Optimising Zn-Ion Solvation Structures for Improved Durability and Performance in Zinc–Bromine Flow Batteries

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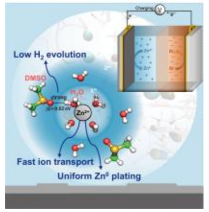
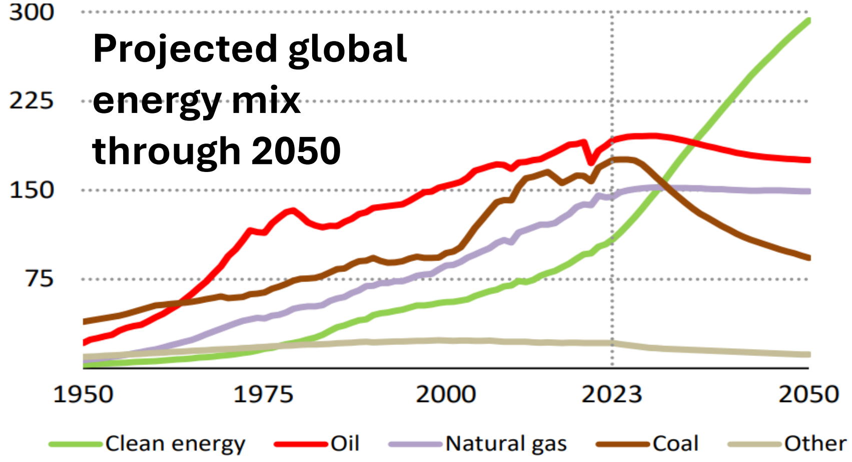
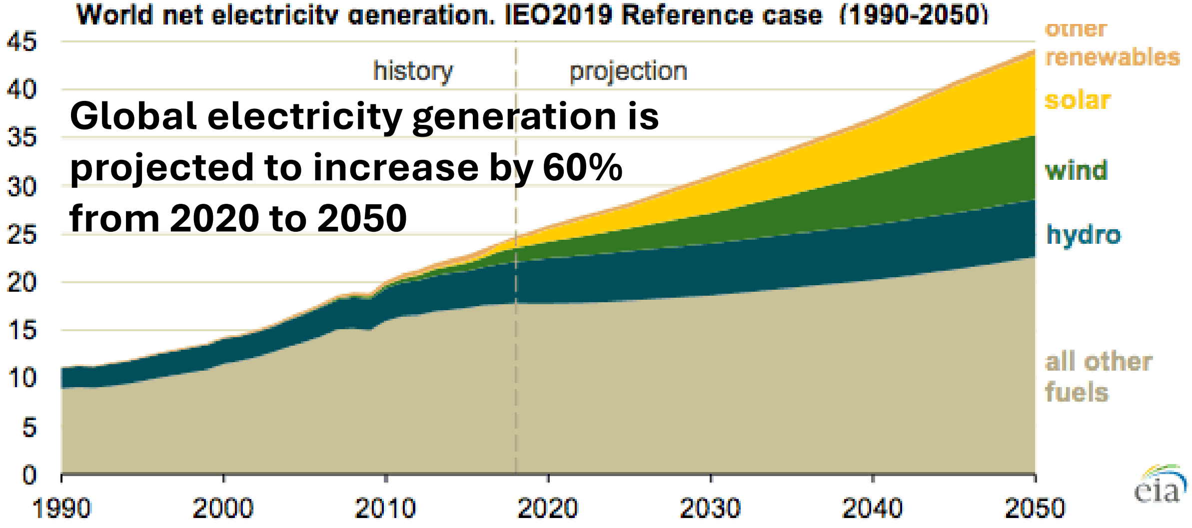


25 June 2025

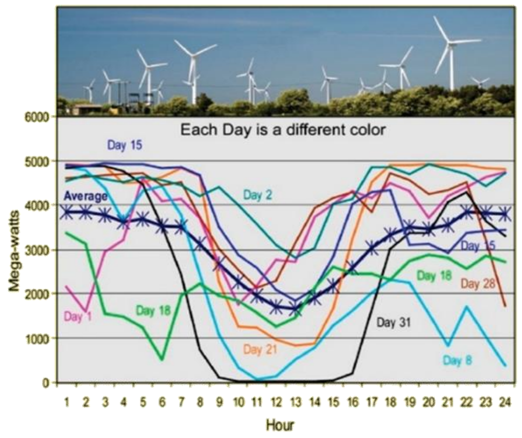
1.1 | Energy Storage in the Global Energy Transition

