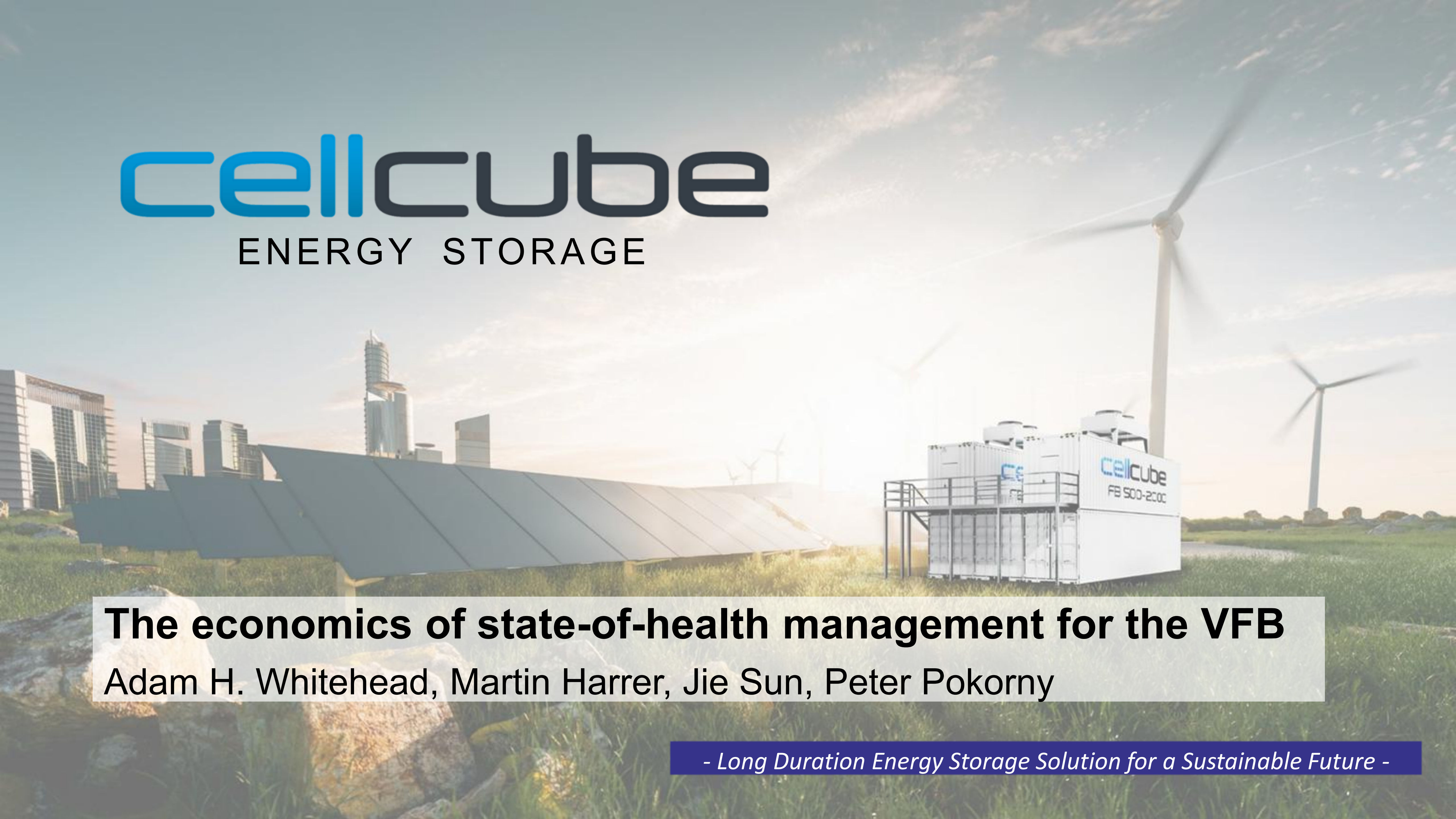

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ENERGY STORAGE

The economics of state-of-health management for the VFB

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