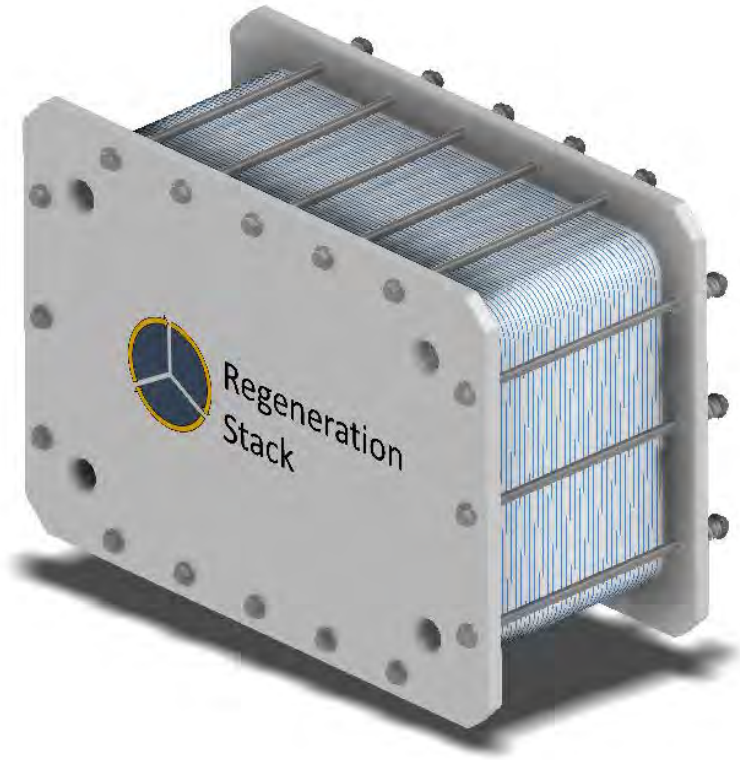
Electrolyte regeneration of vanadium flow batteries



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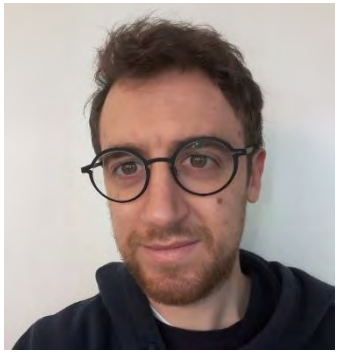

Nicola Poli
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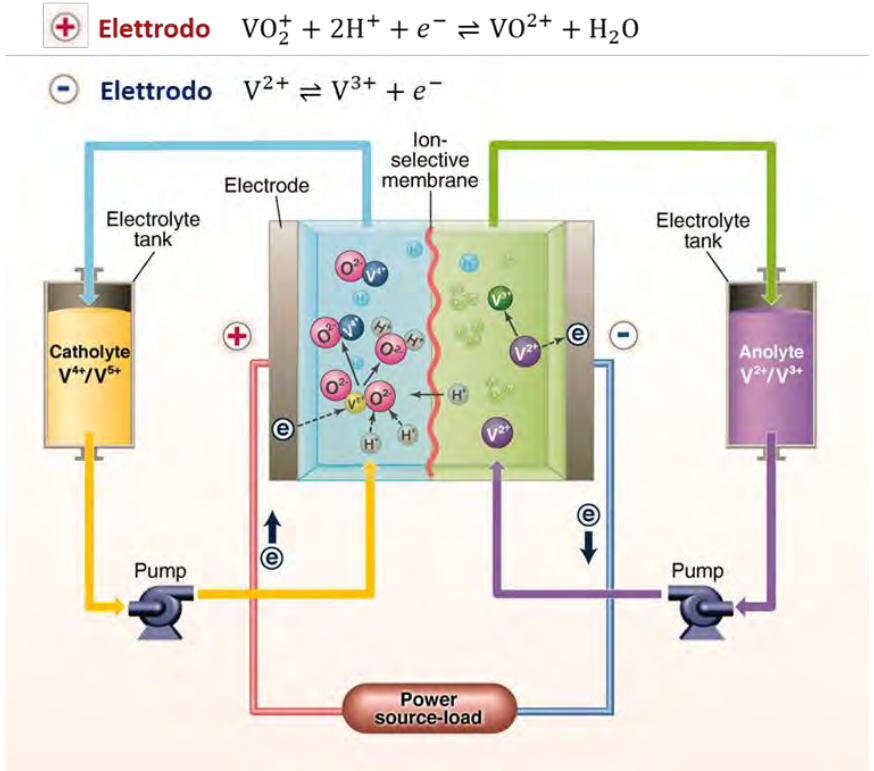
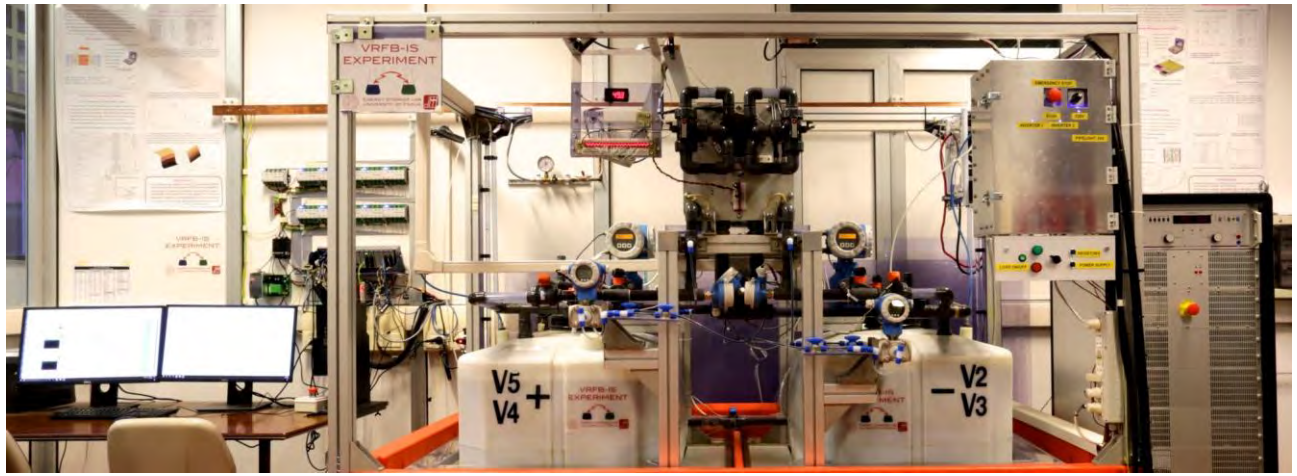
Department of Industrial Engineering
University of Padua
Nicola.poli@unipd.it

