Enhancing Zinc-Iodine Flow Battery Performance: The Role of Ammonium Acetate and Bromide Additives in Cyclability and Current Density Improvement

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Introduction

Zinc-iodine hybrid flow batteries (ZIFBs), characterized by their near-neutral electrolyte pH and high energy density, are gaining traction as potential solutions for grid-scale energy storage. However, the persistent issue of zinc dendrite formation significantly limits their zinc plating capacity and cyclability.

At the anode (Zn side):

$$Zn^{2+} + 2e^- \leftrightarrow Zn$$

$: E^0 = -0.762$ V (vs SHE)

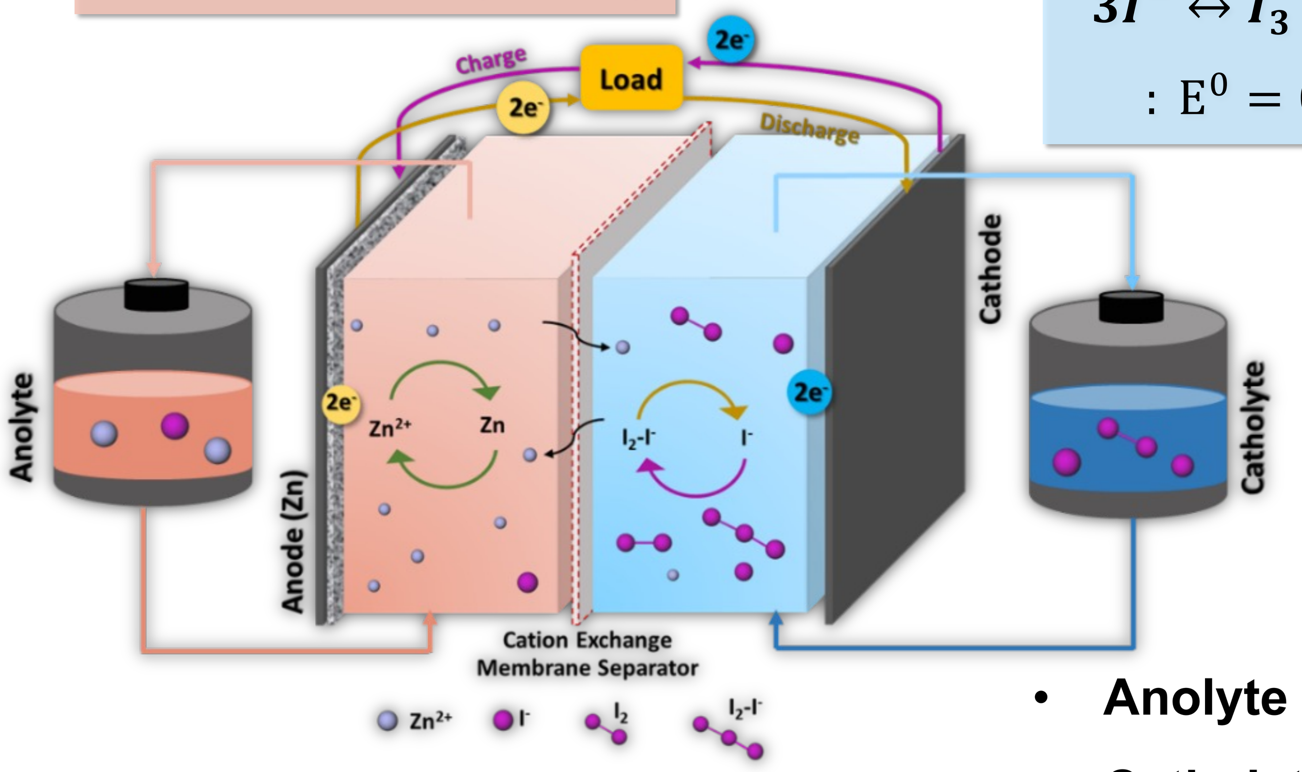
At the cathode (iodine side):

$$2I^- \leftrightarrow I_2 + 2e^- \quad .....(1)$$

$$I^- + I_2 \leftrightarrow I_3^- \quad .....(2)$$

$$3I^- \leftrightarrow I_3^- + 2e^- \quad .....(3)$$

$: E^0 = 0.536$ V (vs SHE)



Overall reaction

$$3I^- + Zn^{2+} \leftrightarrow I_3^- + Zn$$

$: E° = 1.3\ V\ (vs\ SHE)$

- **Anolyte :** 1M ZnI_2 + 1 M NH_4OAc
- **Catholyte :** 1M ZnI2 + 1 M NH4Br

Figure 1: Figure 1. Zinc-iodine redox flow battery.