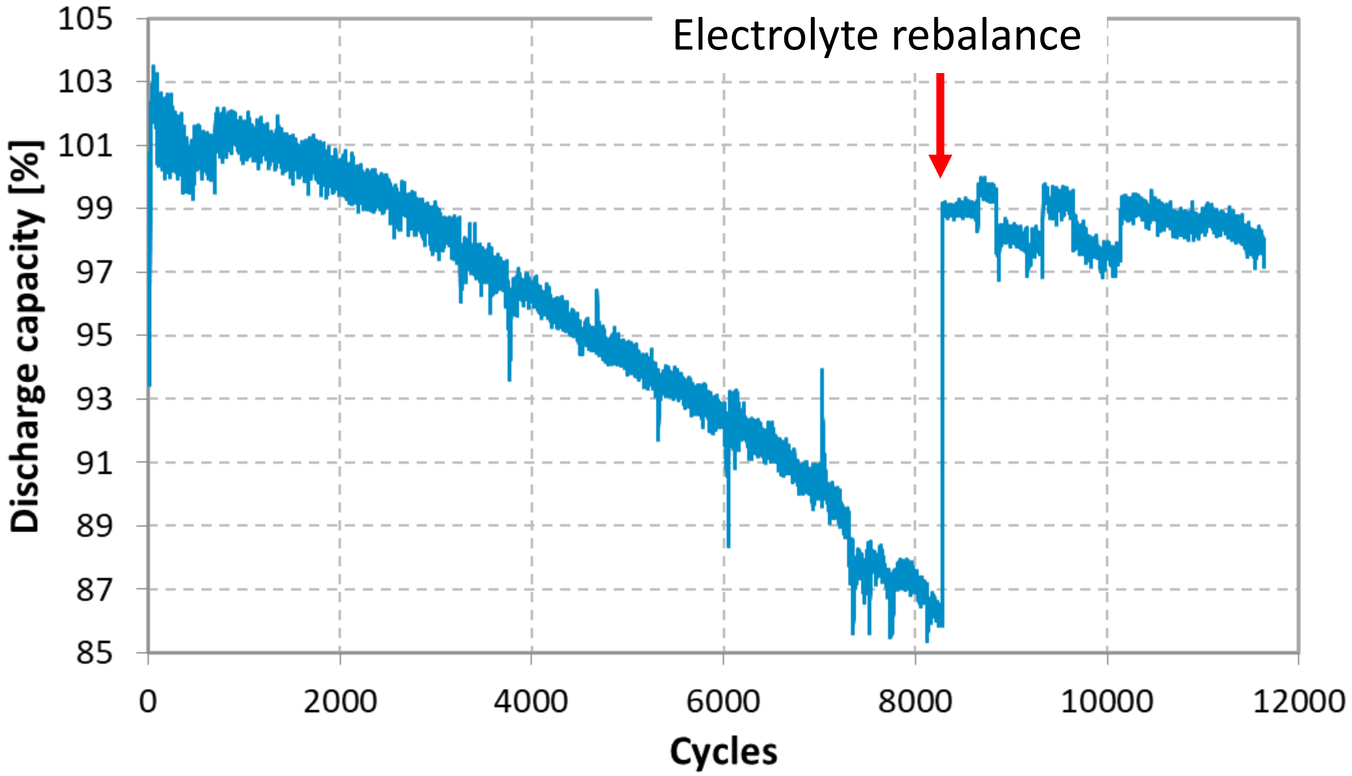
- Long Duration Energy Storage Solution for a Sustainable Future -

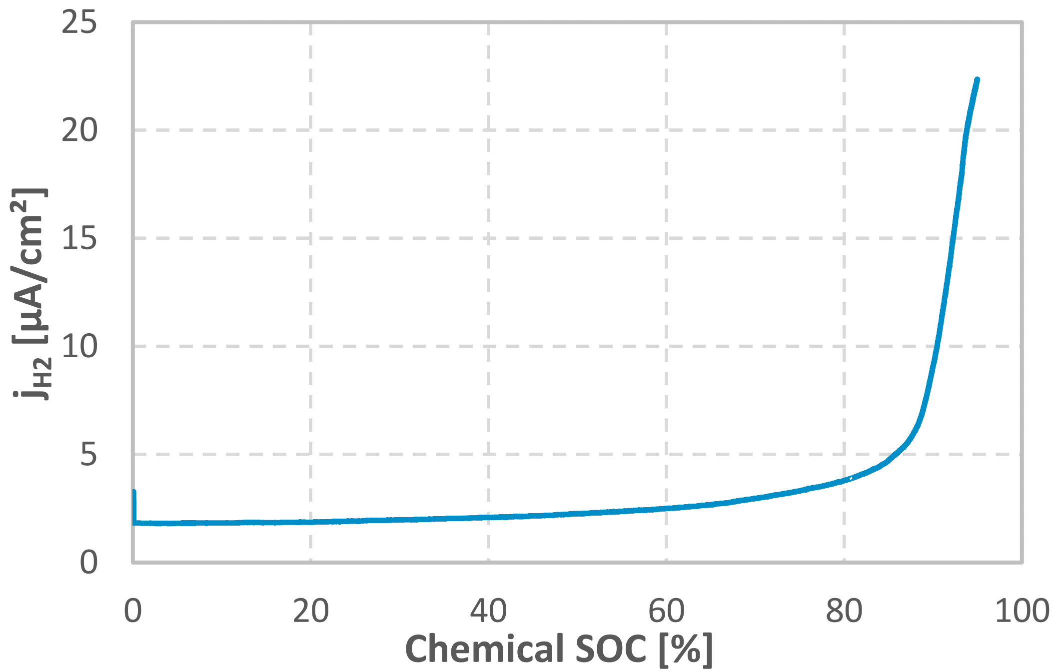
State-of-health (SOH) is a term that is used in many ways.