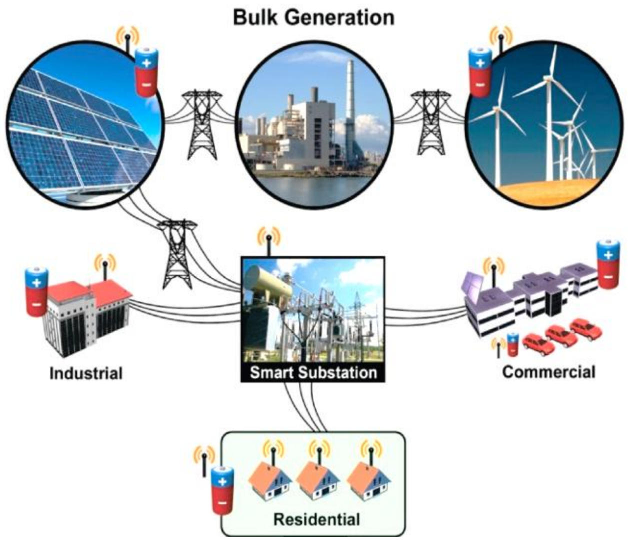
The Growing Role of Renewables





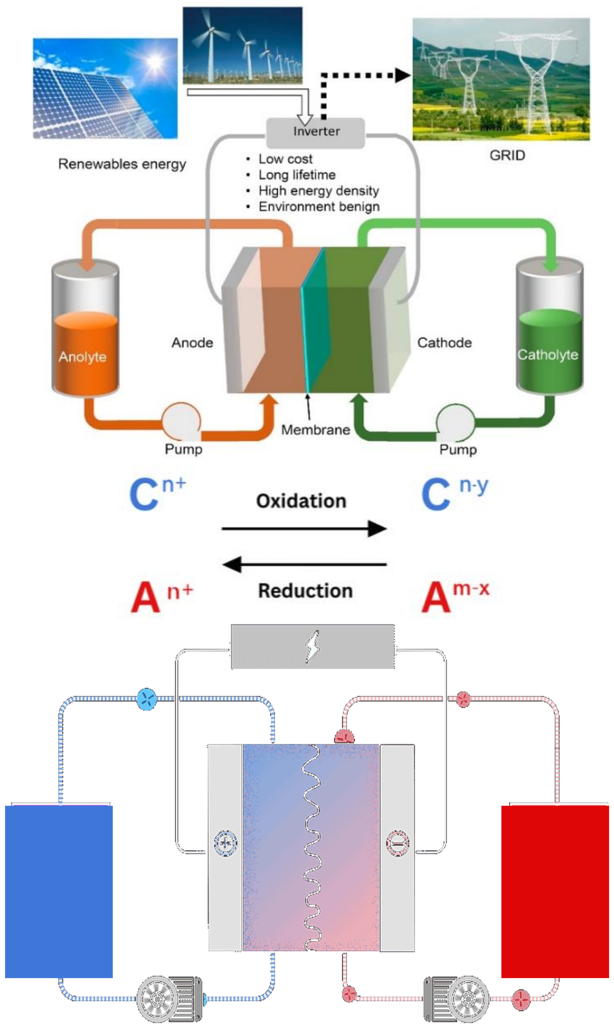
Renewables' Variability



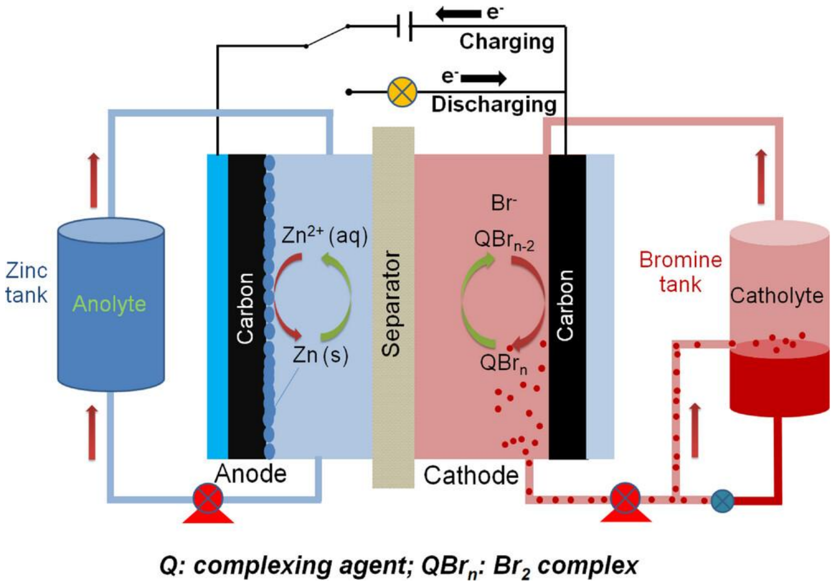


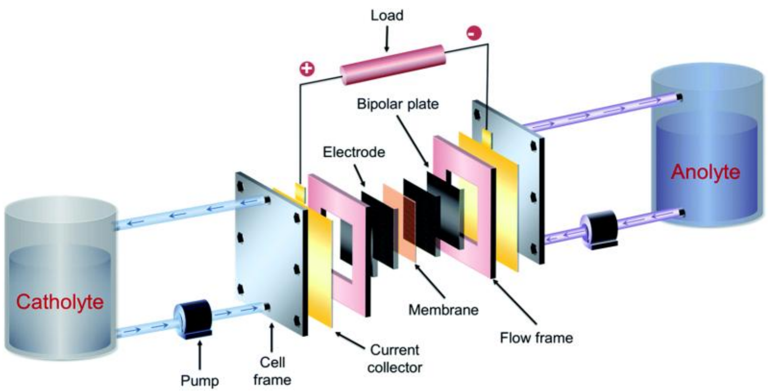
➢ **The deployment of renewables generation requires Energy Storage technology**

Chem. Rev., **2011**, 111, 5, 3577-3613



Long Duration Energy Storage



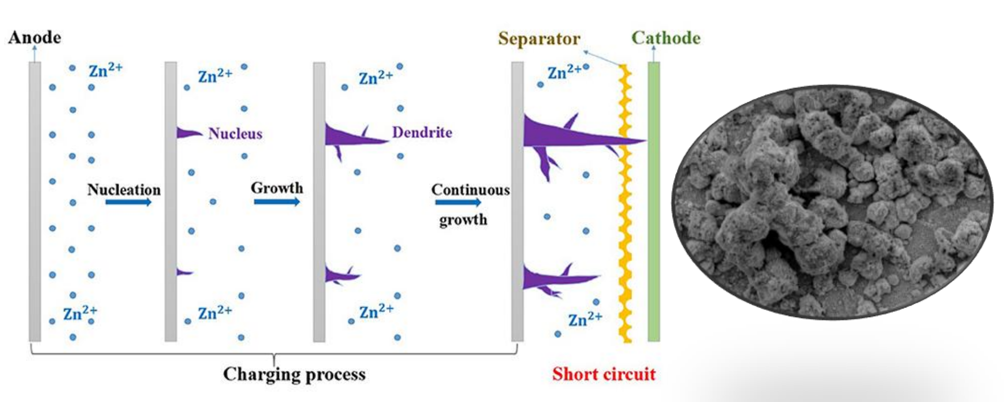


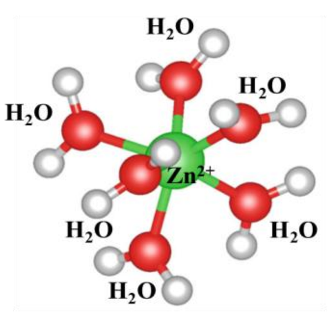
Redox Flow Batteries (RFBs)

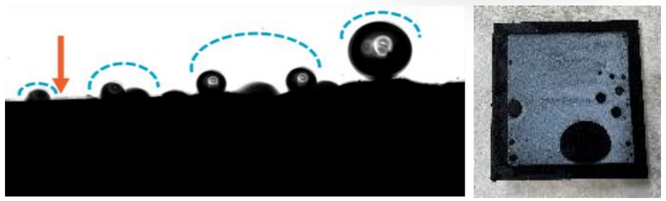
Key features of Zinc-Bromine Flow Batteries

- Higher energy density
- Lower material cost
- safely fully discharged
- Long cycle life
- Non-flammable & safe
- Easy to scale & maintain