Electrolyte characteristics

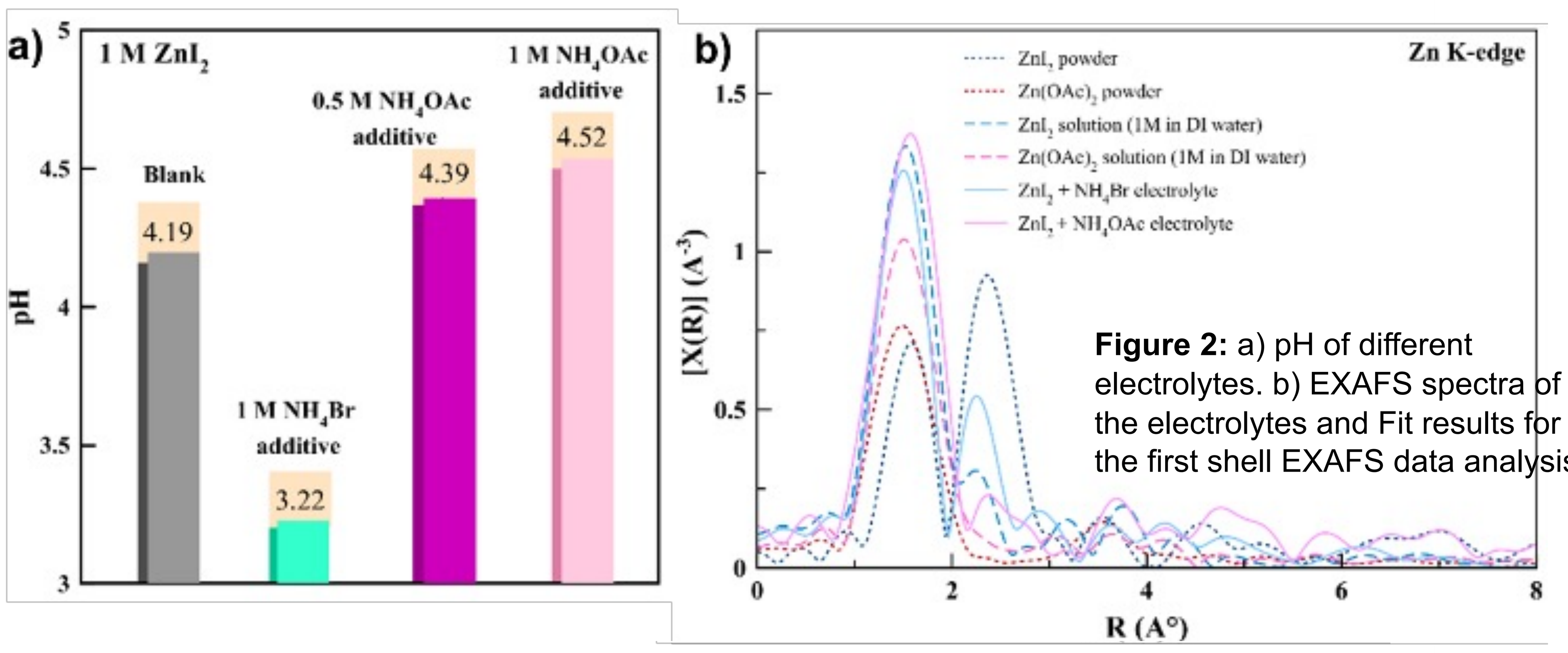


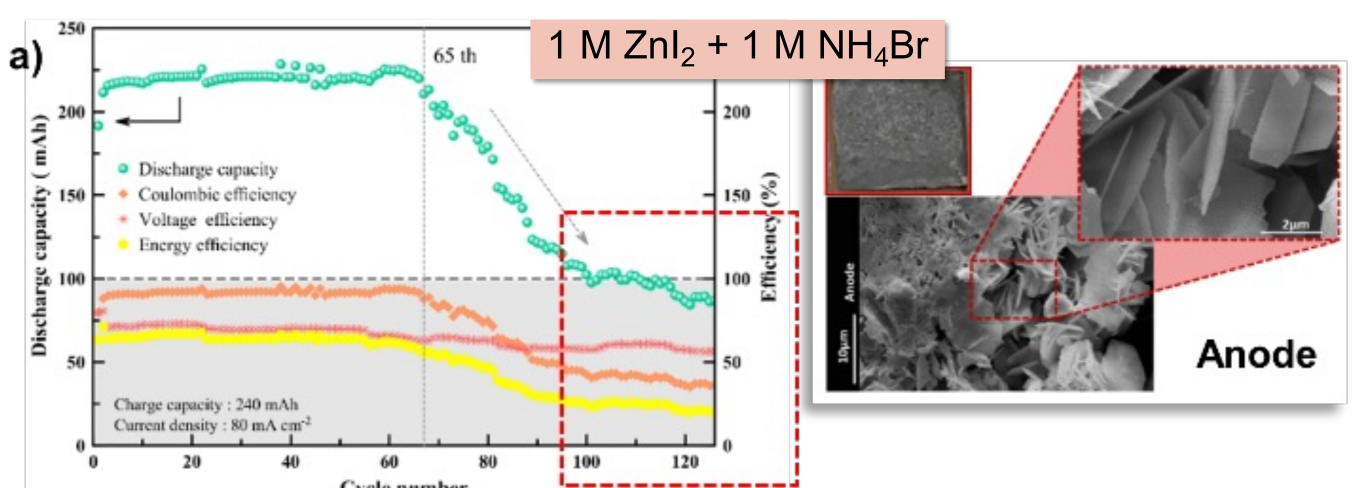
Figure 2: a) pH of different electrolytes. b) EXAFS spectra of the electrolytes and Fit results for the first shell EXAFS data analysis.

Sample	Zn-O CN	R(A°)	$\sigma^2(10^{-3}A^{o2})$	ΔE_0 (eV)
1M $Zn(OAc)_2$ solution	2.9 ± 0.8	2.04 ± 0.02	4.1 ± 4.0	0.04 ± 2.91
