

A promising imidazolium-based bromine-complexing agent for enhancing the overall performance of zinc-bromine flow batteries

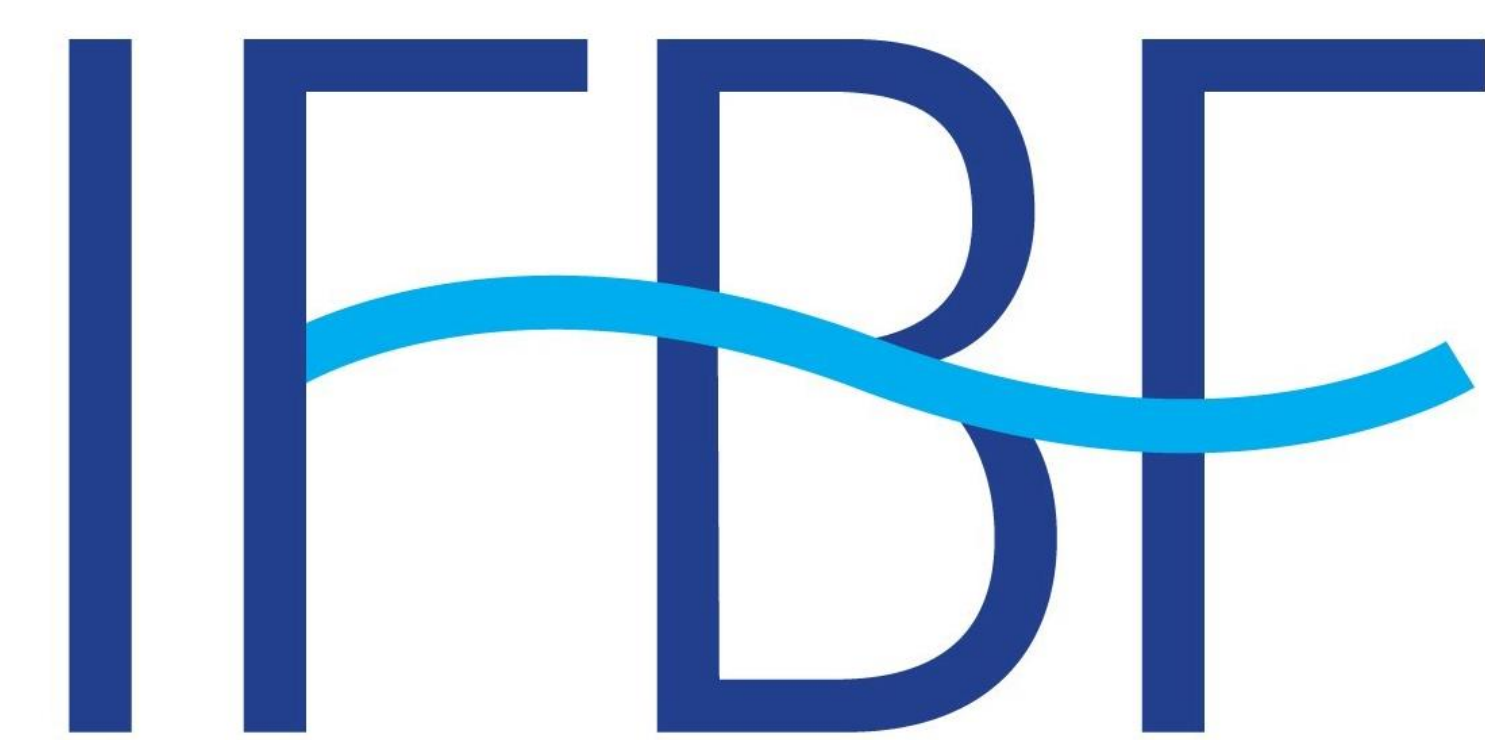
Deokhee Yun¹, Daewon Chung¹, Yunsun Kim¹, Doeun Kim², Youngho Lee³, Joonhyeon Jeon^{1,2} *