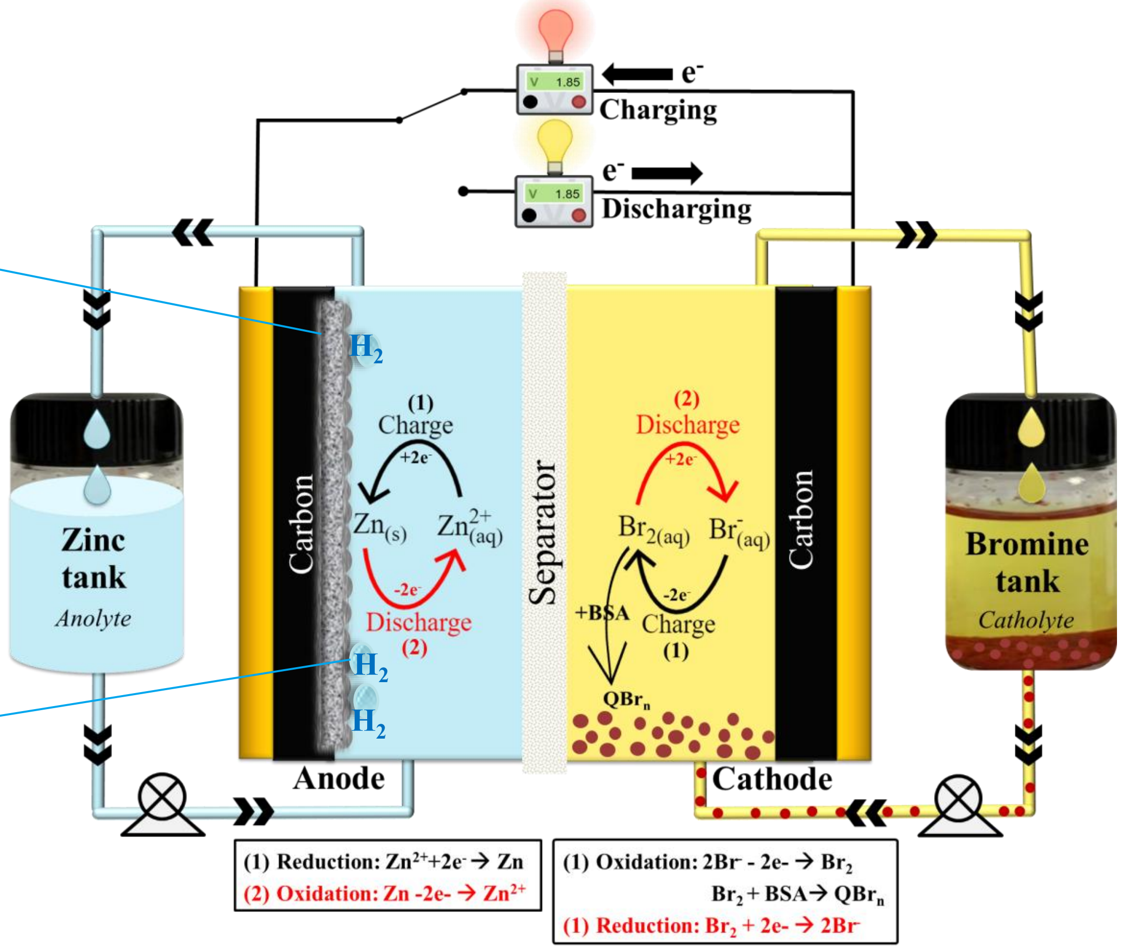
1.3 | Challenges of Zinc-Bromine Redox Flow Batteries





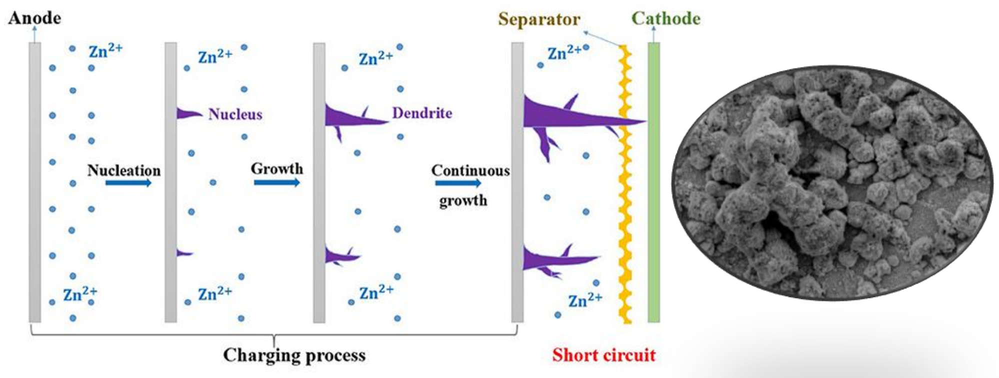


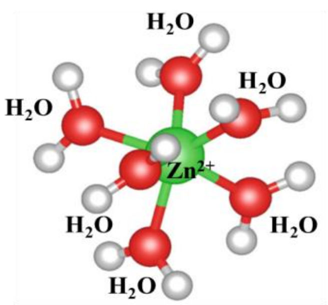
- ✓ HER is thermodynamically preferred in aqueous electrolytes
- ✓ HER compete with zinc plating reduction reaction

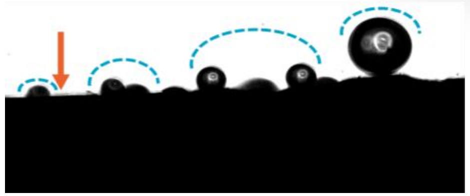


BSA: bromine sequestration agent

Q: complexing agent; QBr_n (n = 3, 5, 7): Br_2 complex







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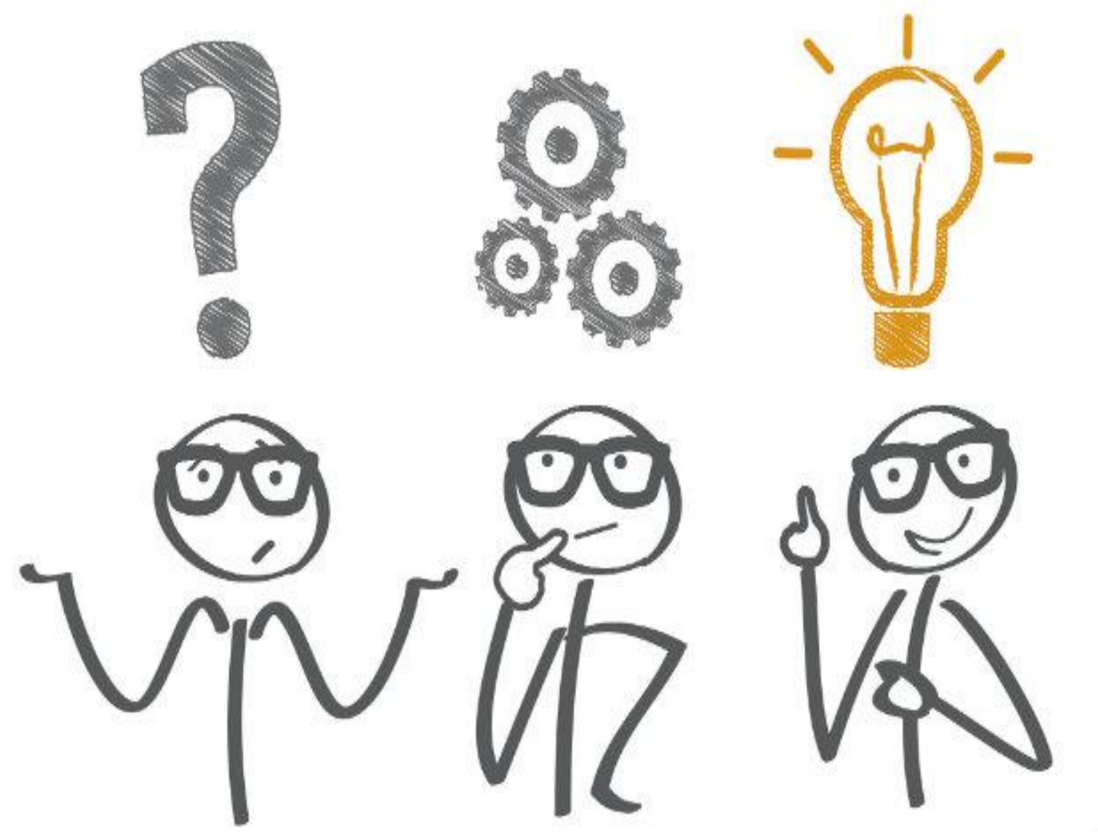
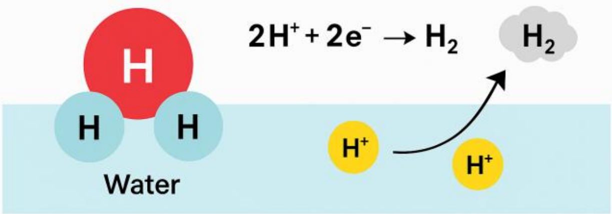