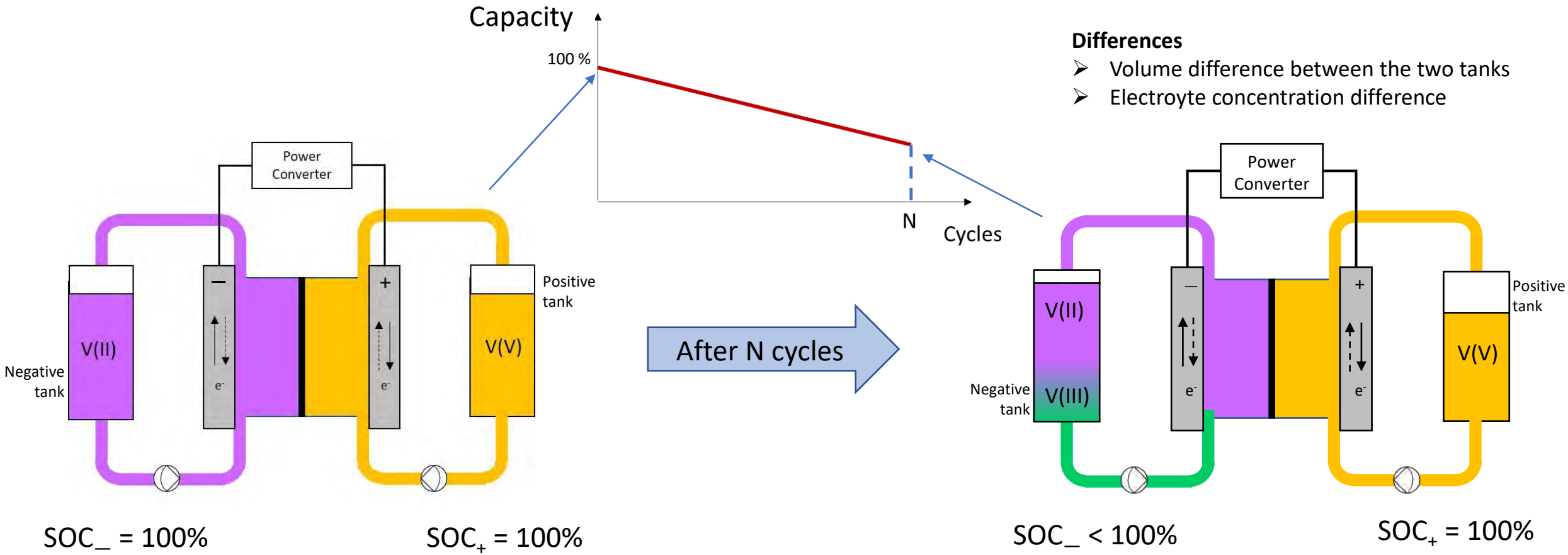
Vanadium flow batteries





9kW/27 kWh VFB

The problem



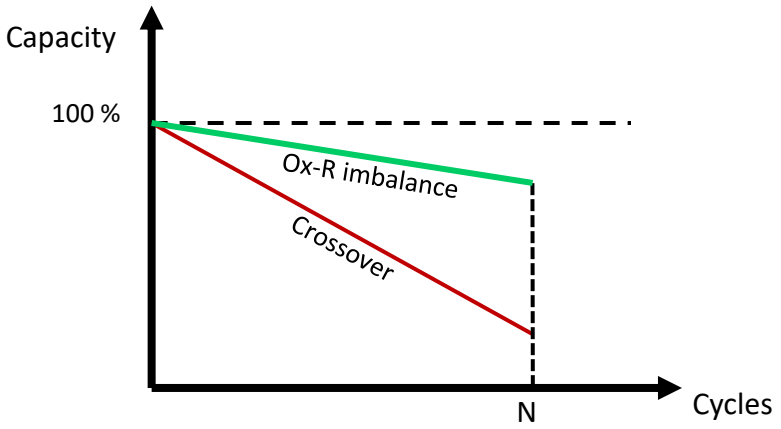
Differences

- Volume difference between the two tanks
- Electroyte concentration difference

$SOC_{-} = 100\%$ $SOC_{+} = 100\%$

$SOC_{-} < 100\%$ $SOC_{+} = 100\%$

The problem

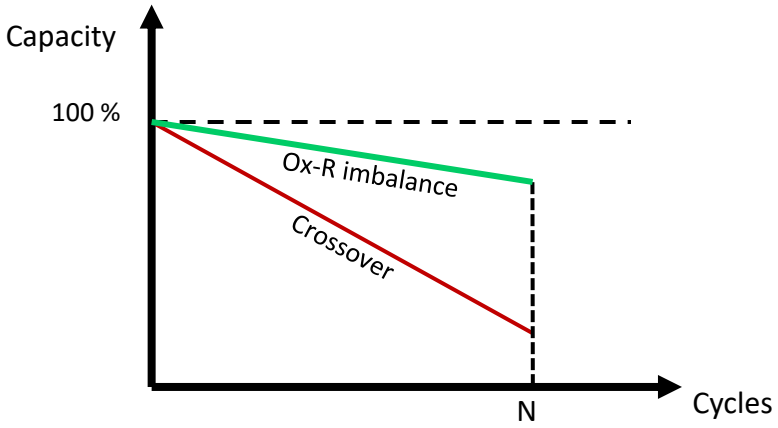


		Causes
Concentration imbalance	•	Crossover of water through the membrane.
	•	Crossover of vanadium species over the membrane.
Oxidative imbalance	•	Hydrogen evolution due to high overpotential.
	•	Oxidation of V(II) electrolyte due to the air
Reductive imbalance	•	Corrosion in V(V) electrolytes accompanied with reduction to V(IV).
	•	Precipitation of V(V) at elevated temperature (If you look more closely, it can be also regarded as concentration imbalance)

M. Skyllas-Kazacos et al. “State of charge monitoring methods for vanadium redox flow battery control” *Journal of Power Sources*, 196 (20) (2011), pp. 8822-8827

Rodby E.K. et al., Assessing the levelized cost of vanadium redox flow batteries with capacity fade and rebalancing, JPS (2020).

The problem



	Causes
Concentration imbalance	• Crossover of water through the membrane. • Crossover of vanadium species over the membrane.
Oxidative imbalance	• Hydrogen evolution due to high overpotential. • Oxidation of V(II) electrolyte due to the air
Reductive imbalance	• Corrosion in V(V) electrolytes accompanied with reduction to V(IV). • Precipitation of V(V) at elevated temperature (If you look more closely, it can be also regarded as concentration imbalance)

Changing the components of the battery

M. Skyllas-Kazacos et al. "State of charge monitoring methods for vanadium redox flow battery control" *Journal of Power Sources*, 196 (20) (2011), pp. 8822-8827

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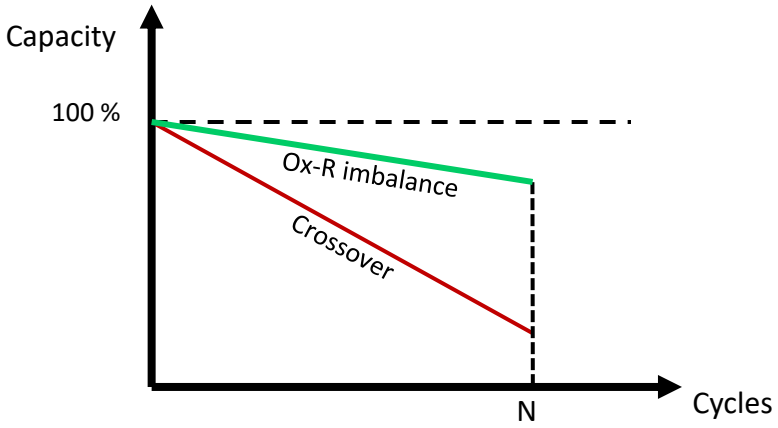
The problem



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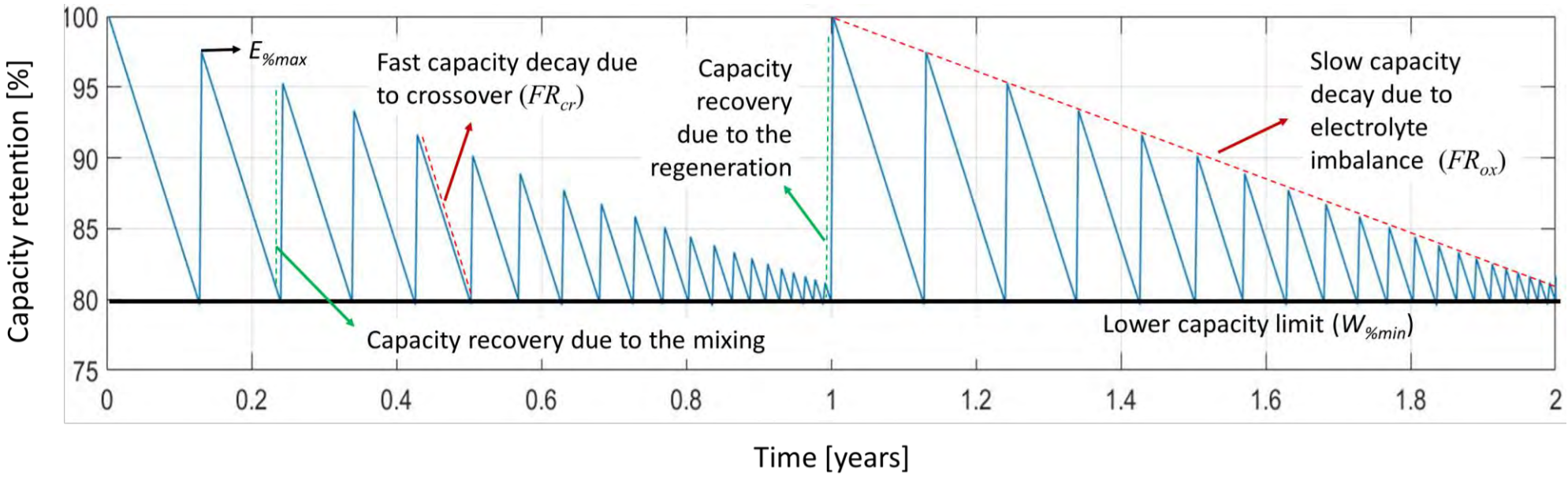
Rodby E.K. et al., Assessing the levelized cost of vanadium redox flow batteries with capacity fade and rebalancing, JPS (2020).

	Causes	
Concentration imbalance	• Crossover of water through the membrane. • Crossover of vanadium species over the membrane.	→ Mixing
Oxidative imbalance	• Hydrogen evolution due to high overpotential. • Oxidation of V(II) electrolyte due to the air	→ Regeneration procedure
Reductive imbalance	• Corrosion in V(V) electrolytes accompanied with reduction to V(IV). • Precipitation of V(V) at elevated temperature (If you look more closely, it can be also regarded as concentration imbalance)	→ Changing the components of the battery

The problem

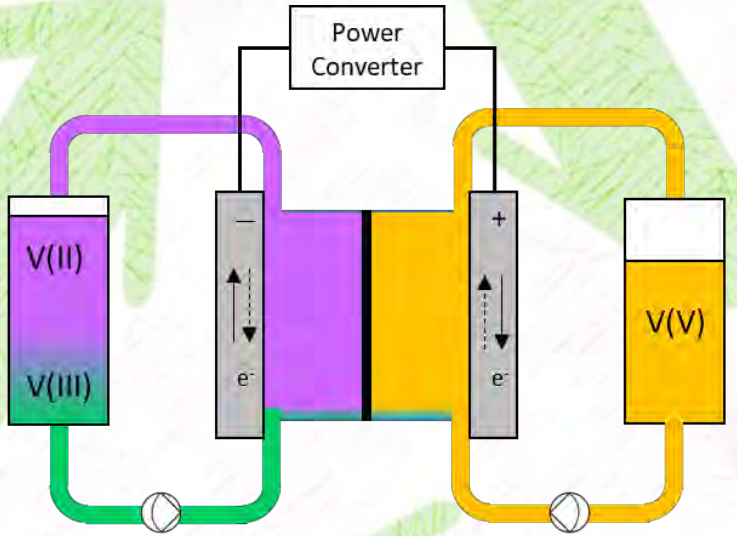


Rodby E.K. et al., Assessing the levelized cost of vanadium redox flow batteries with capacity fade and rebalancing, JPS (2020).