¹ Division of Electronics & Electrical Engineering, Dongguk University, Seoul, Korea

² Department of Advanced Battery Convergence Engineering, Dongguk University, Seoul, Korea

³ Department of Energy and Advanced Material Engineering, Dongguk University, Seoul, Korea

Email: memory@dgu.edu*, thekey916@dgu.edu¹



Introduction

Zinc-bromine redox flow batteries (ZBBs) should use a bromine-complexing agent (BCA) as an additive for bromine stability. However, the weak molecular structure and stability of BCA sometimes negatively affect battery's overall performance, such as electrolyte resistance increase, irreversible interaction between bromine and high-order polybromide anions, redox reaction reversibility decrease and so on [1].

To address this issue, this paper describes an imidazolium-based BCA reported recently by us [2], which is able to enhance the overall electrolyte performance (including stable capture and release of Br₂) in a working ZBB cell.

The proposed 1,2-dimethyl-3-ethylimidazolium bromide (DMEIm·Br, C₇H₁₃BrN₂) significantly contributes to apparently enhancing reaction kinetics and reversibility of Zn²⁺/Zn(s) and Br/Br₂ redox couples by inducing highly reversible zinc-lating/stripping, by strong electrostatic shielding effect and bromine-capture/release (along with strong bromine-binding strength) in anolyte and catholyte solutions, respectively.

This is due to the fact that as compared to other BCAs- MEM·Br, MEP·Br [3], the superior chemical and molecular structural characteristics of the DMEIm·Br lead to a robustly positive impact on all performance indicators, often containing electrolyte-solution and charge transfer resistances, zinc plating/stripping reversibility, and the interaction reaction force between bromine and high polybromide anions.

Further, through CV and cell test, the low steric-hindrance (i.e., large open steric angle between methyl and ethyl groups) due to the planar-molecular structure of the DMEIm·Br is also experimentally proved to undergo fast and reversible interaction reaction of Br₂ ↔ Q·Br Br₃⁻ (i.e., bromine complexation and anion exchange).

Further, the superior chemical and electrochemical properties of the DMEIm·Br in working electrolyte is shown to lead to improved CE and VE of averagely 98.25 (93.4) and 86.19% (88.77%) at the electrolyte temperature of 25 °C (60 °C) which are 5.53 (24.19) and 7.29% (16.99%) higher than the pristine one, respectively.

In particular, owing to the strong molecular-polarisability and low steric-hindrance of the DMEIm·Br, apparently improved discharge-capacity retention of averagely 99.17% for 200 cycles even at the temperature of 60 °C is achieved, along with dramatically ignorable discharge-capacity loss of only 1.46 % vs. 1st cycle at 200th cycle.

This contribution provides new insights into the effects of a planar-molecular structure BCA for highly enhancing the overall performance of ZBBs.

Table 1. Steric bond angle and polarizability of (a) MEM·Br, (b) MEP·Br, and (c) DMEIm·Br

Heterocycle features	(a) MEM·Br	(b) MEP·Br	(c) DMEIm·Br
Molecular geometry diagram (θ : steric bond angle)			
	($\theta = 136.05^\circ$)	($\theta = 125.08^\circ$)	($\theta = 180^\circ$)
Electrostatic potential map			
Molecular polarizability (a.u.)	86.257	73.833	88.933

Results and discussion

The remarkable effectiveness of DMEIm·Br is experimentally compared with those of conventional MEM·Br and MEP·Br and evaluated through the following experimental measurements: cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), open-circuit voltage (OCV), and cyclic cell testing for 200 cycles at the temperatures of 25 and 60 °C.

Experimental results demonstrate that as compared to the conventional MEM·Br and MEP·Br, the DMEIm·Br-supported solution in working ZBB electrolyte exhibits most apparently enhanced reaction kinetics and reversibility of Zn²⁺/Zn(s) and Br/Br₂ redox couples, resulting in not only 4.88(1.73) and 15.14 (5.47) times higher diffusion coefficient and specific capacitance of Zn²⁺ (Br⁻) ion than the pristine one, respectively, but also 2.4 and 3.1 times lower charge-transfer and Warburg-diffusion resistances.