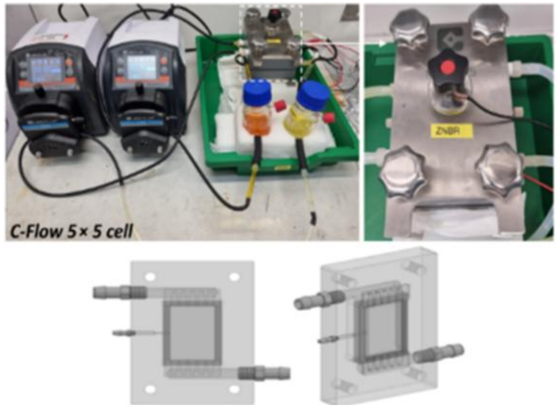
Dimethyl sulfoxide (DMSO) is a strong hydrogen-bond acceptor that helps control the zinc environment, reducing hydrogen gas (HER) and improving zinc plating behaviour.

1.5 | Better Zinc Plating Starts with Better Chemistry

In water-based electrolytes, zinc plating releases free protons (H^+).

These protons can combine to form hydrogen gas — this is called hydrogen evolution reaction, or HER.





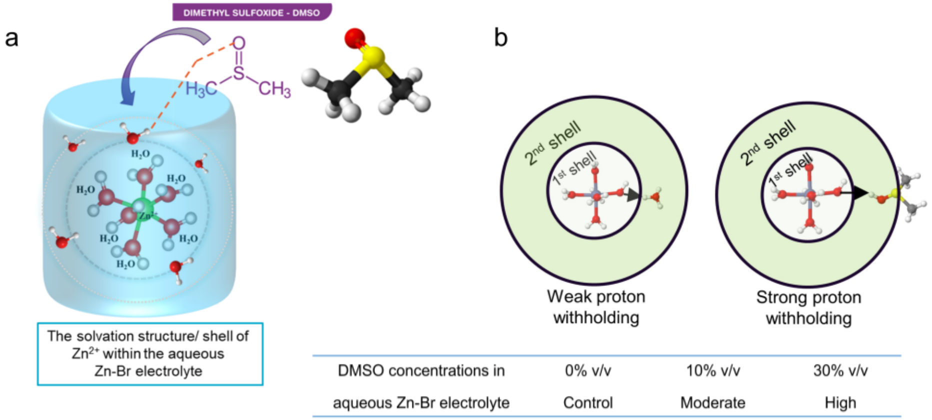
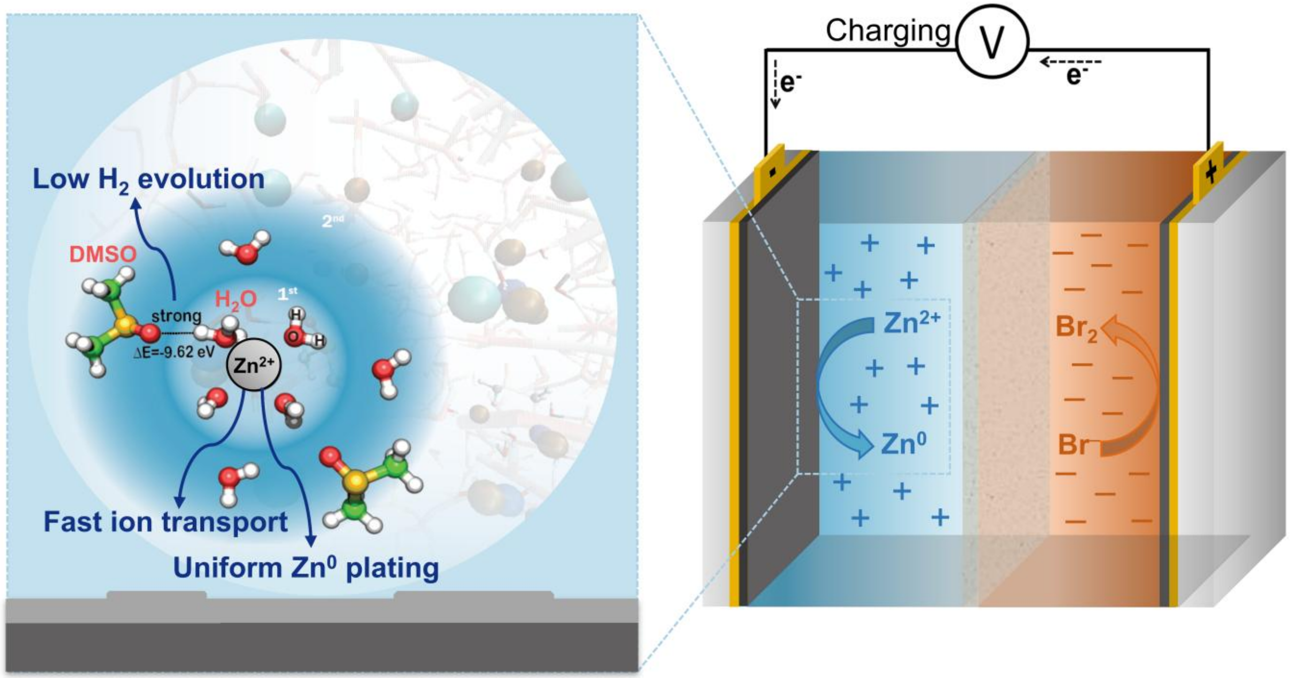


*Fig: **a**. A visual representation of the study's concept demonstrating how the solvation structure is modified in this project. **b**. Proton-withholding mechanism on the oxygen at different coordination shells in different electrolytes.*



Our solvation design:

- Captures free protons
- Keeps pH stable during zinc plating
- Reduces hydrogen evolution (HER)
- Supports fast and uniform Zn^{2+} transport
- Prevents electrode passivation