1M ZnI_2 + 1M NH_4OAc	3.4 ± 0.6	2.07 ± 0.01	2.2 ± 2.4	2.43 ± 1.82
1M ZnI_2 solution	4.3 ± 0.7	2.06 ± 0.01	5.4 ± 3.5	−2.13 ± 1.84
1M ZnI_2 + 1M NH_4Br	-	-	-	-

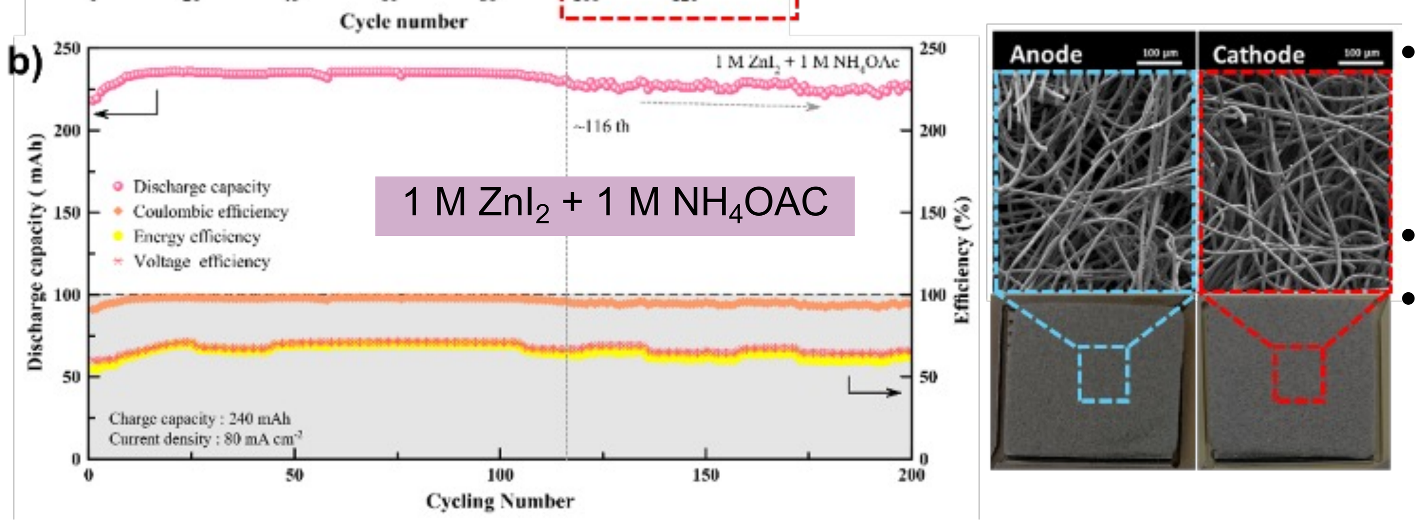
The list parameters reflect the final best fit. (CN, coordination number; R, interatomic distance; σ^2, Debye-*Waller* factor; E_0, the change of threshold energy)