Furthermore, OCV and SEM measurements show that a strong molecular-polarisability of the DMEIm·Br causes not only much higher bromine complex stability and stronger bromine binding strength in charged electrolyte than the MEM·Br and MEP·Br, but also induces a strong electrostatic shielding effect (for a highly uniform electrodeposition of zinc) on the anode surface.

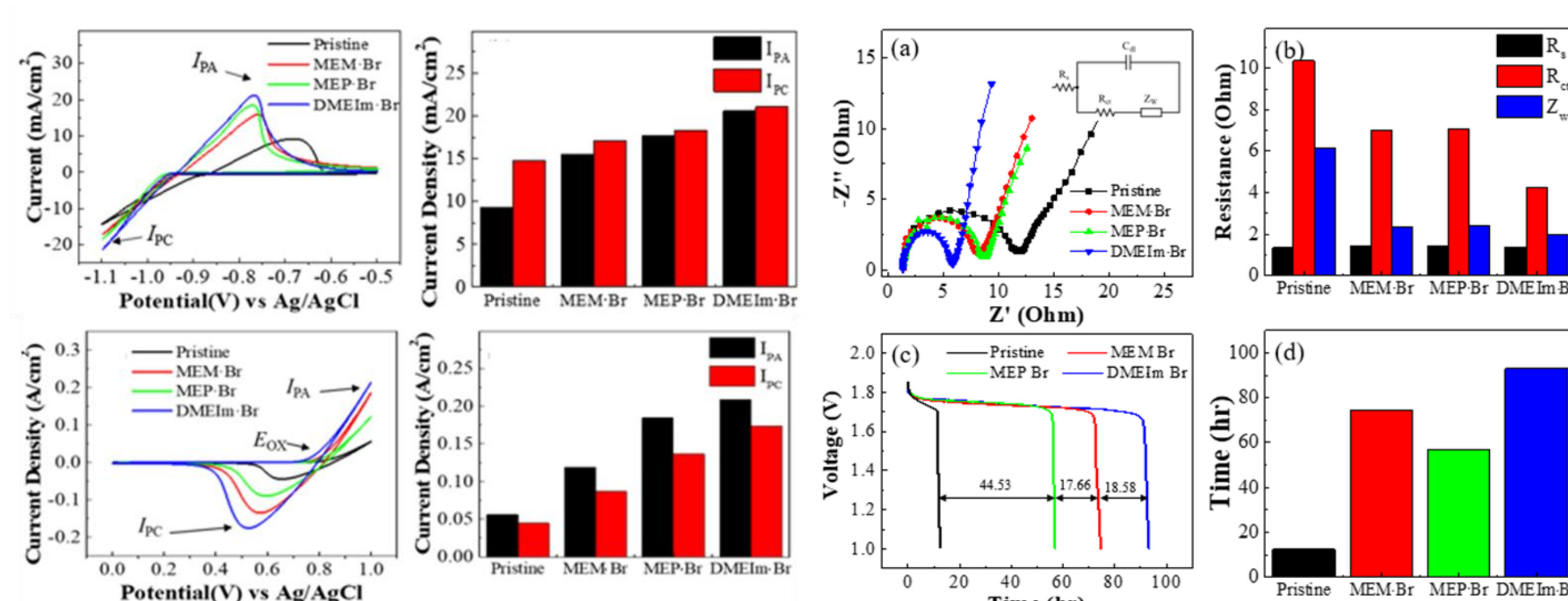


Fig. 1. Electrochemical performance comparison of three BCAs by CV measurements of Zn and Br redox couples for 20 cycles at the scan rate of 20 mV/s⁻¹

