051 V
S	6944 m ²
C _b _in	2000 mM
C _r _in	200 mM
SE	9%

stack_nr	2
P_W_m2	2.9 W/m ²
P_net	19492 W
OCV_mean	748 V
S	6944 m ²
C _b _in	1819 mM
C _r _in	381 mM
SE	16%

stack_nr	3
P_W_m2	1.7 W/m ²
P_net	11270 W
OCV_mean	566 V
S	6944 m ²
C _b _in	1675 mM
C _r _in	525 mM
SE	22%

Conclusions

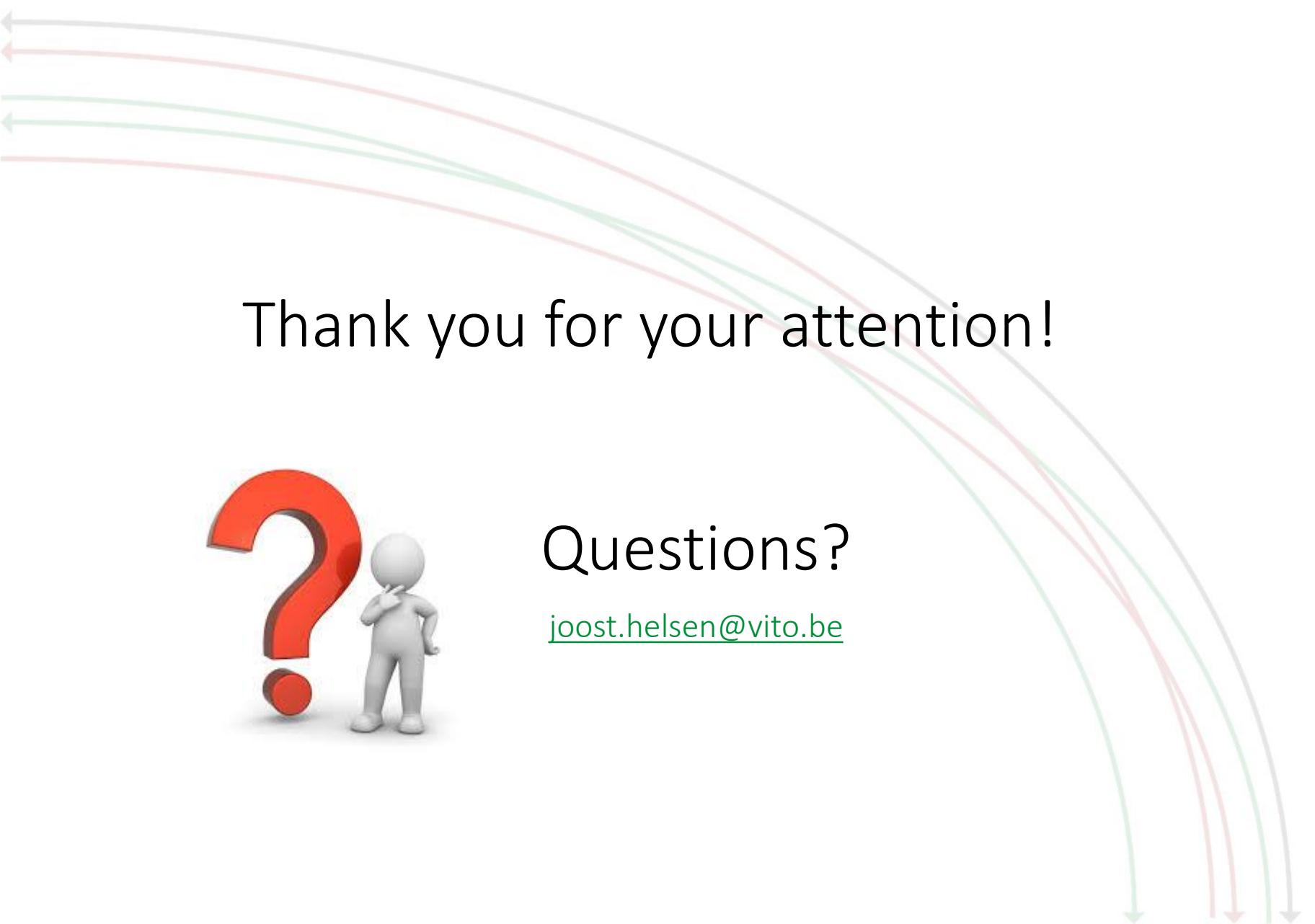
Temperature is on our side

Strong influence of multivalent ions on power density

No pretreatment necessary

Technically feasible with more development needed on stack design and upscaling

Economic feasibility 2030-2050 will depend on specific situation and future market price stack components



Thank you for your attention!



Questions?

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