SELF-DISCHARGE OF ZINC-BASED HYBRID FLOW BATTERIES

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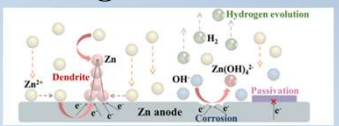
Zinc-air hybrid flow batteries (ZAHFBs)

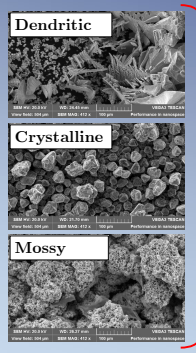
Advantages

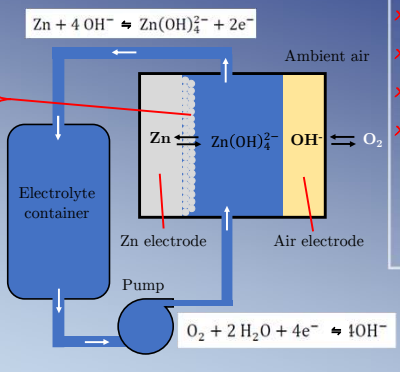
- ✓ High theoretical energy density
- ✓ Cheap and environmentally friendly
- ✓ Non-flammable aqueous electrolytes
- ✓ Possibility of membrane-less arrangement

Challenges



Taken from *Lu, W.; Zhang, C.; Zhang, H.; Li, X., Anode for Zinc-Based Batteries: Challenges, Strategies, and Prospects. ACS Energy Letters* **2021**, *6* (8), 2765-2785.





Self-discharge

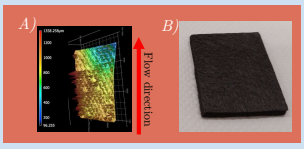
- ✗ Zinc dissolution into zincate ions
  $Zn + 2H_2O + 2\,OH^- \rightarrow Zn(OH)_4^{2-} + H_2$
- ✗ Surface passivation
  $2\,Zn + O_2 \rightarrow 2\,ZnO$
- ✗ Hydrogen evolution (gas formation)
  $2H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$
- ✗ Mechanical detachment of deposited Zn

The GOAL: Understand how morphology, temperature, electrolyte composition, and oxygen exposure influence self-discharge in planar and 3D electrodes.

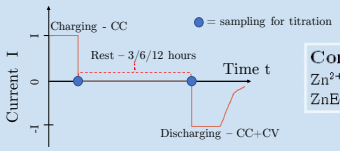
Methodology

Analysis

- Gravimetry (Zn pellets)
- Chelatometric titration (determination of the Zn^{2+} concentration)
- Capacity retention via galvanostatic charge/discharge
- Morphology and surface changes observed by SEM/LSCM



A) Scaled-up 3D visualization of a zinc deposition onto a nickel planar electrode demonstrating uneven and non-homogeneous growth of the deposited zinc. B) An example of a felt electrode.



Complexation reactions

$Zn^{2+} + EBT \rightarrow ZnEBT$ (wine red)
$ZnEBT + EDTA^{4-} \rightarrow Zn(EDTA)^{2-} + EBT$ (blue)

*EBT = Eriochrome black T,
EDTA = Ethylenediaminetetraacetic acid

Controlled variables

- Temperature: 20 vs. 40 °C
- Electrolyte SOC and composition
- Electrolyte flow: 80 ml min^{-1} vs. static
- Gas purging: N_2 vs. ambient air

Standard conditions

Planar nickel:	3D graphite felt:
• 40 °C	• 40 °C
• 80 mA cm^{-2}	• 100 mA cm^{-2}
• 25 mAh cm^{-2}	• 150.1 mAh cm^{-2}
• 250 ml	• 100 ml

ΔQ - difference between charged and discharged capacitance
z - stoichiometric number of electrons
F - Faraday constant

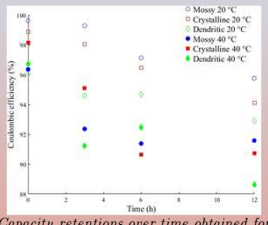
$$n_{Zn} = \frac{\Delta Q}{z \cdot F}$$

Aim of work

- **To develop** a methodology for studying the self-discharge of deposited zinc deposits in alkaline environments
- **To observe** the influence of different operating conditions:
  - **Temperature**
  - Electrolyte **SOC** and **composition**
  - Presence of **oxygen**
- **To reveal** the degree of involvement of different self-discharge processes
- **To compare** the effect of self-discharge for two types of zinc electrodes:
  - Planar substrate – **nickel**
  - **3D electrode** - graphite felt