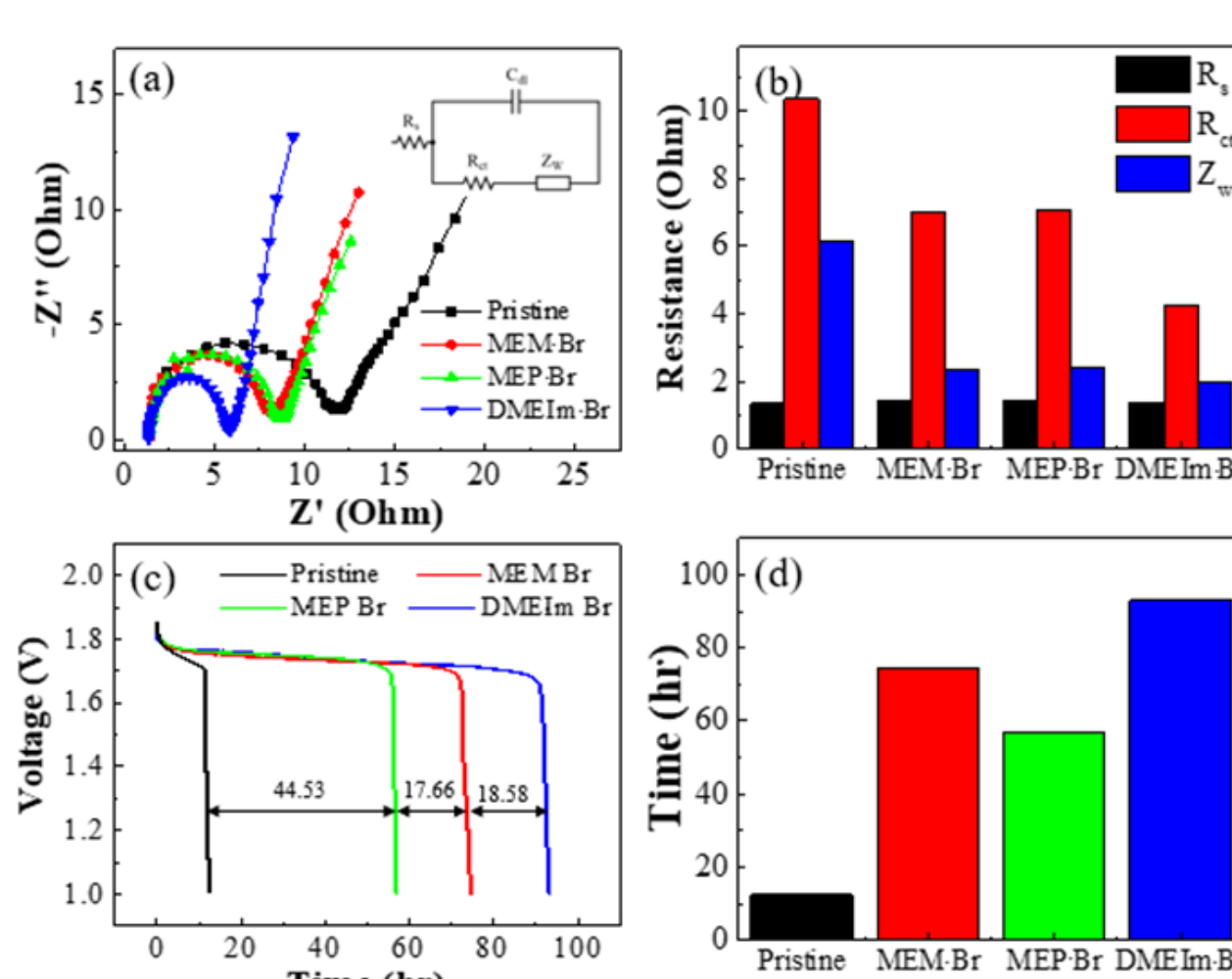


Fig. 2. EIS comparisons due to (a) Nyquist plots and (b) R_s , R_{ct} and Z_w ; (c) OCV curves and (d) OCV maintaining time