The solution

Chemical Regeneration Process

- Methanol
- Ethanol
- Oxalic Acid



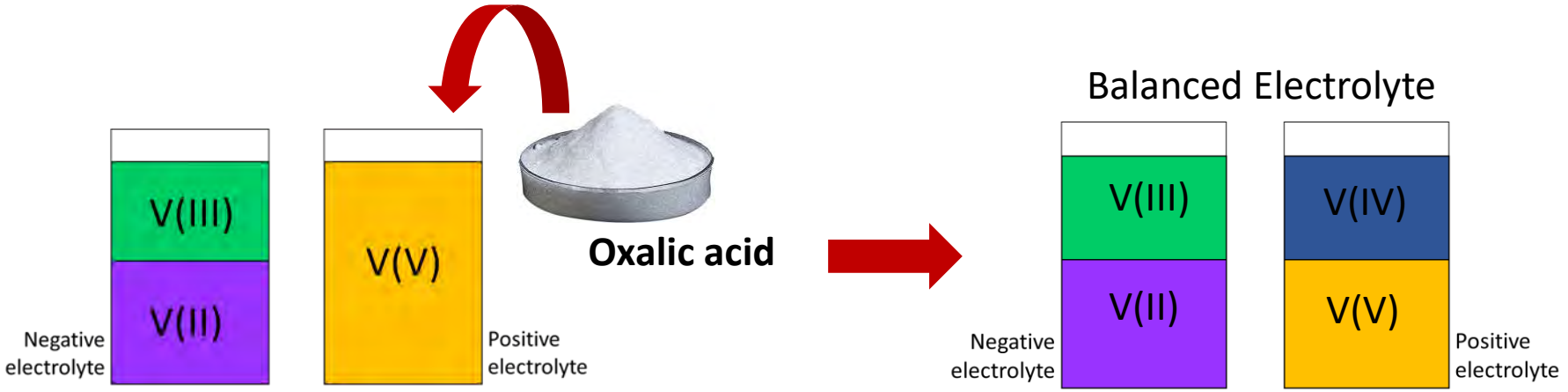
Electrochemical Regeneration Process

- Electrolysis

Chemical regeneration

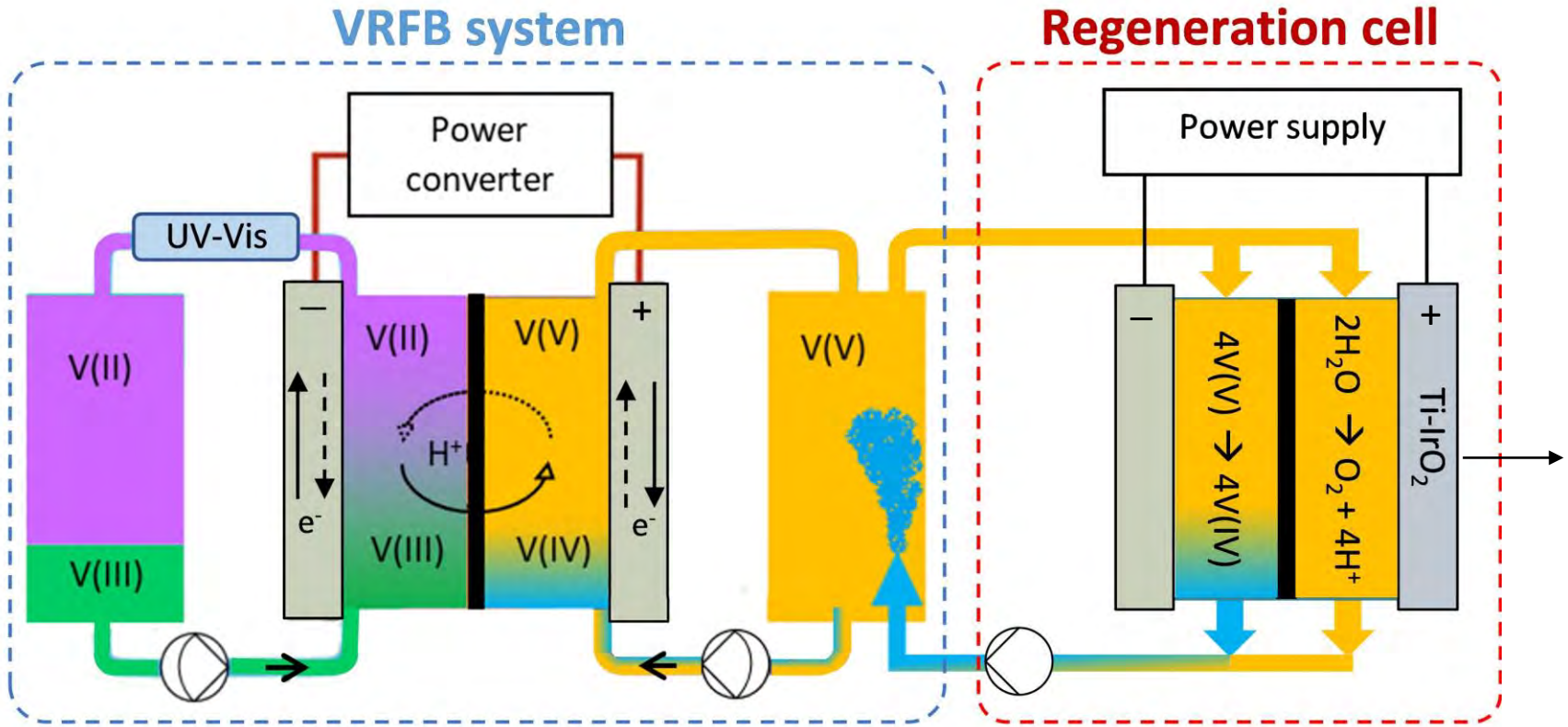
1° step: measuring the imbalance in the tanks

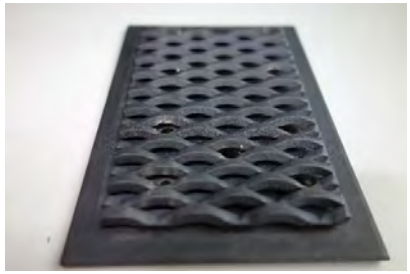
2° step: put the oxalic acid into the tanks



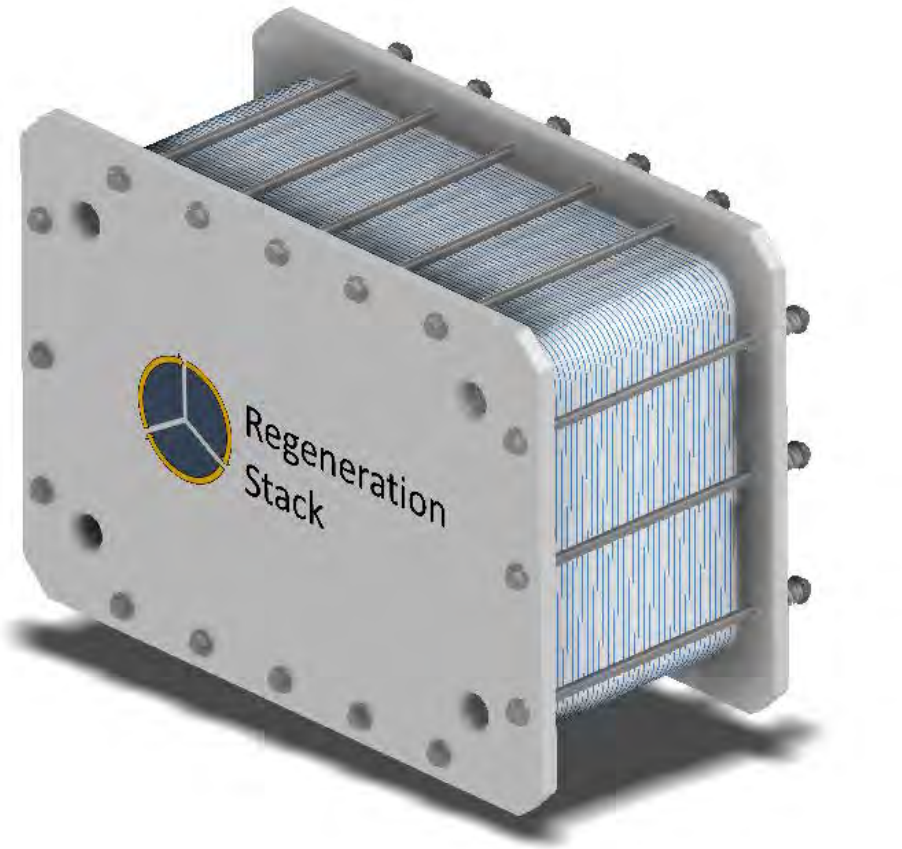
Electrochemical regeneration

Only one step: Electrochemical reduction of the positive electrolyte





Electrochemical regeneration



Number of regeneration cell

$$N_{cell} = \frac{Charge\ to\ provide\ via\ electrolysis}{Charge\ provided\ in\ each\ cell}$$

$$= \frac{\frac{Imbalance[\%] * E[kWh]}{U_{cell}[V]}}{j\ [A\ m^{-2}] * A[m^2] * t(h)} \frac{1}{n_{reg}}$$