In the following it relates to the average oxidation state of the vanadium electrolytes.

- Perfectly healthy = 3.50 average oxidation state
  - this is typically the starting state for a new battery
- Completely unhealthy = 4.00 average oxidation state
  - The battery has no discharge capacity
- We consider rebalance is necessary at 3.60 average oxidation state



Electrolyte oxidation leads to capacity loss, and if not corrected, can lead to stack damage (overcharging of the positive electrodes)



H_2 evolution rates are strongly dependent on the state-of-charge range over which the electrolyte is operated

Therefore, the **use case** affects the rate of oxidation

Additionally, the maximum allowed chemical SOC and stack voltage also have an impact.

Impurities can be grouped as:

1) increase hydrogen evolution rates (e.g. Cu, Ir)

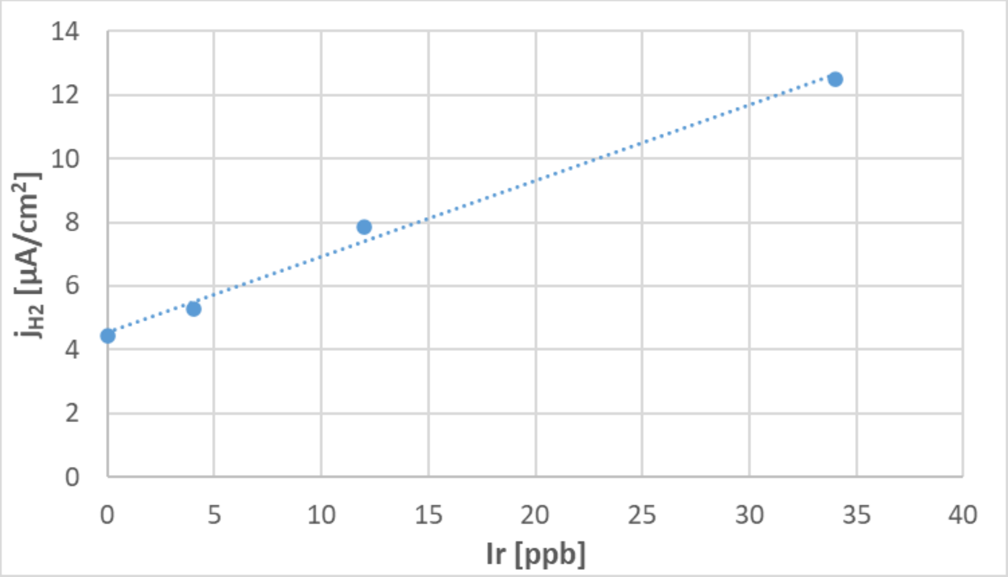
2) block the cell be forming precipitates or deposits (e.g. Si, Bi)