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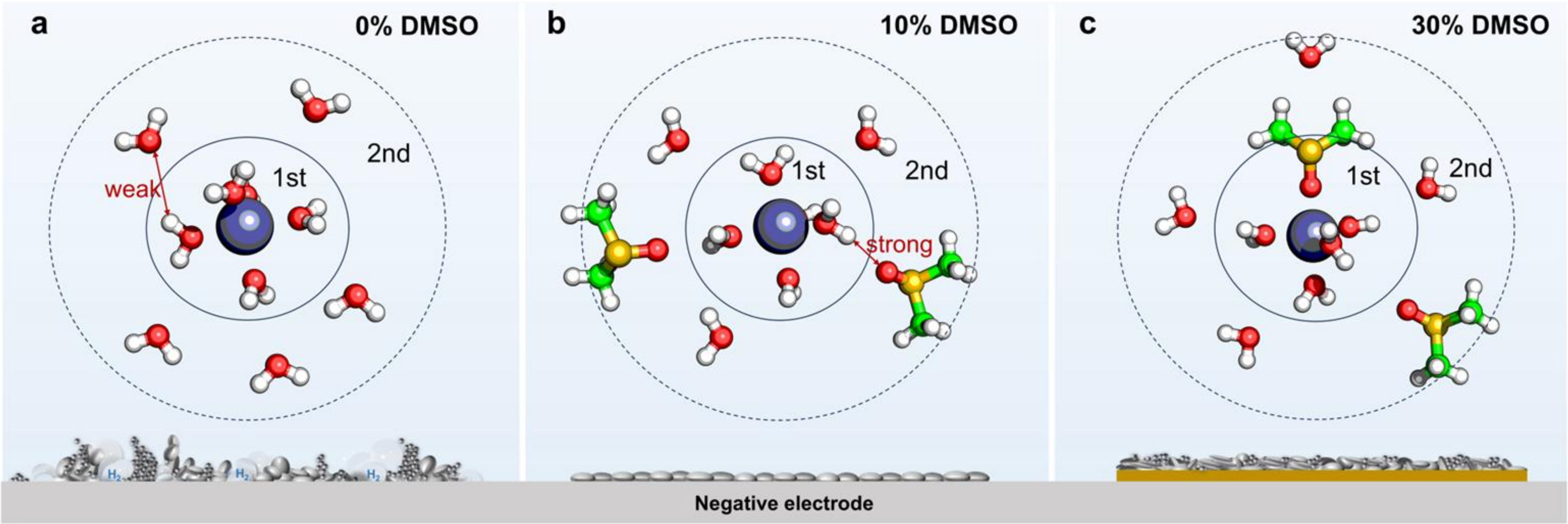
2.1 | Proton withholding mechanism on the oxygen at different Zn^{2+} coordination shells in the examined electrolytes



Advantages:

- Fast ion transport

Drawbacks:

- Intense H_2 evolution
- Zn^0 dendritic plating

Advantages:

- Fast ion transport
- Low H_2 evolution
- Uniform Zn^0 platting

Advantages:

- Low H_2 evolution

Drawbacks:

- Sluggish ion transport
- Ion-insulating interphase

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2.2 | Investigating Changes in Zn^{2+} Solvation Structures

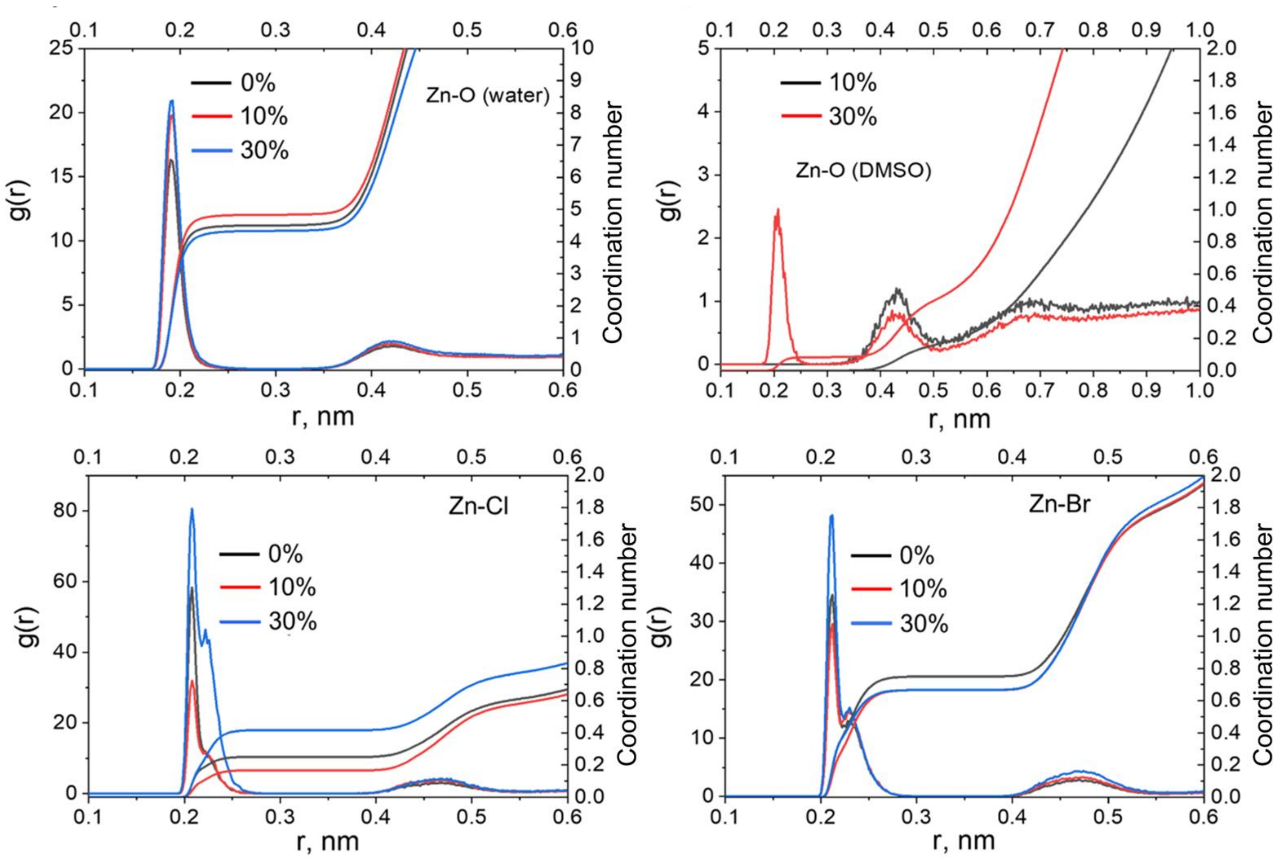


***Fig.** Radial distribution function g(r) for coordination of structure in examined electrolytes at 298 K, specifically, Zn-O (water), Zn-O (DMSO), Zn-Cl, and Zn-Br.*

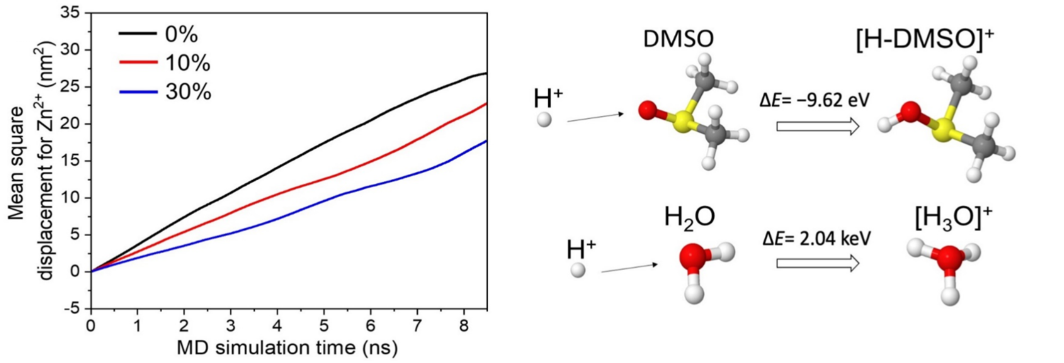


***Fig**. Diffusion analysis for Zn^{2+} by MD simulations for examined cells at 293 K. (i) DFT analysis for the energy of the hydrogen bond with different proton-accepting molecules.*