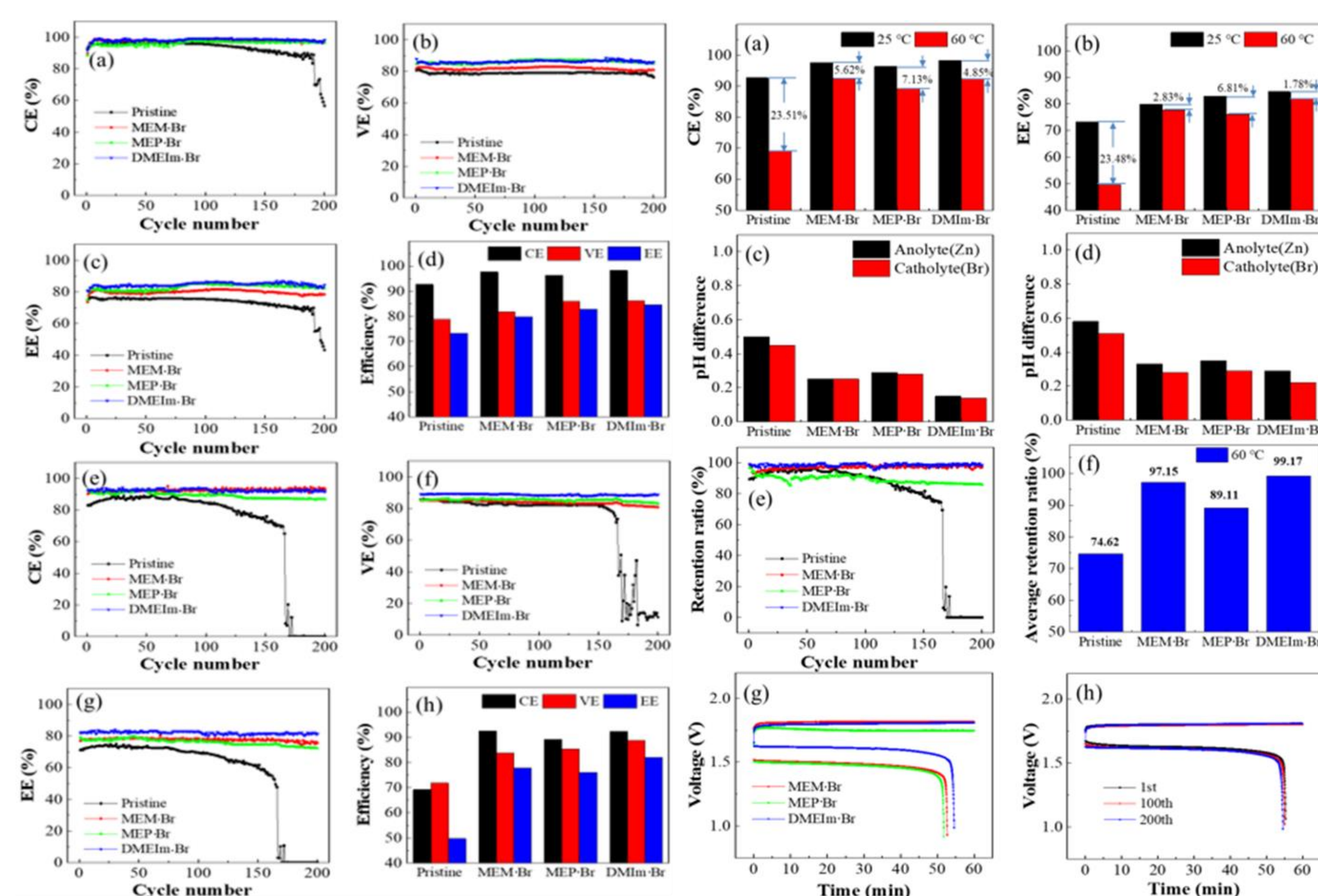


Fig. 3. Performance comparisons: (a) CEs, (b) VEs, (c) EEs and (d) average efficiencies at 25 °C; (e) CEs, (f) VEs, (g) EEs and (h) average efficiencies at 60 °C.