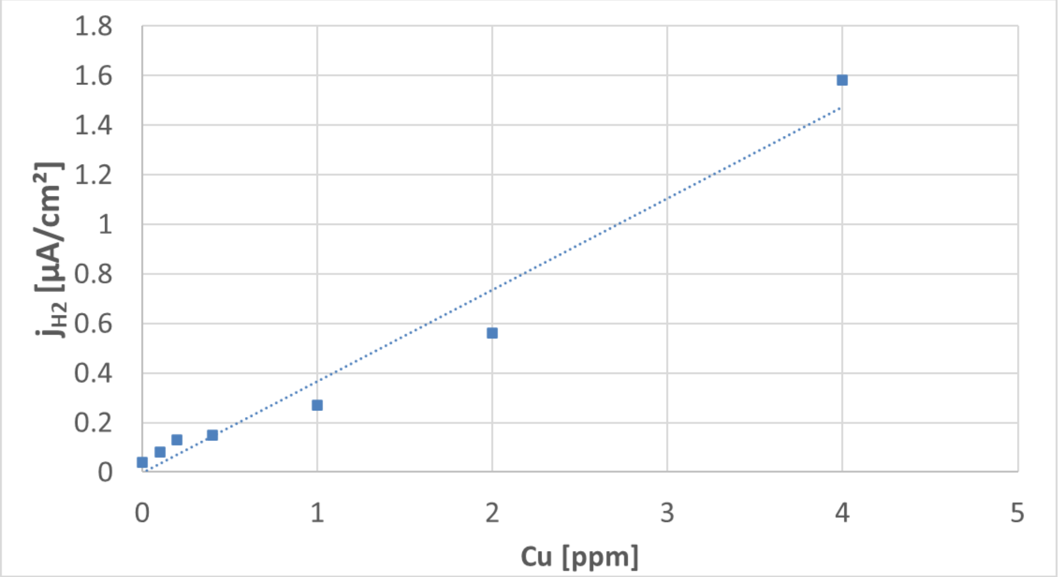
3) reduce the proton concentration → electrolyte/ membrane conductivity (e.g. Na, K)

Of these the (2) must be within specification, (3) can generally be tolerated, but group (1) is of interest here.

Electrocatalytic element concentration can be reduced by a cleaning process, leading to higher purity electrolyte

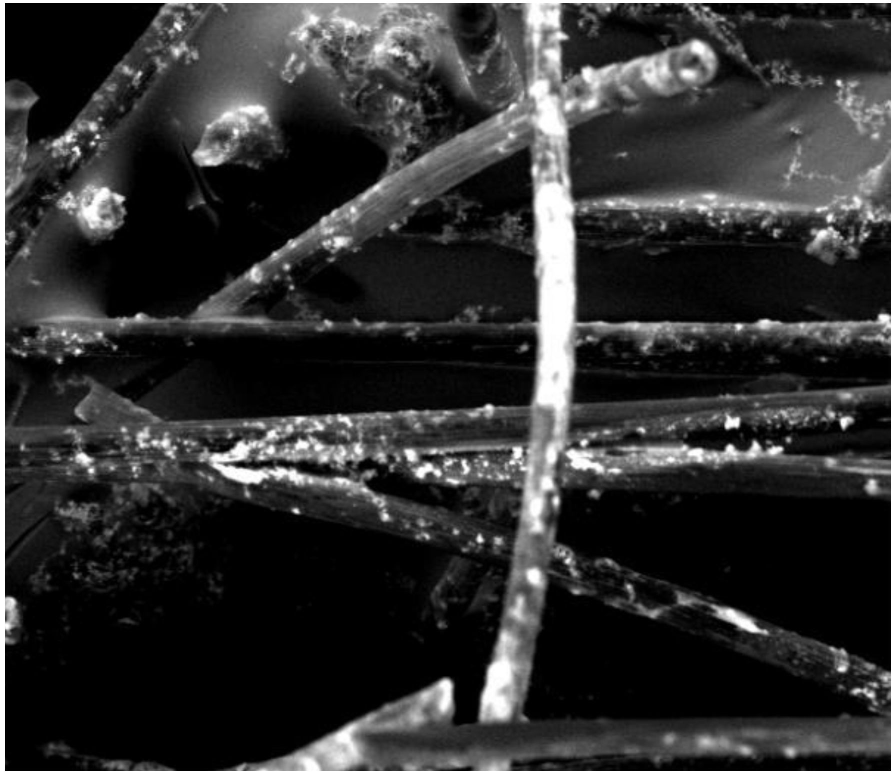
Laboratory investigations were carried out by stepwise addition of impurity elements, from a stock solution. H_2 was detected in a N_2 gas stream through the tanks.





Note the j_{H2} scales cannot be directly compared, because the test conditions differed for these two experiments.
However: $j_{H2} \propto [M]$ at low impurity concentrations

Where j_{H2} increases linearly with concentration of impurity: rate of hydrogen evolution is mainly dependent on the electrolyte volume, not the number of stacks.
This makes sense if the coverage of the deposit increases with the amount of impurity present
Therefore, it is more correct to quote H_2 evolution rates as a function of electrolyte volume rather than electrode area.