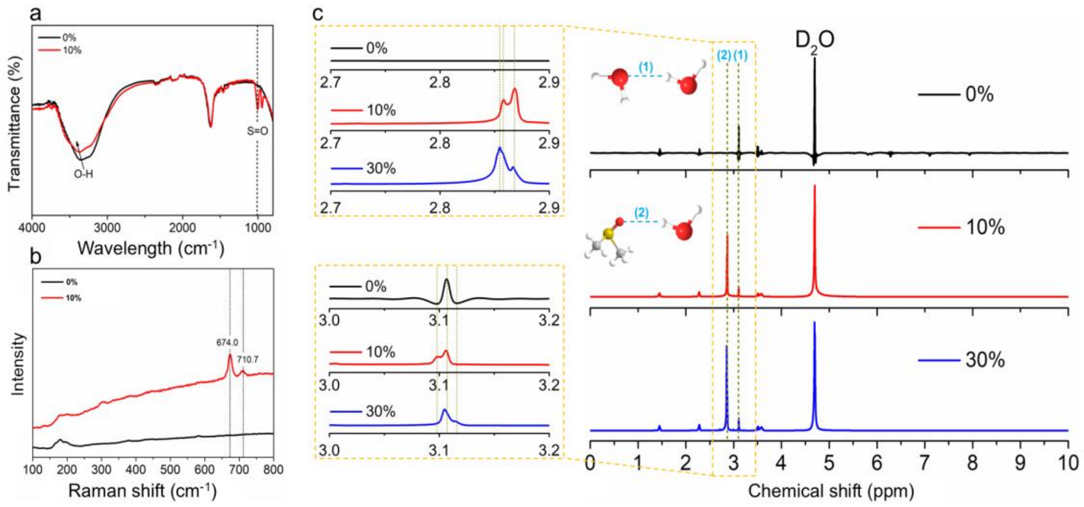


***Fig.** Description of chemical environments of the different electrolytes. Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra of two electrolytes (0% and 10%). Raman Spectra of different electrolytes. 1H nuclear magnetic resonance (NMR) of different electrolytes.*

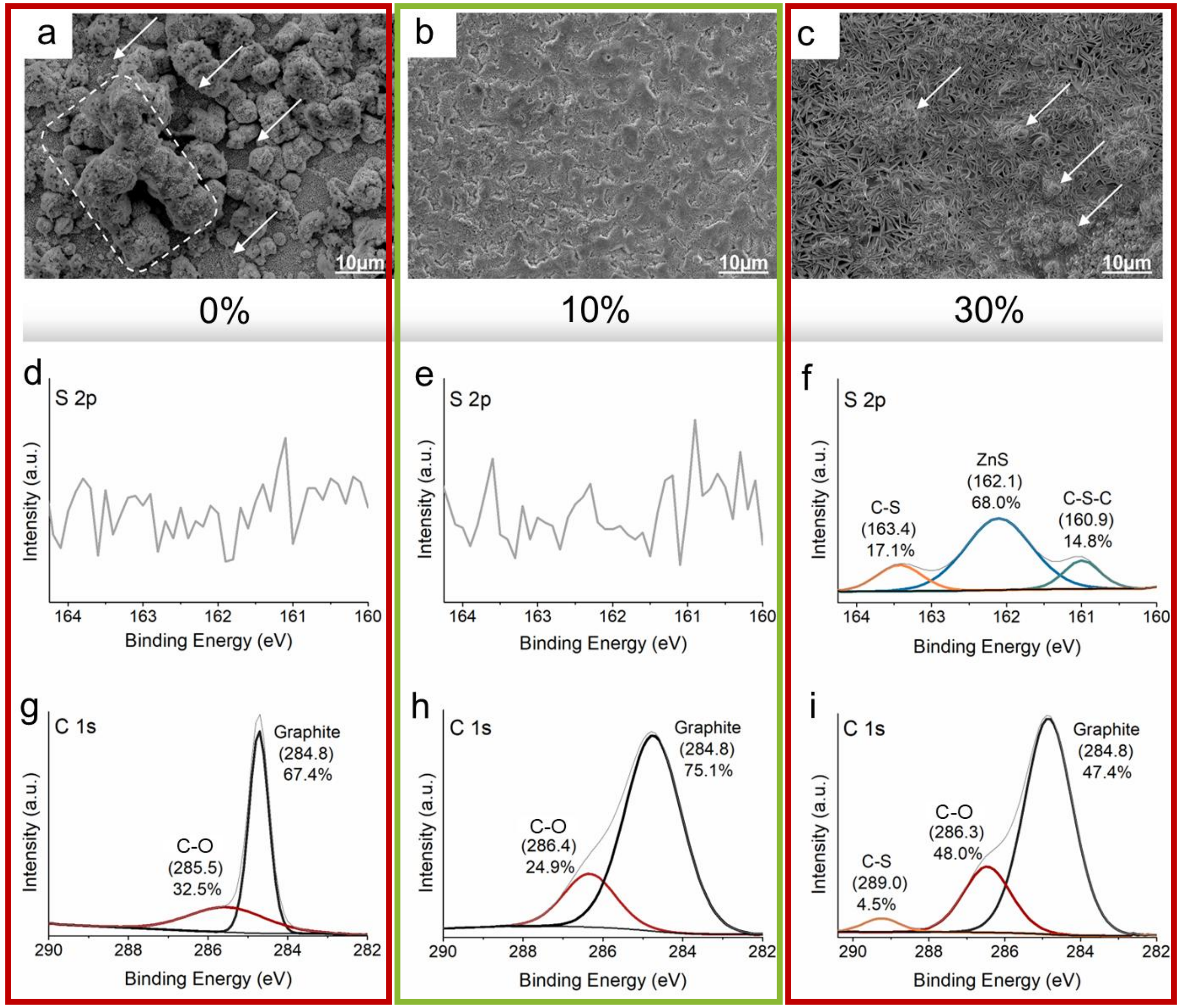


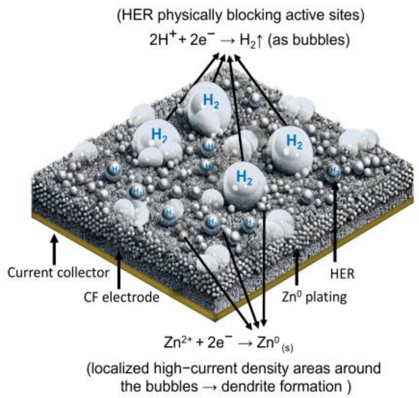
Fig. Characterisation of electrode surfaces after galvanostatic Zn plating/stripping in different electrolytes.

- **Zn Morphology (SEM):**

0% DMSO: H_2 bubbles disrupt plating → vertical Zn^0

10% DMSO: no gas → smooth, compact Zn

30% DMSO: High polarization → uneven, rough plating.



- **SEI Composition (XPS):**

10% DMSO: Stable SEI, no ZnS → DMSO stays intact.

30% DMSO: Thick ZnS-rich SEI → DMSO decomposes, blocks transport

- **Real-Time Plating**

0% DMSO: Bubbles compete with growth.

10% DMSO: Clean, stable deposition.