- The local structure of the first shell in the ZnI_2 + NH_4OAc electrolyte is similar to that of the $Zn(OAc)_2$ solution. These results confirm the coordination of Zn^{2+} with acetate anions in the ZnI_2 + NH_4OAc electrolyte.

Stability of battery



- battery lasted only 65 cycles
- Lower CE
- Flake-like particles on electrode

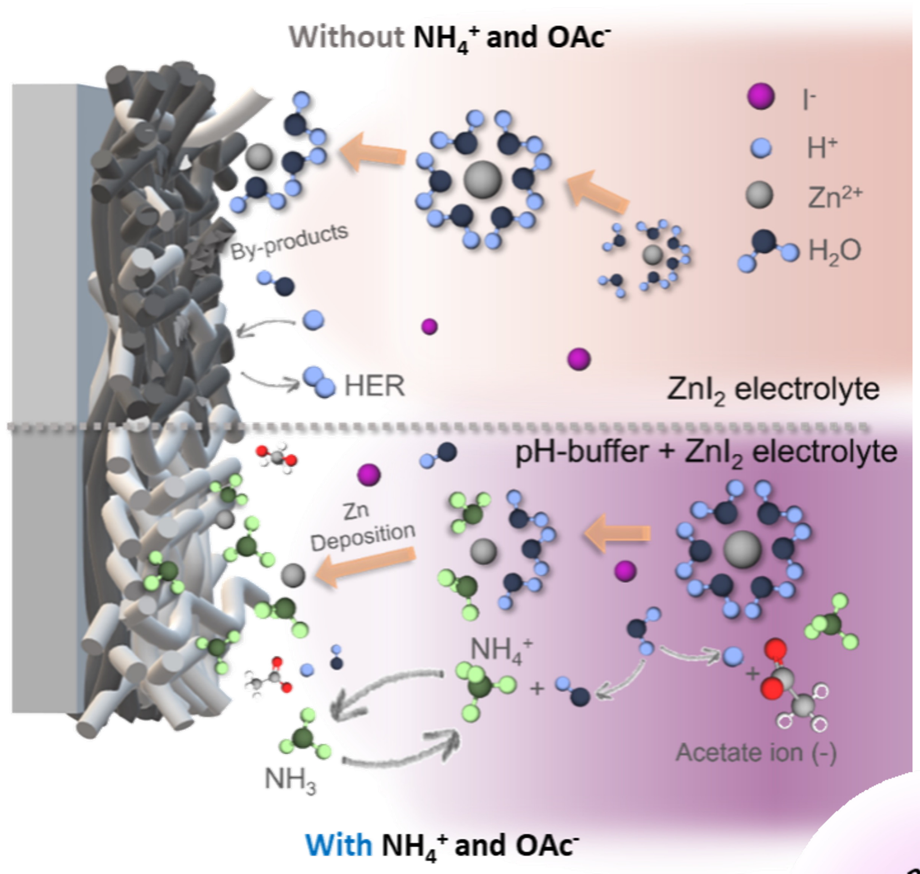


- ZIFBs with NH_4OAc show stable cycling over 200 cycles
- CE of 95%
- No insulating by-products on the electrode cycled