Typical metal deposition on the graphite fibres from unclean electrolyte, by BSE

Patches of thin layer deposit:
more impurity → larger patches

Strategies for keeping the VFB healthy

Baseline electrolyte
Quite high purity, "standard" electrolyte
Meets Chinese grade 1*

or

High purity
Cleaned standard electrolyte

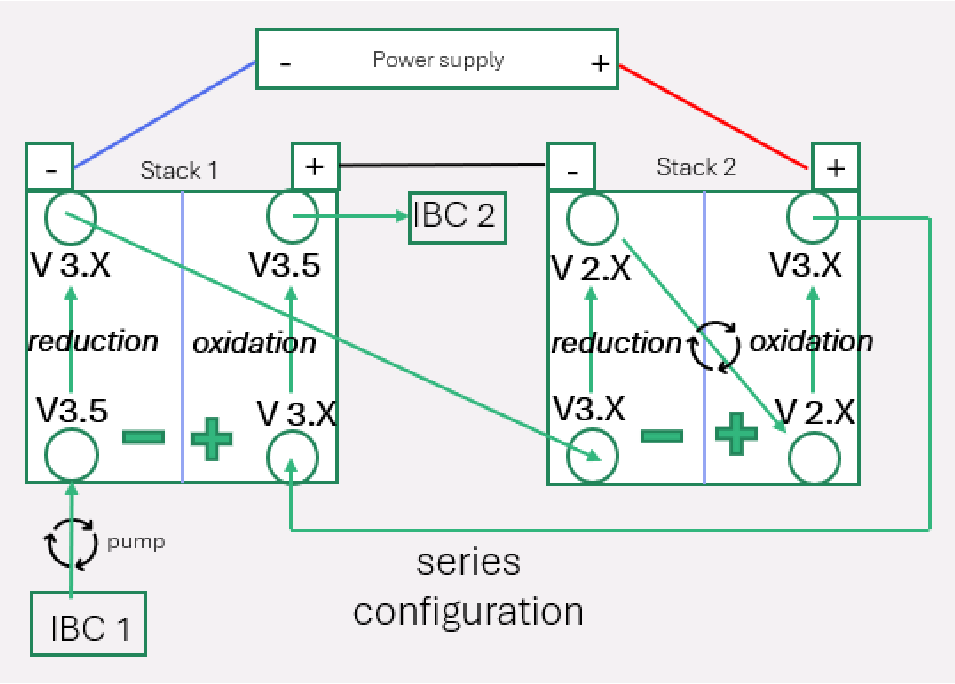
Frequent rebalance

Less frequent rebalance

**Electrolyte for vanadium flow battery, GB/T 37204, State Administration for Market Regulation, Beijing, CN, 28 December 2018.*

How do we raise purity of electrolyte?

CellCube Patent AT 525774



Test electrolyte with
0.6 ppm Sb
1.2 ppm Cu

"Cleaned" electrolyte
0.2 ppm Sb
<0.1 ppm Cu

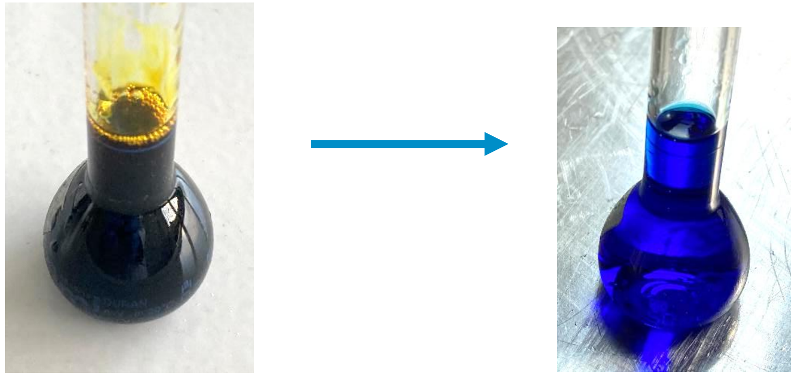
Cost of cleaning step
@ 2 x 10^6 L p.a.