Energy consumed

$$E_c[kWh] = U_{cell,reg.}[V] * N_{cell} * j[Am^{-2}] * A[m^2] * 24h$$

Flowrate

$$Q[L\ s^{-1}] = \frac{\alpha \frac{i\ [A]}{F\ [C\ mol^{-1}]}}{C_v[mol\ l^{-1}]} N_{cell}$$

Electrochemical regeneration

50 kW/500 kWh VFB system

Number of regeneration cell

$$N_{cell} = \frac{\textit{Charge to provide via electrolysis}}{\textit{Charge provided in each cell}}$$

$$= \frac{\frac{\textit{Imbalance}[\%] * \textit{E}[kWh]}{\textit{U}_{cell}[V]}}{j\,[A\,m^{-2}] * \textit{A}[m^2] * \textit{t}(h)} \frac{1}{n_{reg}}$$

CAPEX

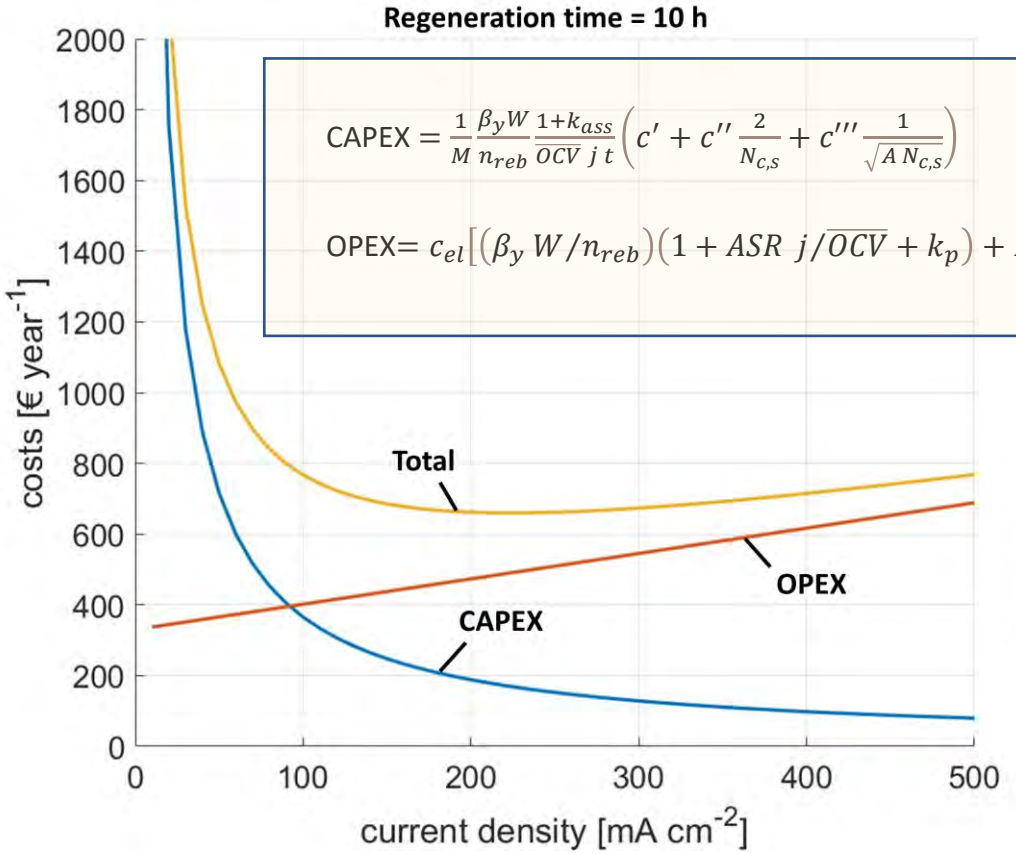
Energy consumed

$$E_c[kWh] = \textit{U}_{cell,reg.}[V] * \textit{N}_{cell} * \textit{j}[Am^{-2}] * \textit{A}[m^2] * \textit{24h}$$

Flowrate

$$Q[L\,s^{-1}] = \frac{\alpha \frac{i\,[A]}{F\,[C\,mol^{-1}]}}{C_v[mol\,l^{-1}]} N_{cell}$$

OPEX



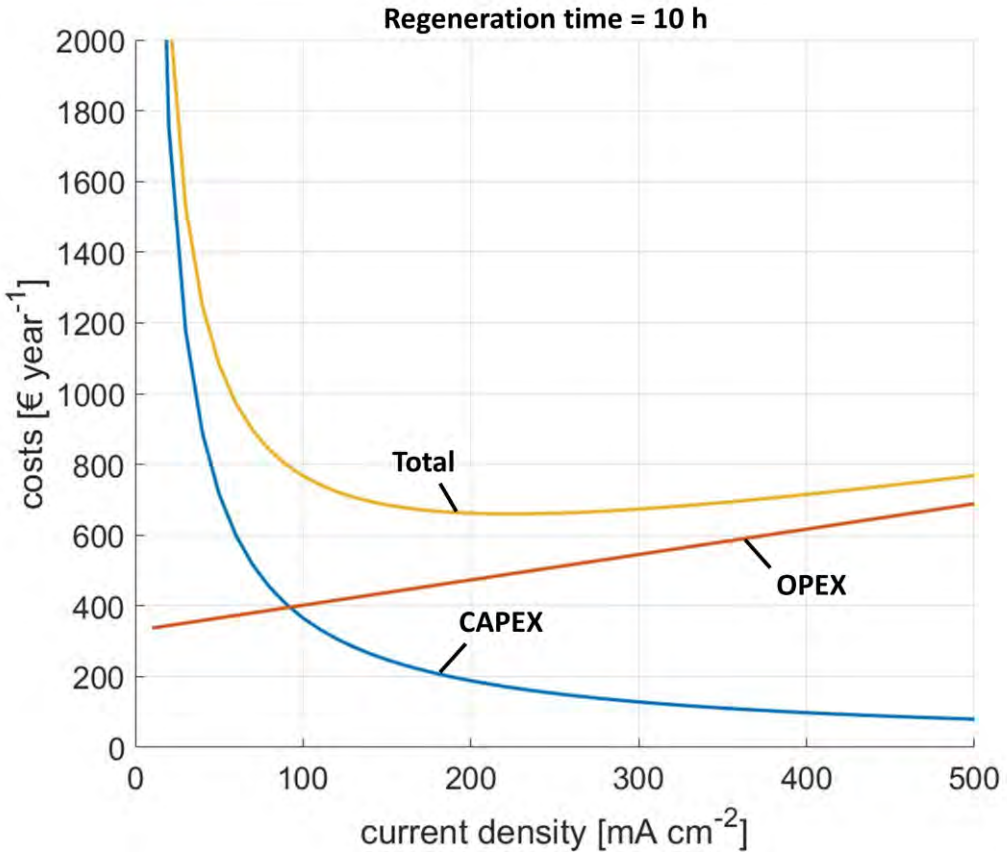
$$\text{CAPEX} = \frac{1}{M} \frac{\beta_y W}{n_{reb}} \frac{1+k_{ass}}{\overline{OCV}\; j\; t} \left(c' + c'' \frac{2}{N_{c,s}} + c''' \frac{1}{\sqrt{A\,N_{c,s}}} \right)$$

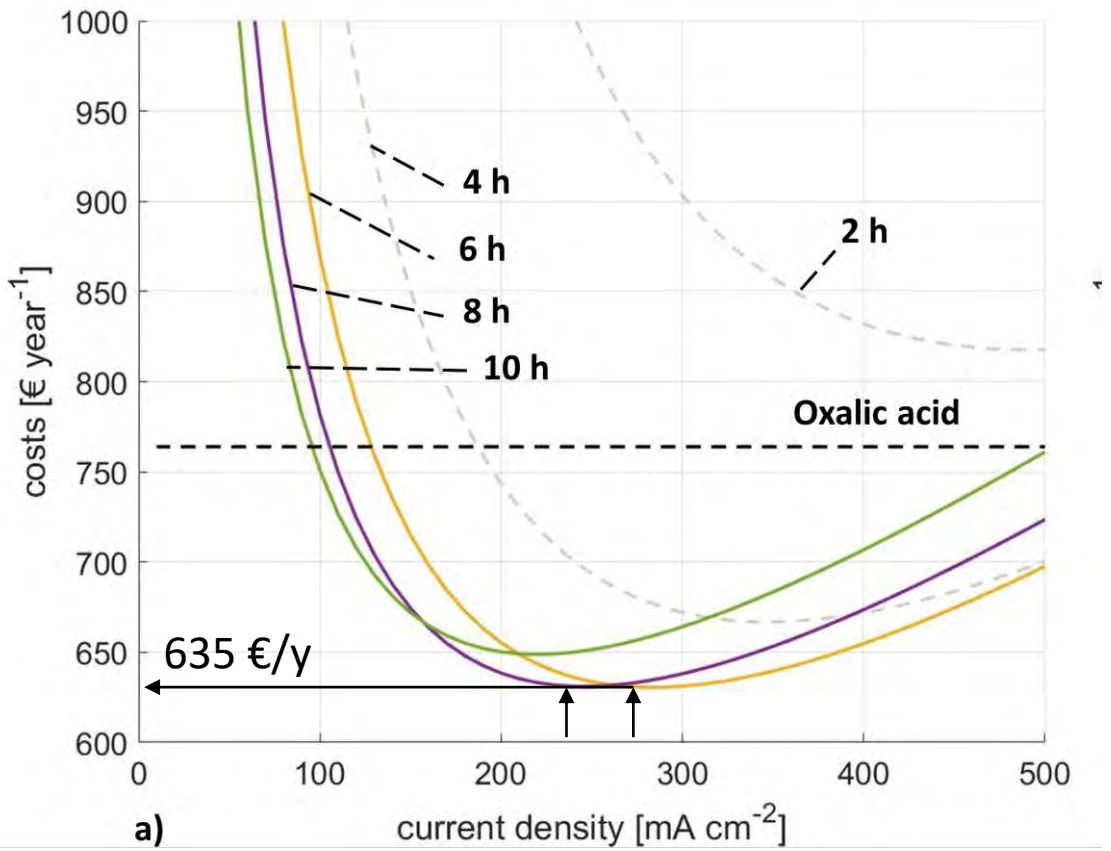
$$\text{OPEX} = c_{el} \left[\left(\beta_y\, W / n_{reb} \right) \left(1 + ASR\; j / \overline{OCV} + k_p \right) + Pt \right]$$