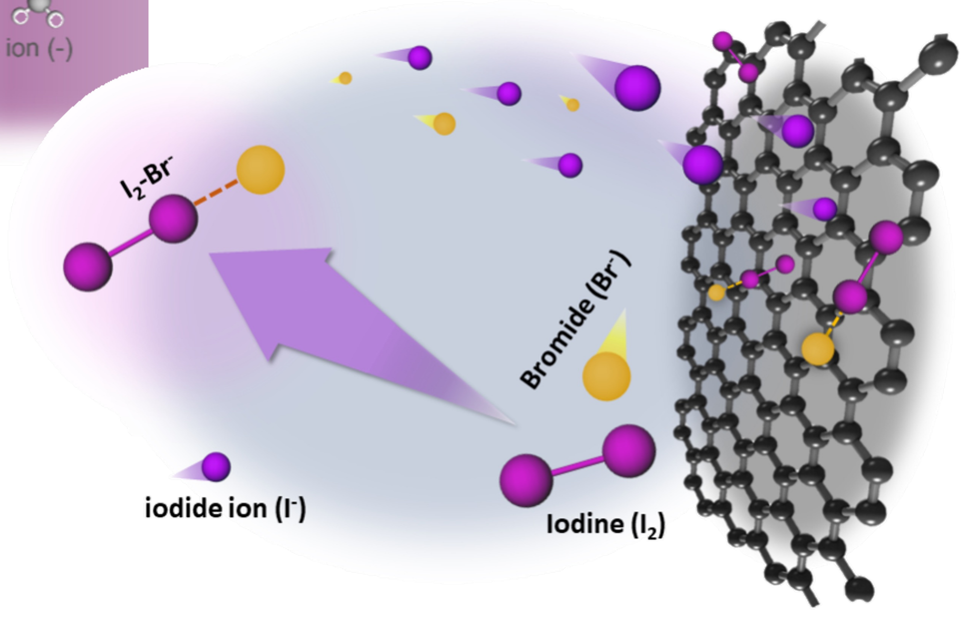
Figure 4: Discharge capacity and efficiencies of the ZIFBs using a) 1 M NH_4Br and b) 1 M NH_4OAc and FE-SEM images of the post-cycled anode at 80 mA cm^{-2} with a capacity of 20 mAh cm^{-2}.

Ammonium acetate & bromide in electrolyte

Our study addresses the challenges by introducing a dual additive strategy, employing ammonium acetate for the anolyte and ammonium bromide for the catholyte. The ammonium ions are instrumental in coordinating with zinc ions, leading to uniform zinc deposition and effectively mitigating dendritic growth. NH_4^+ induces an electrostatic shielding effect on the Zn metal plate, functioning as an ion distributor.



- Acetate ions (OAc^-) stabilize the anolyte pH and suppress undesirable side reactions, aligning with recent advancements in electrolyte modification techniques.
- strategies to maximize the potential of ZIFBs involve adding bromide ions (Br^-) as a complexing agent in catholyte.



- Br^- ion stabilizes I_2 by forming I_2-Br^- complexes, thereby enhancing the battery's capacity.