- Electricity
- CAPEX
- Maintenance/ spare parts
- Process losses
- Labour
- Licenses/ margins

Total €0.07 ± 0.03/ L

Rebalance by:

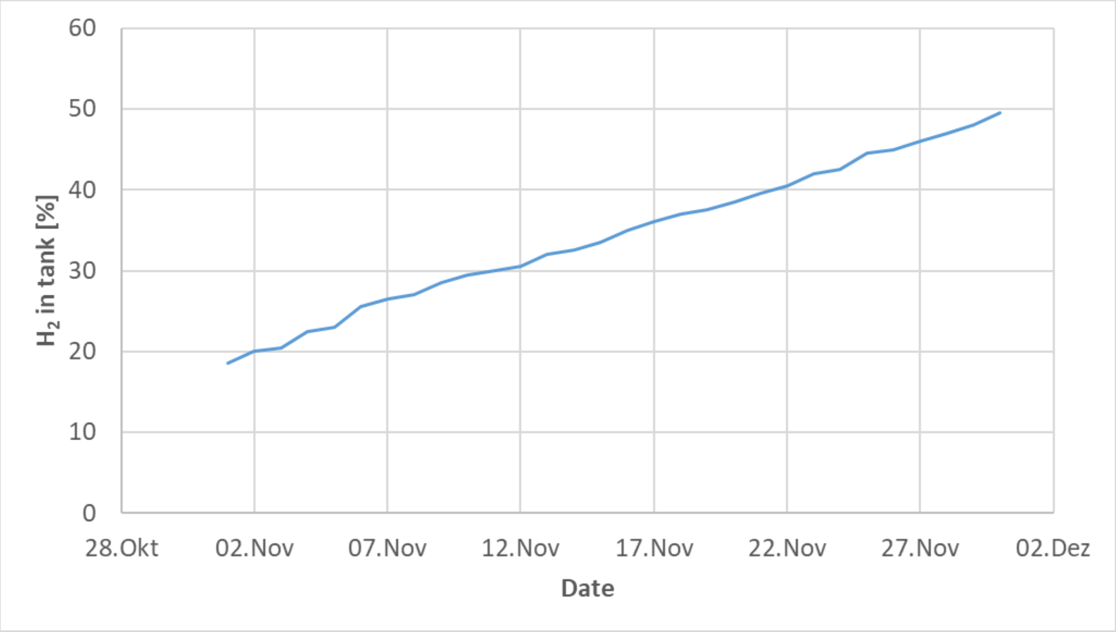
- Partial replacement of charged posolyte
  - This is the most expensive method: requiring fresh electrolyte to be transported, pumped into the system, and charged posolyte to be pumped out and sent for reprocessing
- Adding reducing agents
  - A wide range of reducing agents have been proposed.
  - Carbohydrates are inexpensive and are commonly used
    - – typical bulk prices, ~ €0.008– 0.009 per mol e^-
    - – in small volume, ~ €0.04 per mol e^-



- Use of an electrochemical rebalance cell
  - Oxygen is evolved on one side and vanadium electrolyte reduced on the other.
  - Combined with an SOH detector for autonomous operation.
  - Estimate for rebalance cell, control electronics, cables, power supplies & detector based on medium scale
  - Electrodes need periodic replacement

Field data from many historical systems

Electrolyte purity	Equivalent H_2 evolution rate [mL_{H2}/L_{VEL} per day]	Time to reach 3.60 average oxidation state [months]
High purity electrolyte	0.1 – 0.5 (average ~0.4)	40 – 200, **average 50**
Standard "uncleaned" electrolyte	0.5 – 5 (average ~2)	4 – 40, **average 10**
Contaminated electrolyte	>5	<4



The spread of oxidation rates is due in part to operating conditions & oxygen ingress, partly due to range of impurity concentrations