Results:

Morphology effect (Ni plate)



Capacity retentions over time obtained for each morphology after different self-discharge periods at 20 and 40 °C

Morphology	Rate of self-discharge (μmol h^{-1})	
	20 °C	40 °C
Mossy	23.8	29.3
Crystalline	29.1	45.5
Dendritic	20.0	49.5

Different SoC (plate vs. felt)

SoC (%)	Rate of self-discharge (μmol h^{-1})	
	Nickel	Graphite
20	60.1	163.0
40	121.8	109.0
60	110.8	222.4
80	262.2	225.1
Areal capacity (mAh cm^{-2})	190.3	150.1

The **planar** electrode showed **lower self-discharge at low SoC**, but degradation increased sharply at 80% SoC. In contrast, graphite **felt improved with increasing SoC** and ultimately outperformed planar Ni at high charge levels.

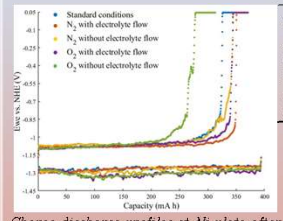
Effect of SoC (crystalline morphology)

SoC (%)	Zn^{2+} concentration (M)	Rate of self-discharge (μmol h^{-1})
100	0	159.4
75	0.175	37.6
50	0.35	42.9
25	0.525	27.5
0	0.7	49.4

Self-discharge was highest at 100% SoC, indicating that zincate-free electrolyte promotes rapid zinc degradation. Intermediate SoCs showed inconsistent behaviour, indicating complex competing effects between dissolution kinetics and passivation.

Atmosphere composition

Ni plate

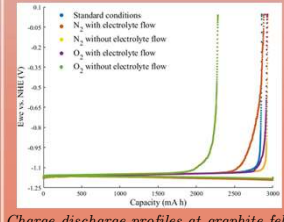


Charge-discharge profiles at Ni plate after 12 hours of self-discharge at 40 °C.

Setup	Rate of self-discharge (μmol h^{-1})
Standard conditions	45.5
$1/6$ with electrolyte flow	29.1
$1/6$ without electrolyte flow	25.2
O_2 with electrolyte flow	25.1
O_2 without electrolyte flow	114.7

- **Nitrogen atmosphere reduced self-discharge**
- No flow improved electrode stability
- Direct oxygen caused severe degradation
- **Air bubbling mimicked nitrogen effect**
- Gas-phase oxygen triggered parasitic reactions
- Dissolved oxygen had weaker impact

Graphite felt



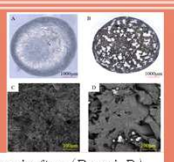
Charge-discharge profiles at graphite felt after 12 hours of self-discharge at 40 °C.

Setup	Rate of self-discharge (μmol h^{-1})
Standard conditions	145.5
N_2 with electrolyte flow	67.5
N_2 without electrolyte flow	21.3
O_2 with electrolyte flow	21.5
O_2 without electrolyte flow	1037.9

- Oxygen exposure reduced zinc dissolution
- Residual zinc remained after discharge
- **Passivation increased under oxygen presence**
- Passivation hindered zinc utilisation efficiency

Zn pellets

Zincate concentration (M)	Absolute weight difference (g)	Relative weight difference (%)	The rate of dissolution (μmol h^{-1})
0	0.049	16.6	0.248
0.14	0.027	8.7	0.117
0.175	0.027	7.9	0.125
0.35	0.029	10.7	0.127
0.525	0.028	10.0	0.137



Representative images of zinc pellet before (A and C) and after (B and D) dissolution. Used temperature: 20 °C, solution: 8M KOH

Conclusion

- This study quantifies how zinc self-discharge in zinc-based hybrid flow batteries, especially in alkaline zinc–air hybrid flow batteries is influenced by deposition morphology, temperature, electrolyte composition, and oxygen exposure.
- Crystalline and dendritic zinc layers exhibited increased degradation rates, with self-discharge rising from 29.1 to 45.5 μmol h^{-1} at 40 °C. **Direct air introduction caused up to 1037.9 μmol h^{-1} Zn loss in porous electrodes.**
- Flow conditions enhanced parasitic reactions, while nitrogen purging suppressed them. Zinc dissolution reached **3.6% after 12 h in 3D felt.**
- These results emphasise that targeted control of gas environment, morphology, and electrolyte dynamics is critical to minimising idle-state energy losses.

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