Electrochemical regeneration

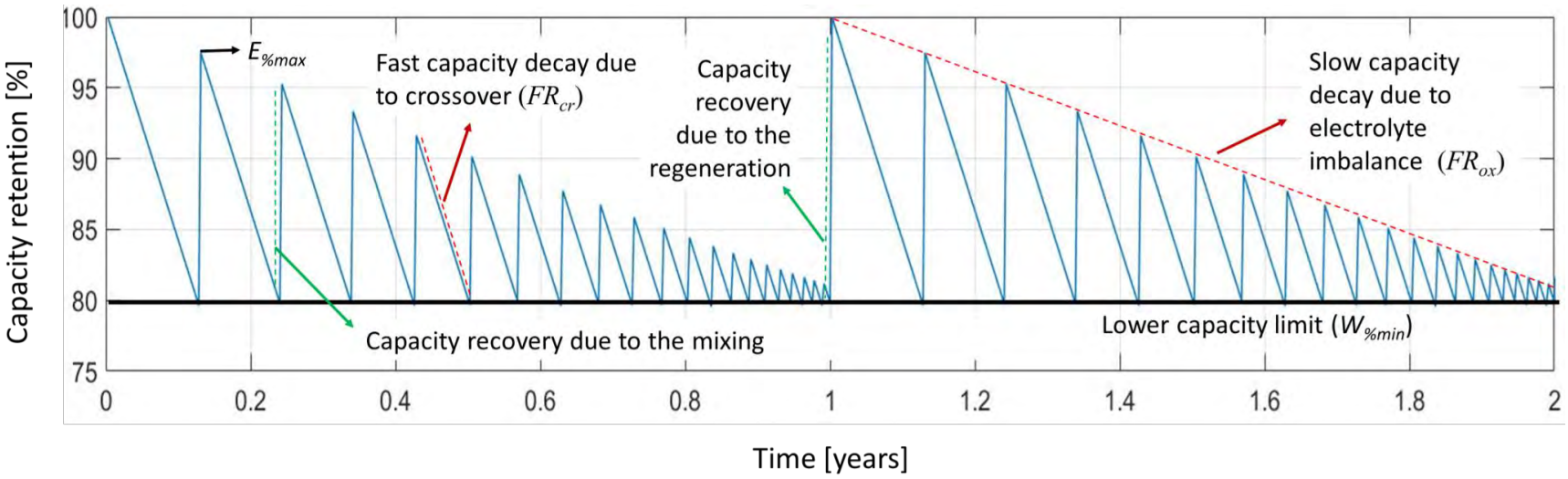
Cost of OA = 1.10 €/kg
Labor costs = 5 €/kWh
(for dosing the additive)

Rodby E.K. et al., Assessing the levelized cost of vanadium redox flow batteries with capacity fade and rebalancing, JPS (2020).