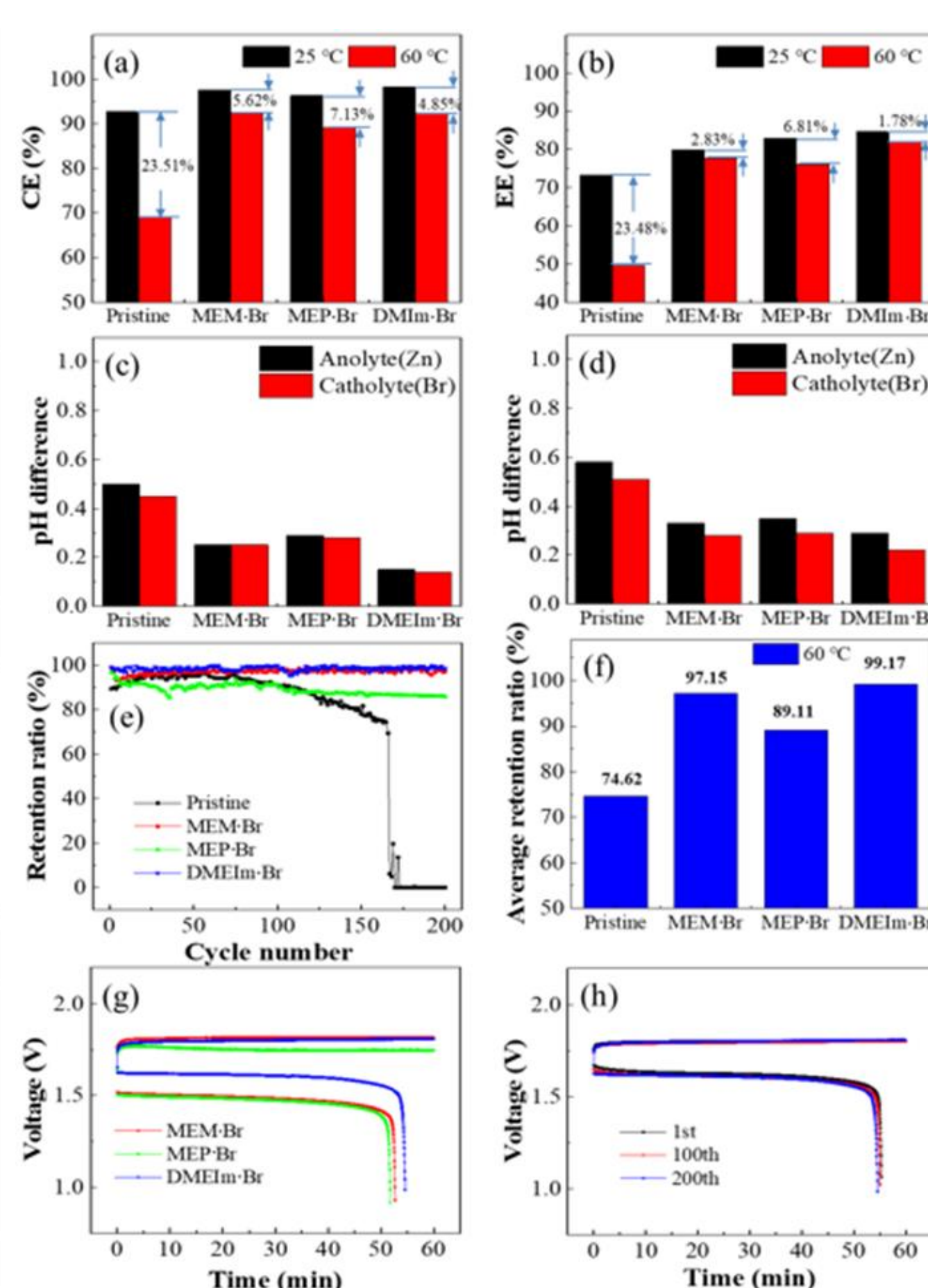


Fig. 4. Performance profiles: (a) average CEs and (b) EEs due to the temperature rise of 25 to 60 °C; pH difference (initial pH = 1.0) between before and after 200 cycling at (c) 25 and (d) 60 °C; Discharge capacity comparisons (at 60 °C) of (e) discharge capacity retention curves, and (f) average discharge capacity retention; Charge-discharge curves (capacity vs. potential) of (g) 200th and (h) DMEIm·Br's charge-discharge curves of 1st, 100th, and 200th cycles.