H_2 sensor in the tank, or periodic measurements of electrolyte samples

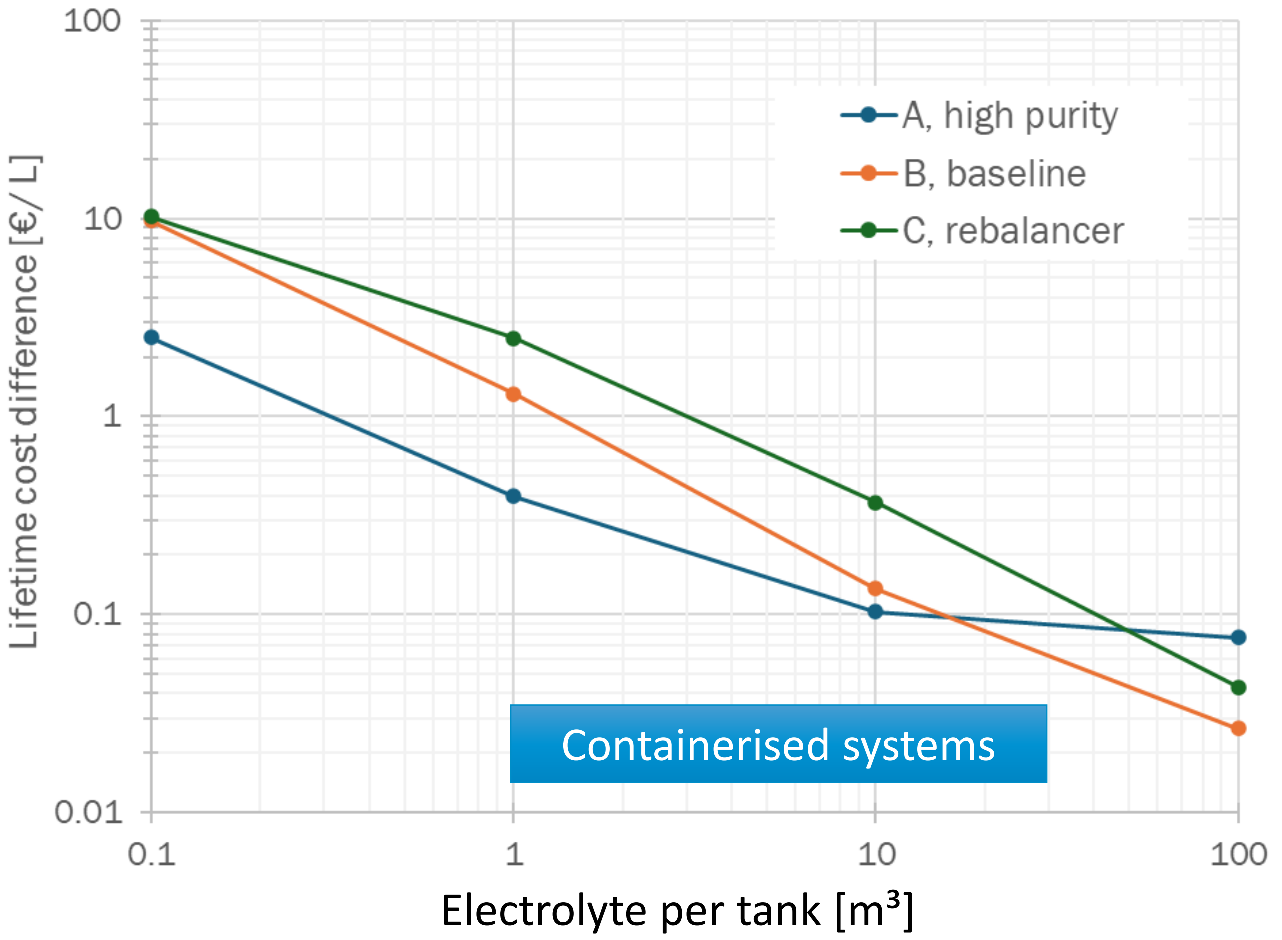
Additional costs
in comparison to baseline electrolyte quality and no extra service operations

Electrolyte purity	High	Lower	
Approach	A	B (baseline)	C
Rebalance method	Reducing agent	Reducing agent	Rebalance cell
Additional CAPEX	Cost of electrolyte cleaning	None	Cost of rebalance cell /detector
OPEX impact	+ extra cost during every 4th annual service	+ extra cost during annual service actions	Maintenance of rebalance cell/ detector
End of life electrolyte	Less contamination than B	May be contaminated Reprocessing cost	May be contaminated Reprocessing cost

Real weighted average cost of capital, calculated using the US DOE model

Costs vary with tank size

e.g. adding reducing agent to one large tank is about the same service effort as adding to a small tank



Taking 6% WACC - real

Ignores difference in end-of-life electrolyte value

Conclusions

- “Standard” electrolyte must be of a relative high purity, but there is a wide range of SOH degradation rates
- The rebalancer approach makes least economic sense
- “Cleaned” electrolyte is economically advantageous for electrolyte ≤ 15 000 L per tank

Final word:

- Cleaned electrolyte made of less expensive, lower-purity oxides than “baseline” grade, may bring even more benefit

Thank you!