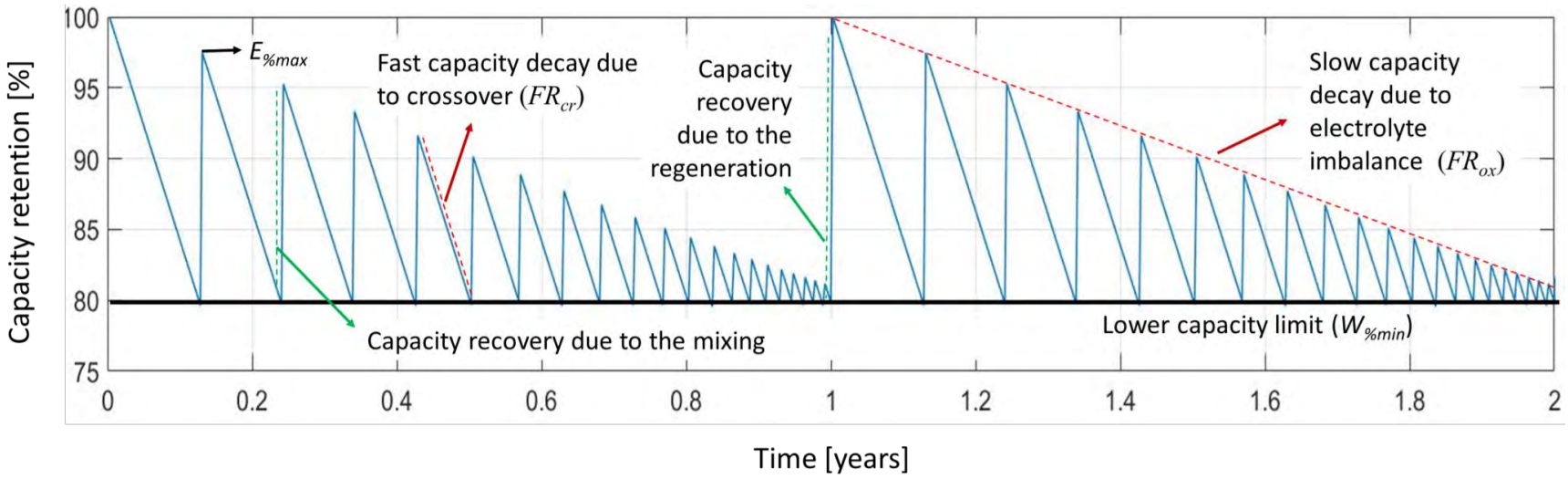


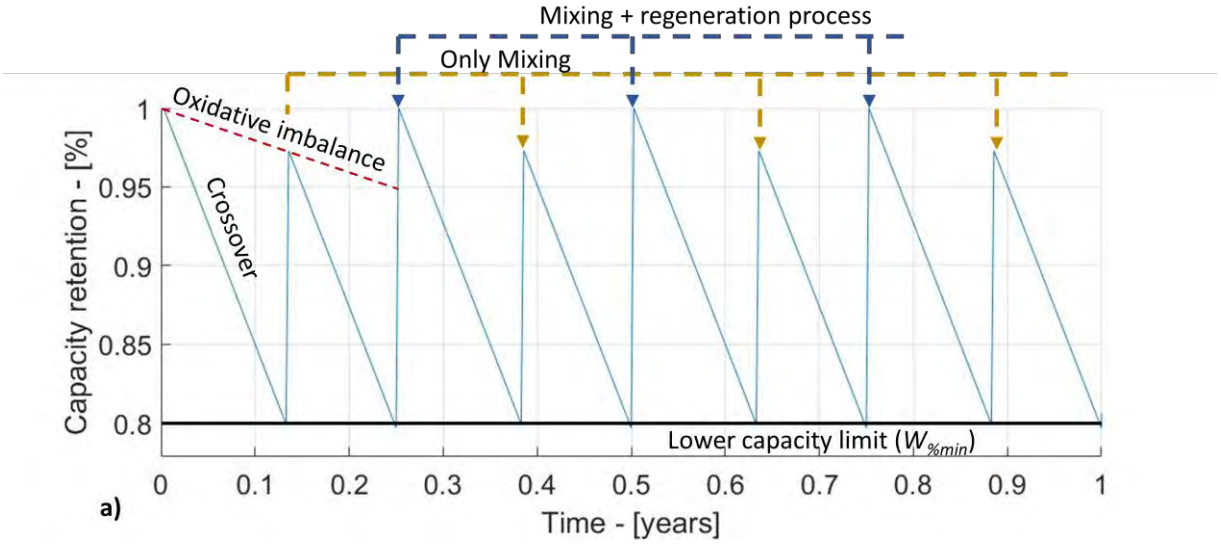


Electrochemical regeneration

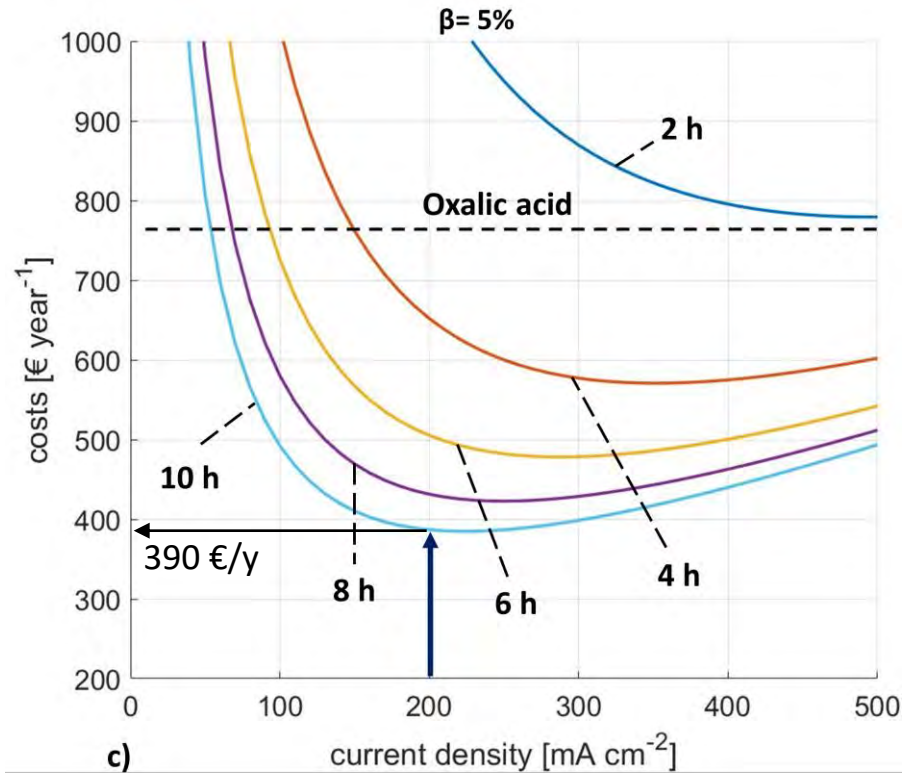


Electrochemical regeneration

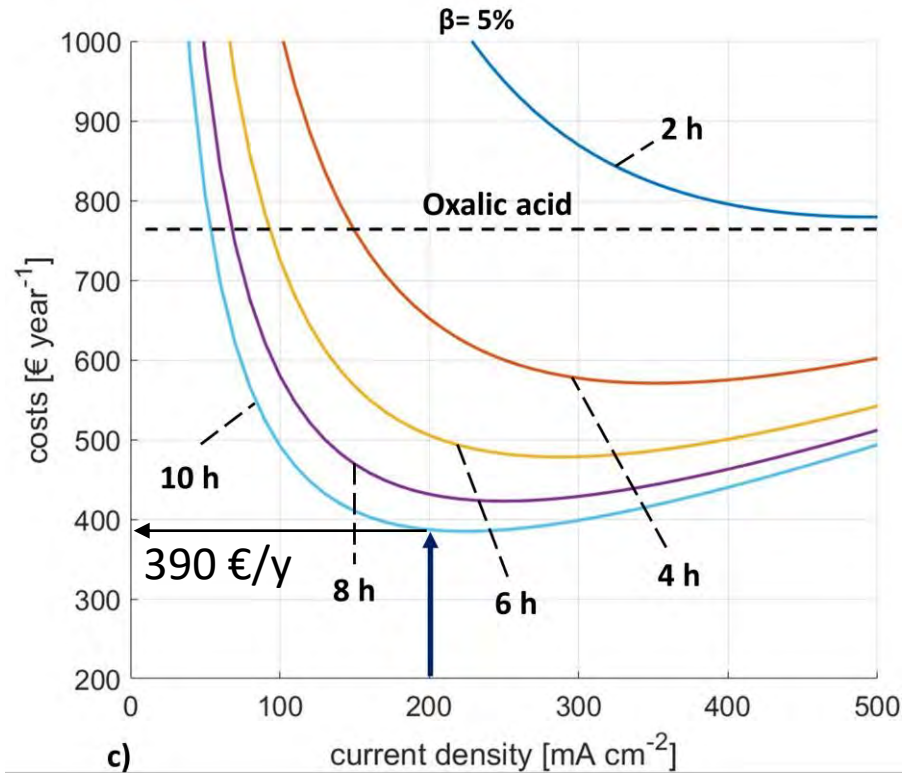


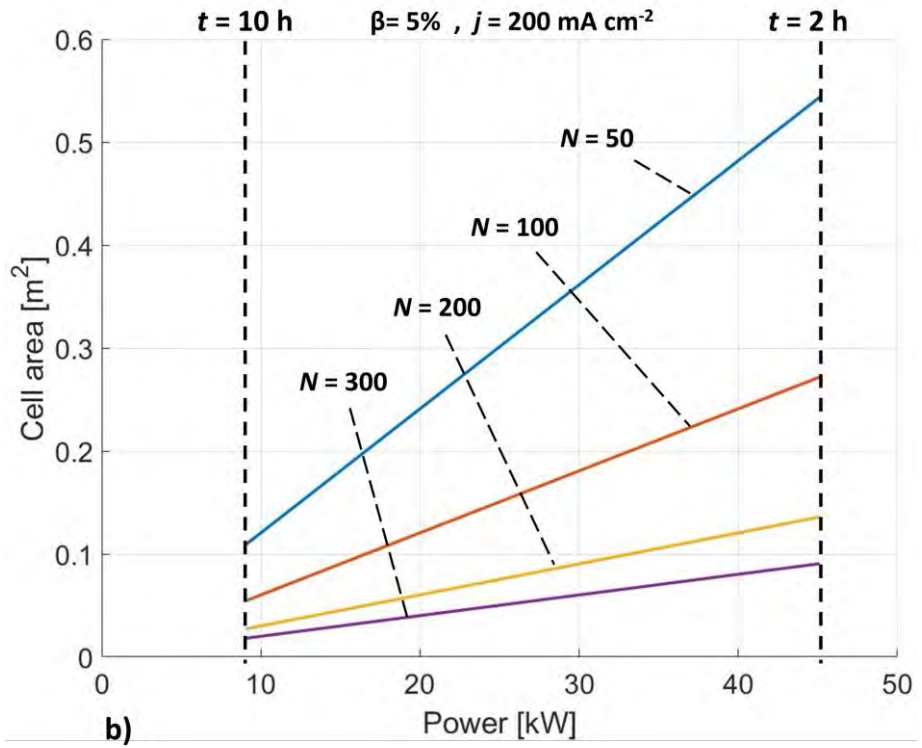


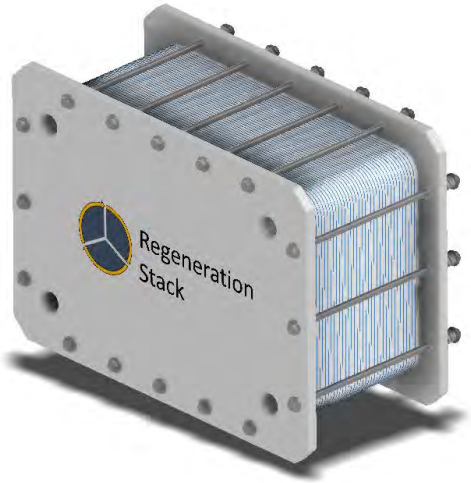
Electrochemical regeneration



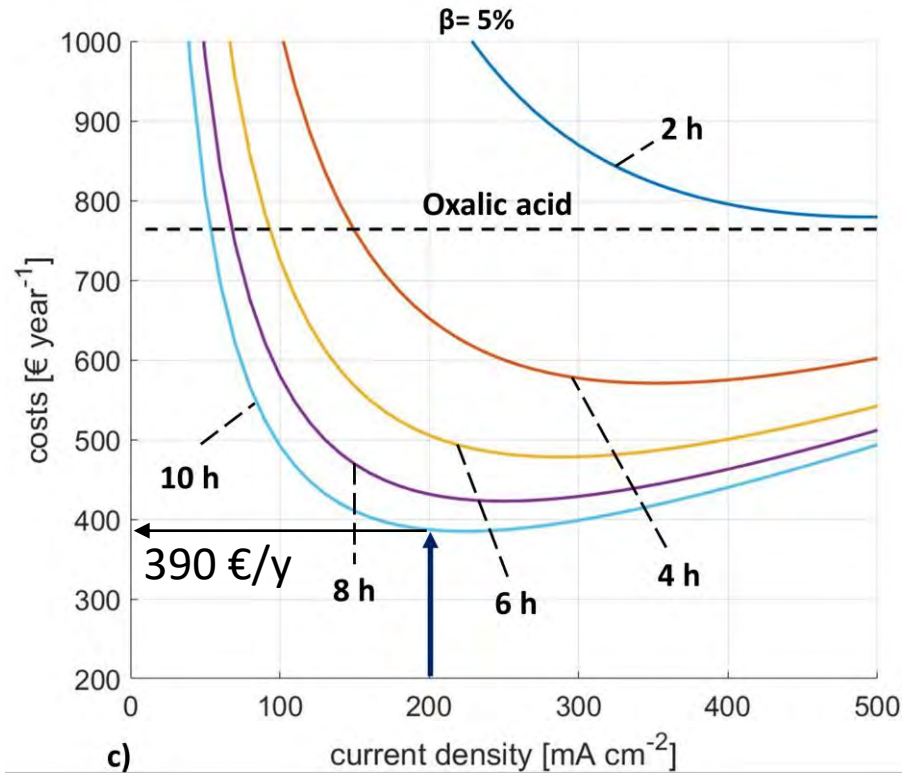
Electrochemical regeneration

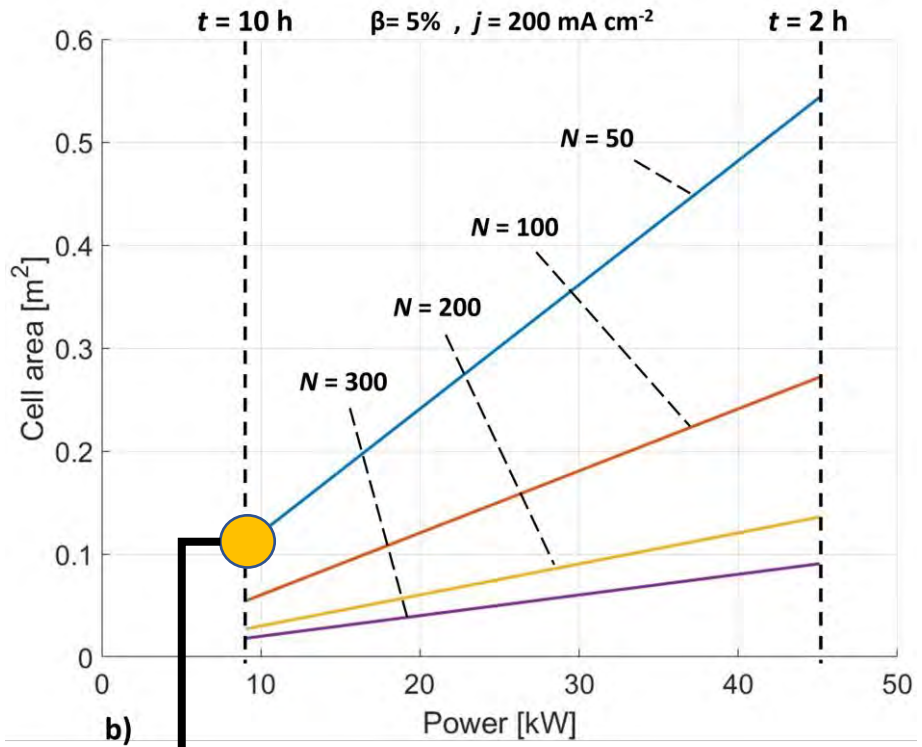


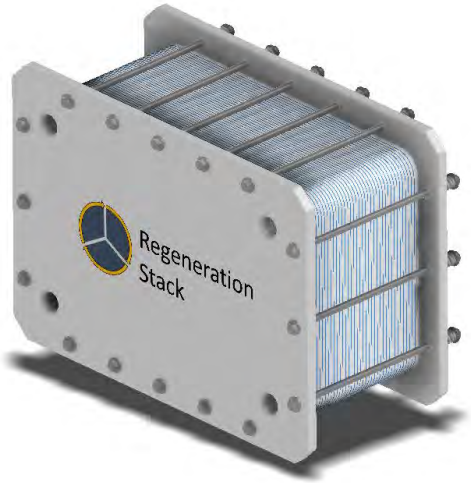




Electrochemical regeneration







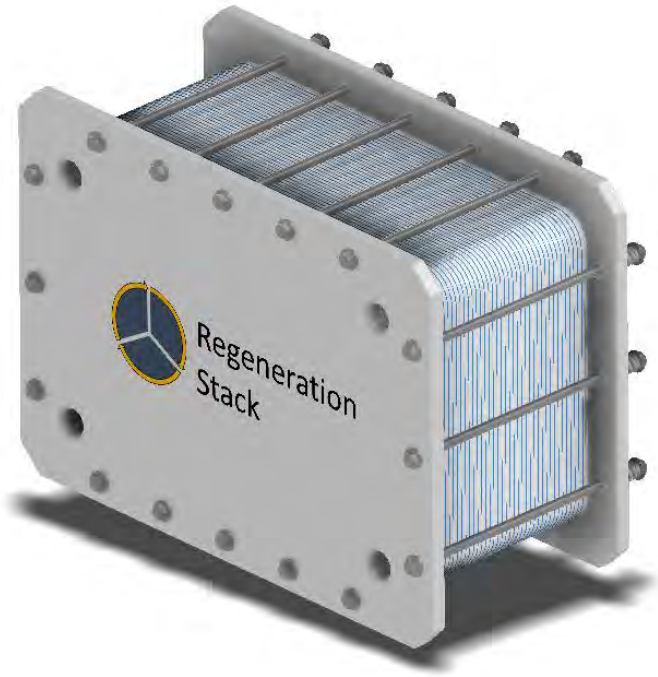
$$Q[L\ s^{-1}] = \frac{\alpha \frac{i\ [A]}{F\ [C\ mol^{-1}]}}{C_v [mol\ l^{-1}]}\ N_{cell}$$ = 19 l/min (with α = 5)

Conclusion

- The model was used to investigate optimal configurations of minimum costs in terms of rebalancing reactor design and system operation.

- Interestingly, the electrochemical rebalancing process here studied, if properly optimized, can present a total cost (investment plus operation) lower than a chemical rebalancing process using oxalic acid as reducing agent.

- In the case of a VFB rated 50 kW/500 kWh affected by a yearly imbalance rate of 20 %, it was found that a rebalancing process performed once a year result suitable only with slow regeneration process, lasting 5–10 h.



Papers

Chemical Engineering Journal 405 (2021) 126583

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Novel electrolyte rebalancing method for vanadium redox flow batteries

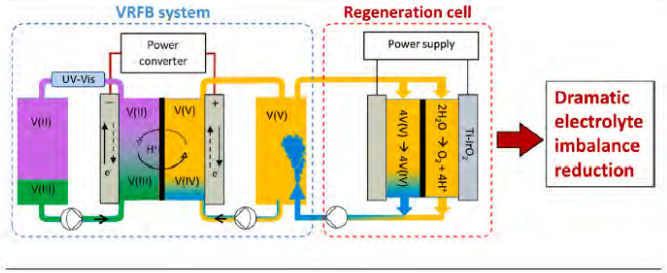
Nicola Poli[a,b], Michael Schäffer[c,d], Andrea Trovò[a,b], Jens Noack[c,d], Massimo Guarnieri[a,b,*], Peter Fischer[c,d]

[a] Department of Industrial Engineering, University of Padua, Via Gradenigo 6/a, 35131 Padova, Italy