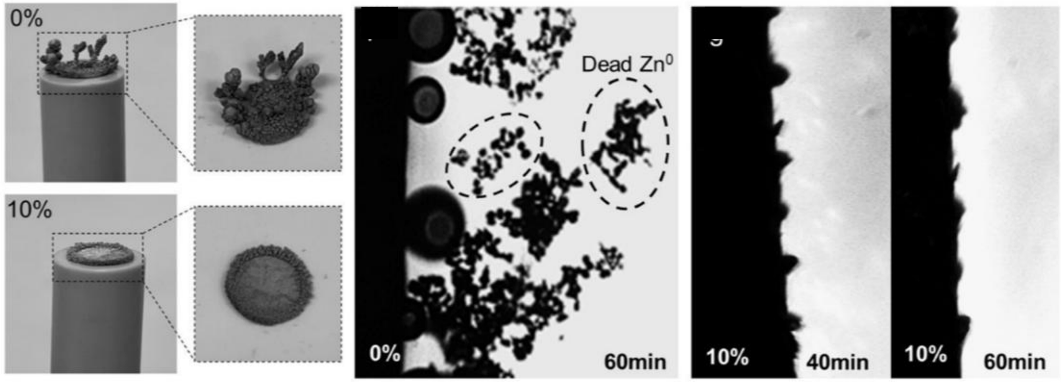


Fig. (left) *Digital images of electrodes charged for 1 hour at 5 mA cm^{-2} in ZBRBs with 0% and 10% DMSO, respectively.* ***(Right)*** *Optical images of Zn plating morphology over 1h charging time in an operando optical cell with 0% and 10% DMSO.*

2.4 | Electrochemical Analysis of Competitive Reduction Reactions

- **pH test:** 10% DMSO keeps pH stable, less H_2 gas.
- **CA test:** 10% DMSO shows better HER suppression.
- **CV plot:** higher current& lower overpotential = Zinc plates more easily with 10% DMSO
- **LSV:** 10% DMSO lowers HER onset, increasing overpotential and favoring Zn^0 plating over HER

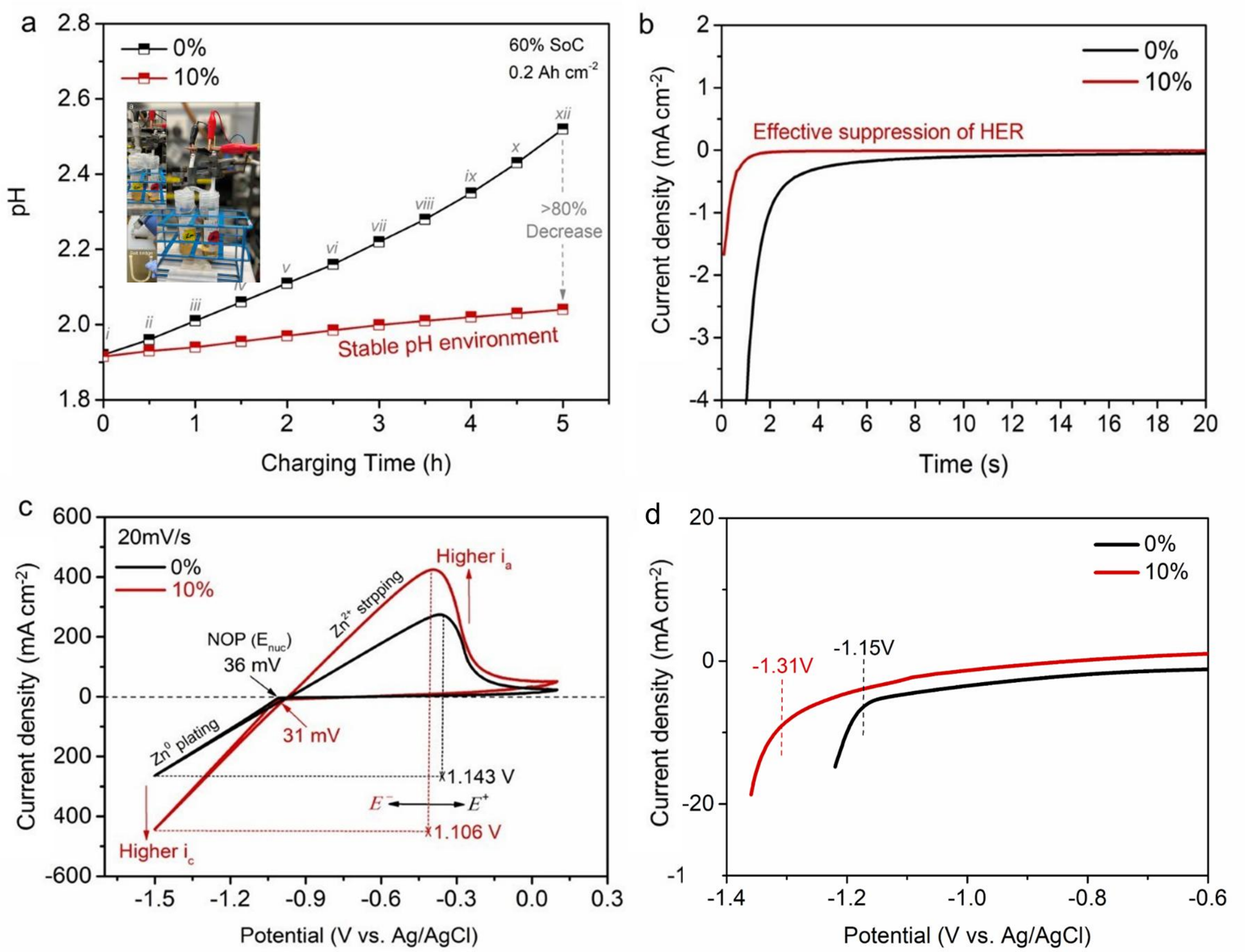
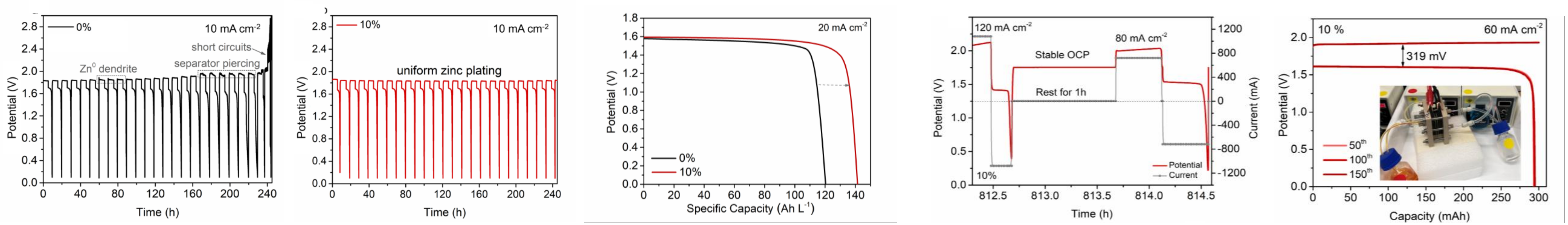
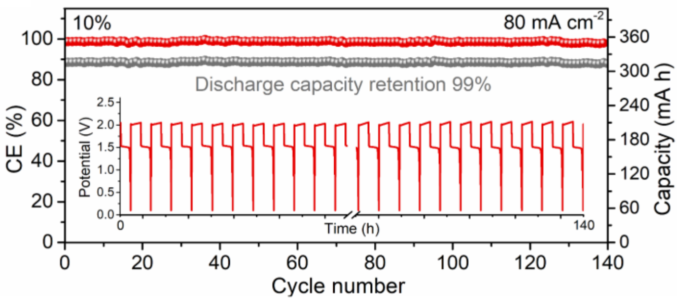
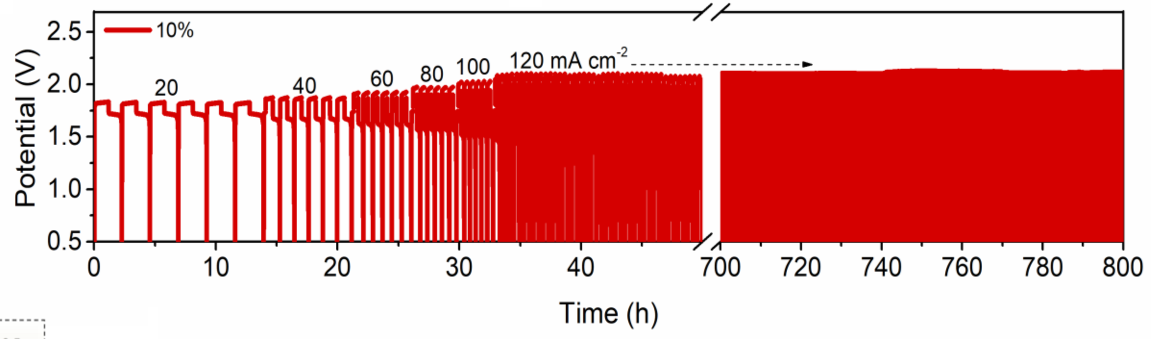