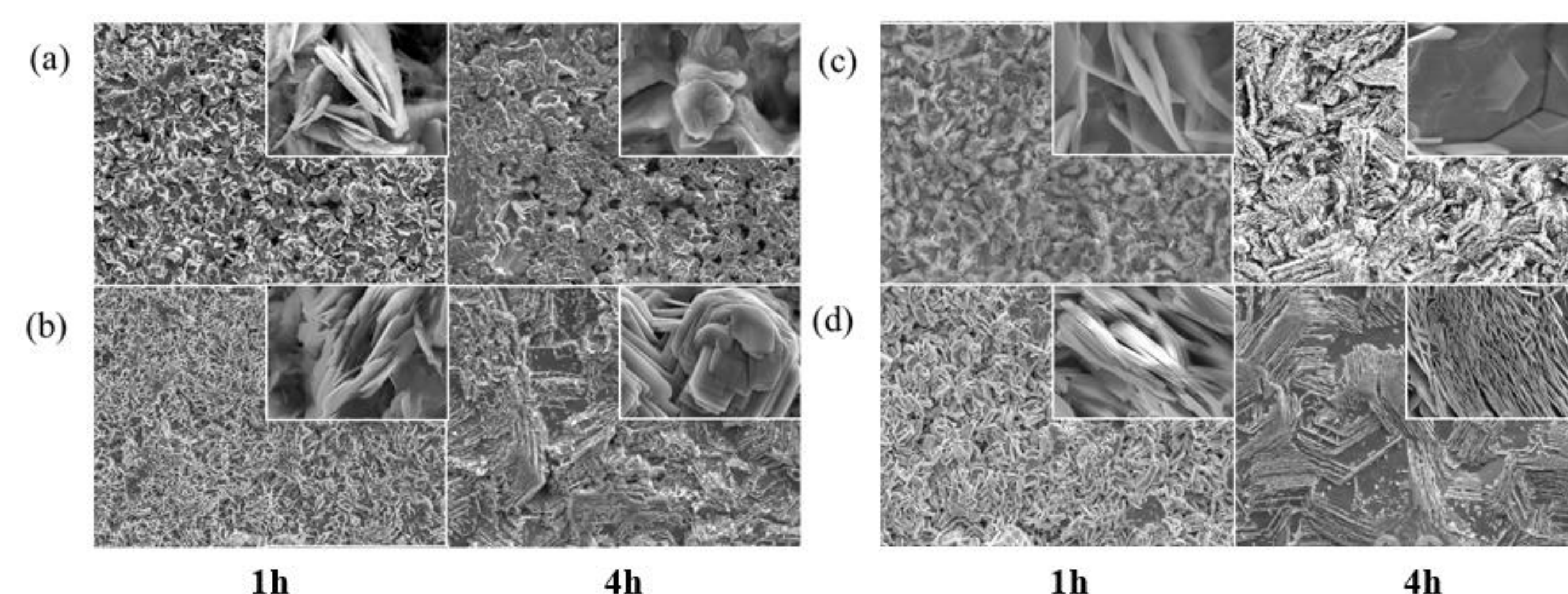


Fig. 5. SEM images: for x500/x10000 (inset image) magnification morphologies of electrodeposited zinc due to charge time and BCA type: (a) Pristine, (b) MEM·Br, (c) MEP·Br, and (d) DMEIm·Br.

Conclusion

This paper provides new insights into the development of a chemically and electrochemically stable and superior BCA for highly enhancing the overall performance of ZBBs, and a planar-molecular structure BCA has to be considered for electrolyte solutions more suitable to ZBB systems.

Acknowledgements

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References

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