Battery performance

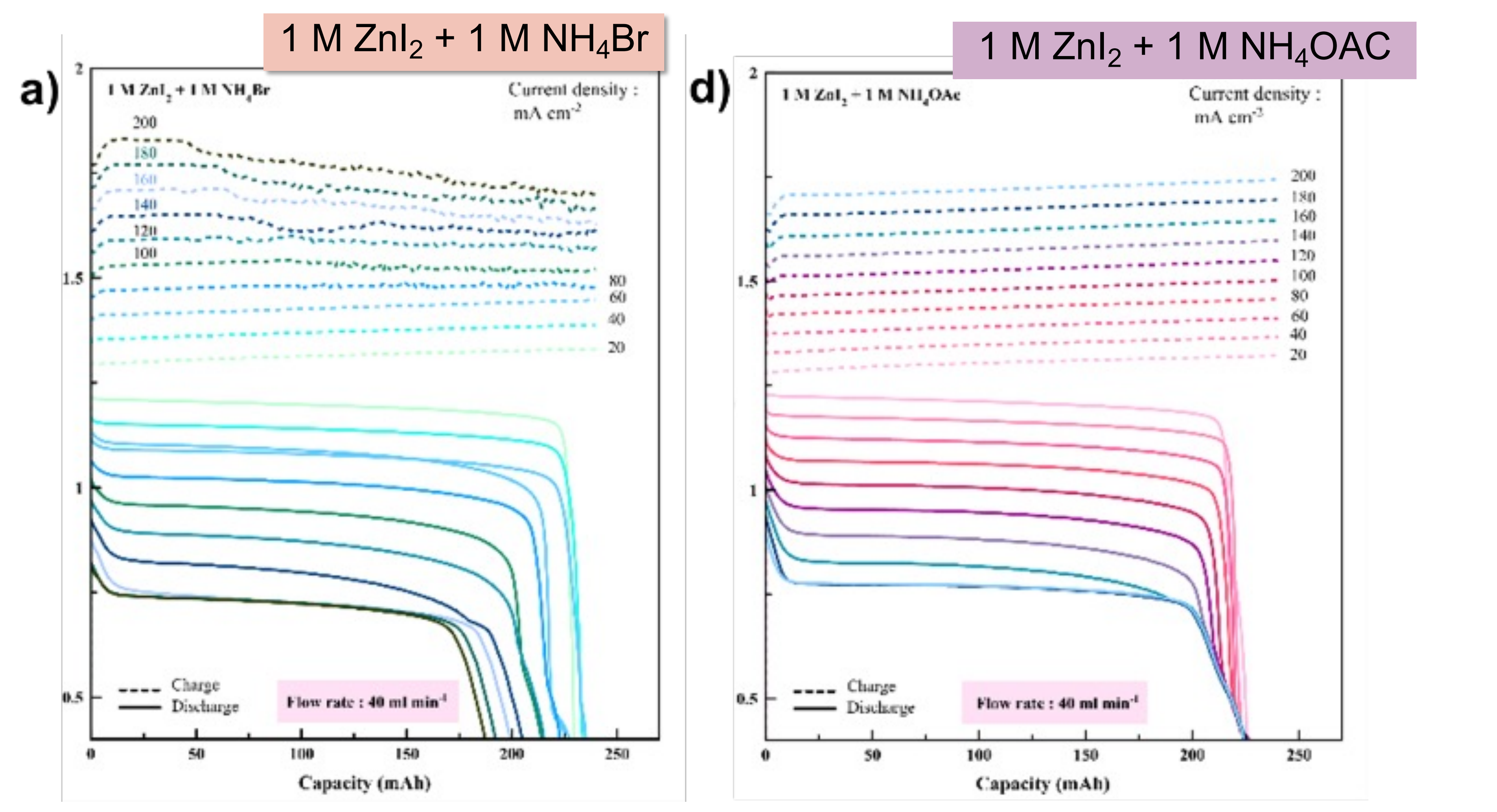


Figure 3: Galvanostatic voltage profiles of the ZIFBs using a) 1 M NH_4Br and b) 1 M NH_4OAc at different current densities between 20-200 mA cm^{-2} with a capacity of 20 mAh cm^{-2}.

- The battery with 1 M NH_4OAc as an additive electrolyte displays a lower overpotential compared to 1 M NH_4Br and maintains consistent discharge capacities even at a current density of 200 mA cm^{-2}.

Conclusions

We incorporated NH_4^+, OAc^-, and Br^- ion into the electrolyte of ZIFB. NH_4^+ ions serve as competing cations, creating a dynamic electrostatic shielding layer on the zinc electrode to mitigate dendrite growth. Concurrently, OAc^- ions act as a pH buffer, maintaining an optimal pH of 5.14. These combined effects enabled charging/discharging at a current density of 200 mA cm^{-2} with an areal capacity of 20 mAh cm^{-2}. Remarkably, the cells maintained consistent performance over 200 cycles, with a coulombic efficiency of 95% at 80 mA cm^{-2}.

These findings significantly contribute to the field of ZIFBs, offering a novel method to enhance performance and extend battery viability for practical applications.

Acknowledgements

P.T. acknowledges the funding from the Chulalongkorn Academic Advancement into its Second Century Project: C2F.

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