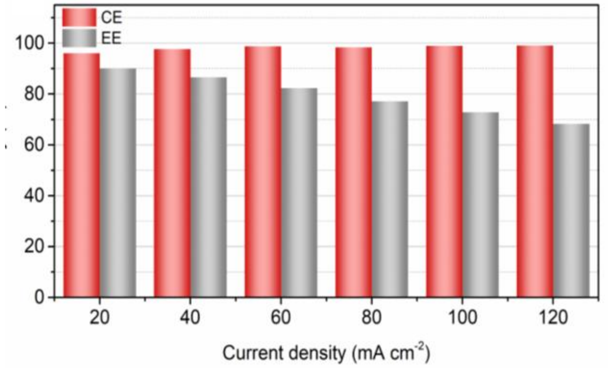
***Fig**. Analysis of pH levels and electrochemical performance of Zn plating and HER activity. **(a)** pH levels during galvanostatic Zn plating in examined electrolytes. **(b)** Chronoamperometry (CA) measurements illustrating the current response over time, assessing the stability of Zn plating and HER suppression under the applied potentials. **(c)** Cyclic voltammetry (CV) profiles showing the redox behaviour and potential window of the zinc electrode at a scan rate of 20 mV s^{-1}. **(d)** Linear sweep voltammetry (LSV) for HER polarisation in different electrolytes.*

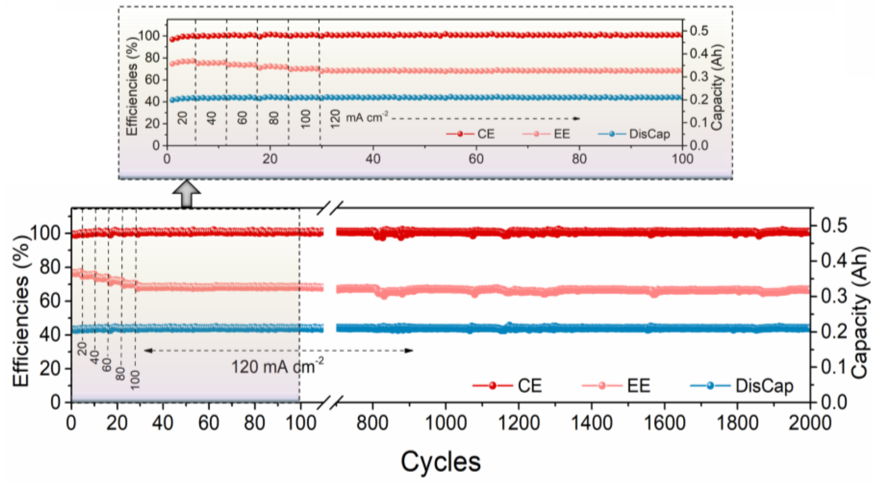
2.5 | High-Performance Zn–Br Flow Battery Enabled by DMSO



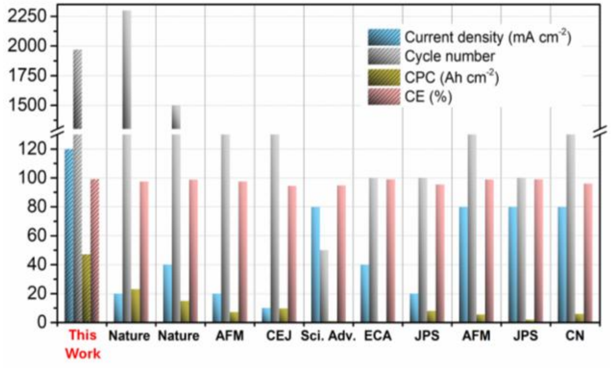








- **Efficient at scale:** Stable cycling in 9 cm² and 25 cm² flow cells.
- **High discharge capacity: 35.6 Ah cm⁻² at** 80 mA cm⁻² with >99.8% Coulombic efficiency.
- **Low voltage hysteresis: 0.3 V** (stable over 150+ cycles).
- **Outstanding Performance:** CPC of **47.2 Ah cm⁻²** over ~2000 cycles at 120 mA cm⁻².



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3 | Conclusion

IFBF

GDCh **Research Article** Angewandte Chemie International Edition www.angewandte.org

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Zinc-Bromine Flow Batteries ***Hot Paper***

Tailoring Zn-ion Solvation Structures for Enhanced Durability and Efficiency in Zinc–Bromine Flow Batteries

Norah S. Alghamdi, Dmitrii Rakov, Xiyue Peng, Jaeho Lee, Yongxin Huang, Xingchen Yang, Shuangbin Zhang, Ian R. Gentle, Lianzhou Wang, and Bin Luo**

- Intense H_2 evolution
- Zn^0 dendritic plating

- Low H_2 evolution
- Uniform Zn^0 platting
- Fast ion transport

“By carefully tuning zinc solvation with just the right amount of DMSO, we unlocked smooth plating, suppressed hydrogen evolution, and achieved one of the highest zinc capacities ever reported, 47.2 Ah cm^{-2}, even at high current.”

4 | Acknowledgments

- My PhD supervisors (Prof. Bin Luo and Prof. Ian Gentle)
- Dr. Dimitrii Rakov
- My PhD group members at UQ
- The audience
- IMSIU funding & Saudi support

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Better Battery Performance Starts with Better Chemistry

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