Understanding the degradation process in zinc-iodine hybrid flow batteries

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Motivation:

- Flow batteries are promising stationary energy storage due to modularity and inherent safety
- Zinc-iodine hybrid flow battery (ZIHFB): high theoretical energy density and zinc abundancy

Aims of study:

- Understatement of degradation mechanism in ZIHFB
- Identification of the safe conditions for stable and efficient battery operation

Cell

Conclusions:

- Detailed study of irreversible ZIHFB cell failure due to "voltage bugle"
 - \rightarrow Irreversible efficiency loss due to membrane penetration

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- → Several mitigation strategies tested to regenerate performance/prevent degradation
- Hydraulic connection of electrolyte tanks and reduced SOC range (0-50% of negolyte) \rightarrow Efficient (EE \approx 85%) and mid-term stable single-cell operation at 100 mA cm⁻²



1.6

 $0.8 \times 0.05 \text{ dm}^3$

 \times 0.07 dm⁻

20

80

SoC / %

Cell voltage development during cycling at

100 mA cm⁻² for different negolyte volumes.

100

1.5

utilization

Capacity

60

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Voltage

Averaged cycling parameters at different SOC charging limits:

SOC limit	Coulomb. efficiency	Voltage efficiency	Energy efficiency	Capacity utilization
60% SoC	98.7%	78.4%	77.4%	59%
80% SoC	89.4%	76.4%	68.2%	72%



- ✓ High efficiencies and capacity utilization (SoC 0-60%)
- × Voltage bulge at 70% SOC (\approx 125 mAh cm⁻²)
- \rightarrow Gradual disappearance of voltage bulge
- \rightarrow Irreversible coulombic efficiency decay
- \rightarrow Membrane penetration by Zn dendrites (pressure tests)

Voltage bulge is:

... only slightly manifested on potential development of both electrodes ... evidently (EIS) related to a steep increase of ASR_{CT} (not an ohmic effect!) ... primarily related to the amount of deposited Zn (not the negolyte composition!) ... caused by limited reactant accessibility within the negative felt electrode due to **compact Zn layer** formation forcing grow towards the membrane. (supported by increased ohmic overvoltage at the begging of discharge). - Membrane pierced by Zn dendrites enables fast permeation of I₃⁻ (pressure tests) \rightarrow Enhanced self-discharge reaction: **Zn+I₃** \rightarrow **3I⁻ + Zn²⁺**







Time / seconds

-U_{Cell-dif} $3I^- \rightarrow I_3^- + 2e^-$ ∗ E_{REF-} \geq × E_{REF+} Voltage_{cell} <u>ج</u> 0.2 خ -0.4 -0.6 1.2 -0.8 d $Zn^{2+}+2e^- \rightarrow Zn$ 50 150 200 100 Specific capacity / mAh cm^{-2} Cell voltage and electrode potentials development during charging at 100 mA cm^{-2.} Charge



SOC charging limit and after membrane exchange.

Mitigating efficiency losses – electrolyte composition

× Increased initial SOC of posolyte (self-healing) \rightarrow **does not prevent** the efficiency fade

 \times Omitting of **Zn²⁺** ion in posolyte \rightarrow voltage bulge at higher specific capacites

*Photo of Zn compact layer deposited on felt (left); Reconstructed μ-*Computed Tomography image of deposited Zn within the felt (right).

The half-cell pressure test tightens without bulge and after the voltaic bulge appeared.

Mitigating efficiency losses – construction modifications

Non-conductive felt insertion to:

- negative electrode chamber
- positive electrode chamber
- \rightarrow no effect on the bulge position
- \rightarrow increased ASR_o when at positive side





Hydraulic connection of electrolyte tanks

- \rightarrow Continuous volume equalization
- \rightarrow Improved and stabilized efficiencies and capacity

Stable operating conditions identified:

- Galvanostatic cycling within 0-50% SOC range (negolyte)
- Regenerative "full-discharge" periodically implemented



ZIHFB single-cell parameters for different electrode set-ups:

	•	ASR _Ω	ASR _{LC}	Coulomb. efficiency	Voltage efficiency	Capacity fade
		$\Omega \ cm^2$	$\Omega \ cm^2$	%	%	%Q _{theor.} /cycle
	STD	0.68	0.96	89.4	76.4	-0.19
150	Neg. el.	0.60	1.24	83.4	81.1	-0.27
150	Pos. el.	1.54	2.06	85.0	69.6	-0.01

ASR from ES and load curve measurements at +50% SOC Efficiencies CC-CV cycling at 100 mA cm⁻² in 0-80% SOC range



Hydraulic connection of electrolyte tanks



Voltage development during cycling at 100 mA cm⁻² for STD and modified initial posolyte composition.

Acknowledgement:

50 100 150 Specific capacity / mAh cm⁻² Voltage development during cycling at 100 mA cm⁻² for STD and modified initial posolyte composition.

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Efficiency and capacity development during cycling at 0-50% SOC without (left) and with (right) hydraulic shunt between the electrolyte tanks. Working conditions: current density 100 mA cm⁻², temperature 40 °C, electrolyte volumes 0.06 dm³.