[b] Interdepartmental Centre Giorgio Levi Cases for Energy Economics and Technology, University of Padua, Via Gradenigo 6/a, 35131 Padova, Italy
[c] Department of Applied Electrochemistry, Fraunhofer Institute for Chemical Technology, Joseph-von-Fraunhofer-Strasse 7, 76327 Pfinztal, Germany
[d] German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy – CENELEST, University of New South Wales, Sydney, Australia

HIGHLIGHTS

- A novel electrolyte rebalancing method for vanadium redox flow batteries is presented.
- The method uses a rebalancing cell fed from the positive electrolyte tank.
- The rebalancing cell reduces the concentration of V(V) ions in the catholyte.
- A multi-physical numerical model is used to control and optimize the process.
- The effectiveness of the method has been tested and validated on a real VRFB.

GRAPHICAL ABSTRACT



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Journal of Energy Storage 58 (2023) 106404

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Research Papers

Electrochemical rebalancing process for vanadium flow batteries: Sizing and economic assessment

Nicola Poli [a,b], Andrea Trovò [a,b], Peter Fischer [c], Jens Noack [c,d], Massimo Guarnieri [a,b,*]

[a] Department of Industrial Engineering, University of Padua, Padova, Italy
[b] Interdepartmental Centre Giorgio Levi Cases for Energy Economics and Technology, University of Padua, Padova, Italy
[c] Fraunhofer-Institut für Chemische Technologie, Pfinztal, Germany
[d] University of New South Wales, Sydney, Australia

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UNIVERSITÀ DEGLI STUDI DI PADOVA
DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

Thank you

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PhD student
Department of Industrial Engineering
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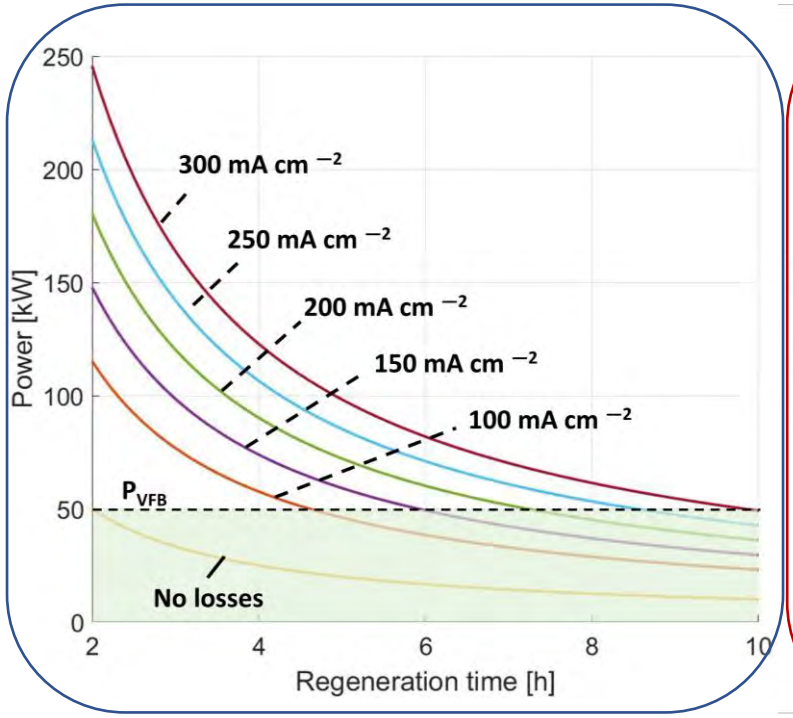
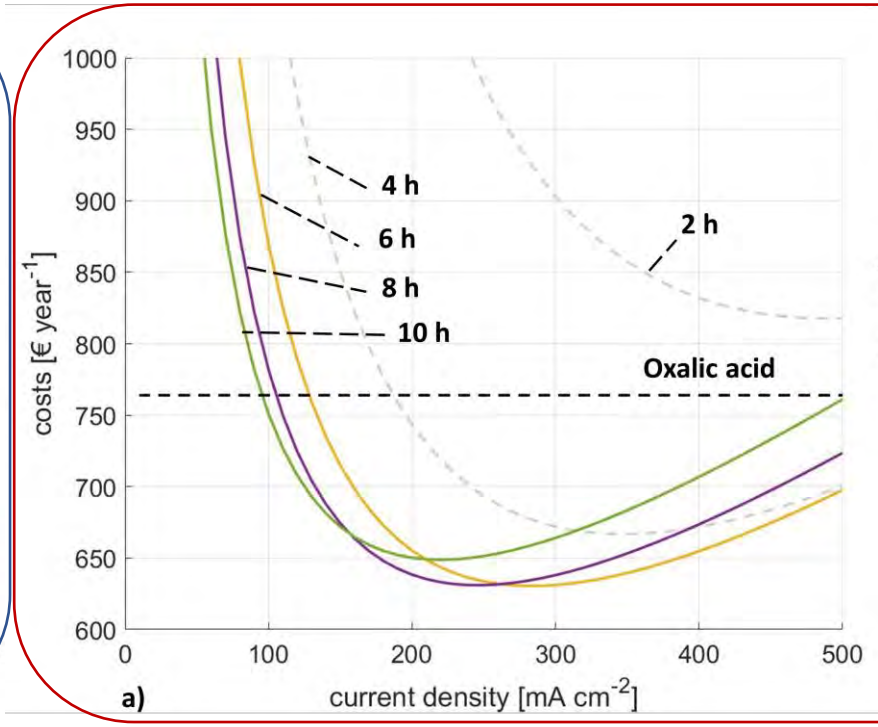
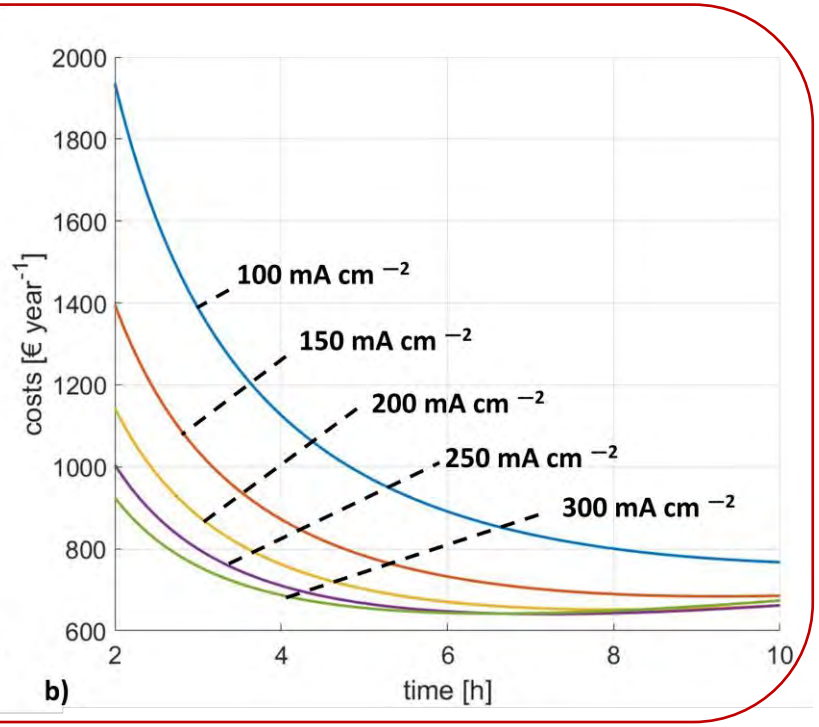
Electrochemical regeneration

Power



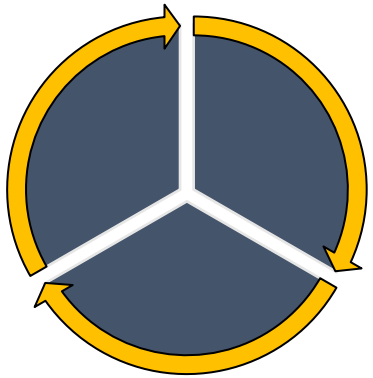
CAPEX





Cost of OA = 1.10 €/kg
Labor costs = 5 €/kWh
(for dosing the additive)

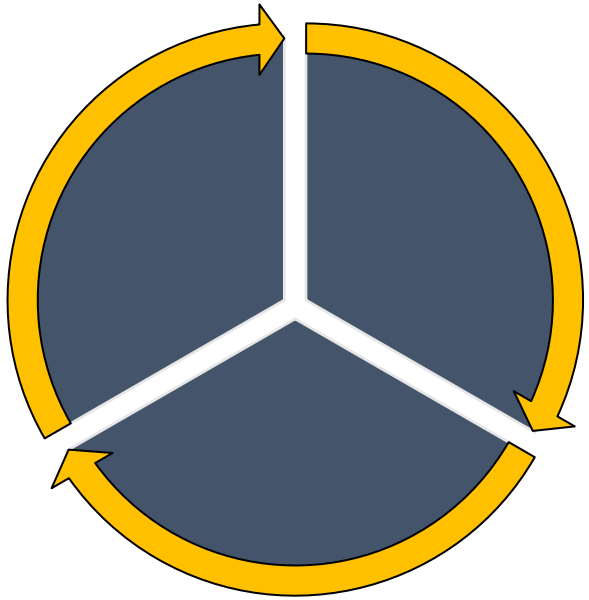
Costs



Regeneration Stack

10 kW / 30 kWh

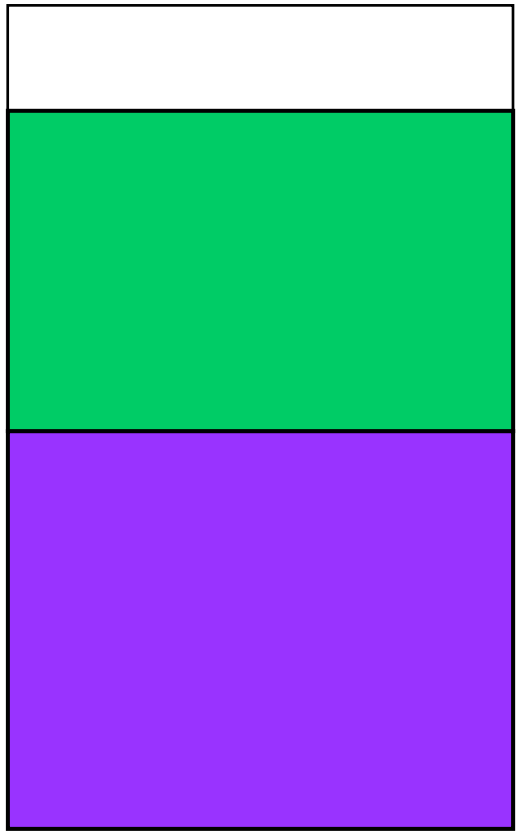
Costs

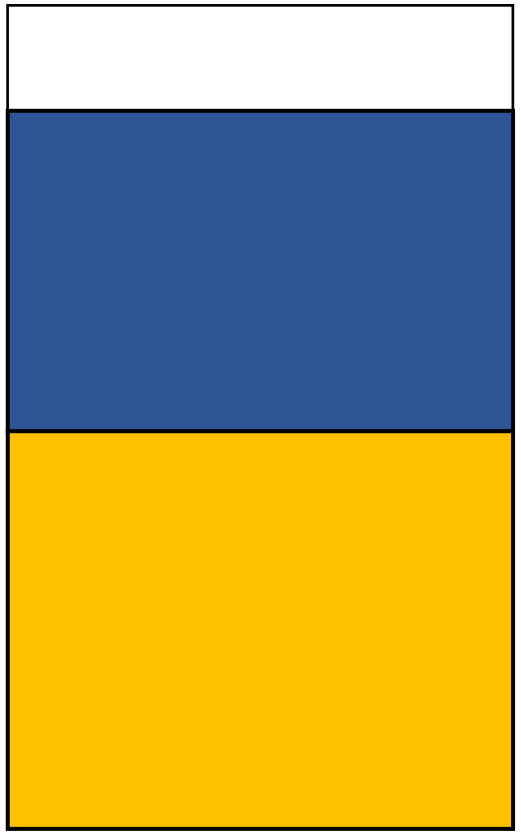


Costs

50 kW / 500 kWh

Negative electrolyte





Positive electrolyte