Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information

Supporting Information

for

A High-Energy Efficiency Membraneless Flowless Zinc Bromine Battery Enabled By High Concentration Hybrid Electrolyte

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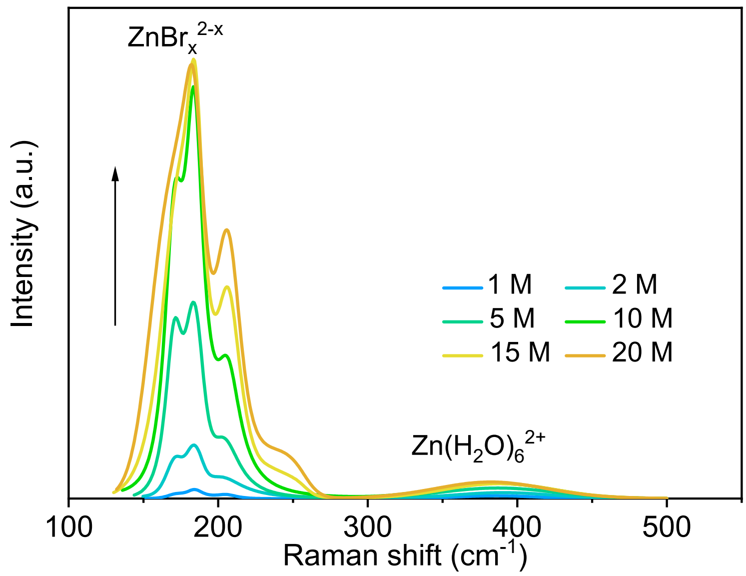

Figure S1. Raman spectra of $ZnBr_2$ solution of different concentrations.

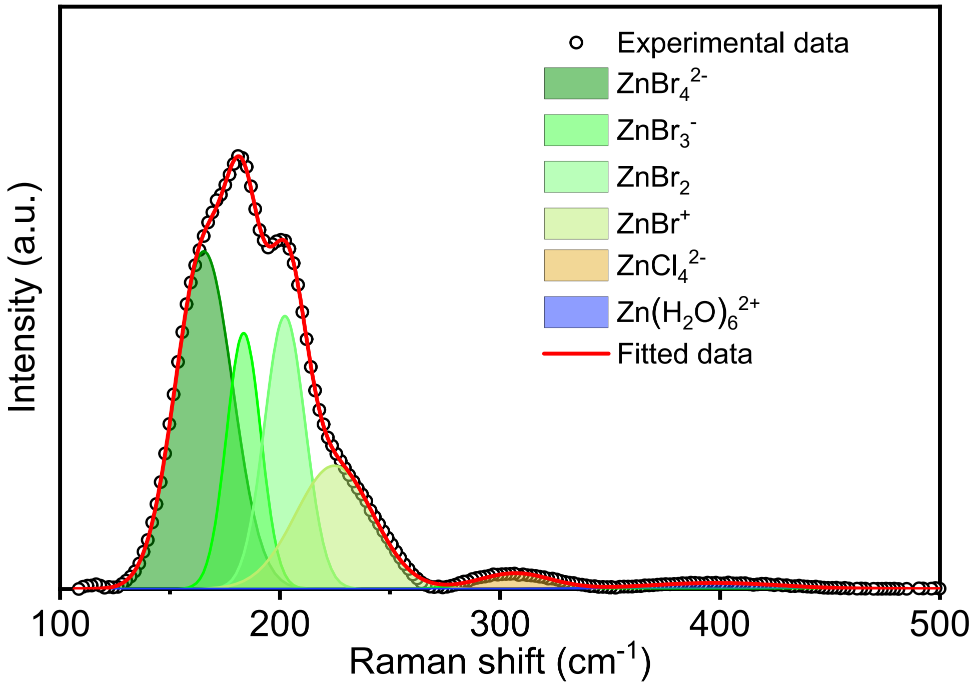

Figure S2. The Raman spectrum of 20 M $ZnBr_2$ + 10 M LiCl electrolyte.

The impact of the LiCl to the solution structure was investigated by Raman spectrum. The full spectrum from 100 cm^{-1} to 600 cm^{-1} can be fitted to six peaks, which represents $ZnBr_4^{2-}$, $ZnBr_3^{-}$, $ZnBr_2$, $ZnBr^{+}$, $ZnCl_x^{2-x}$ and $Zn(H_2O)_6^{2+}$, respectively. New complex species of $ZnCl_x^{2-x}$ formed and the relative quantity of $Zn(H_2O)_6^{2+}$ complex species reduced after the addition of 10 M LiCl.

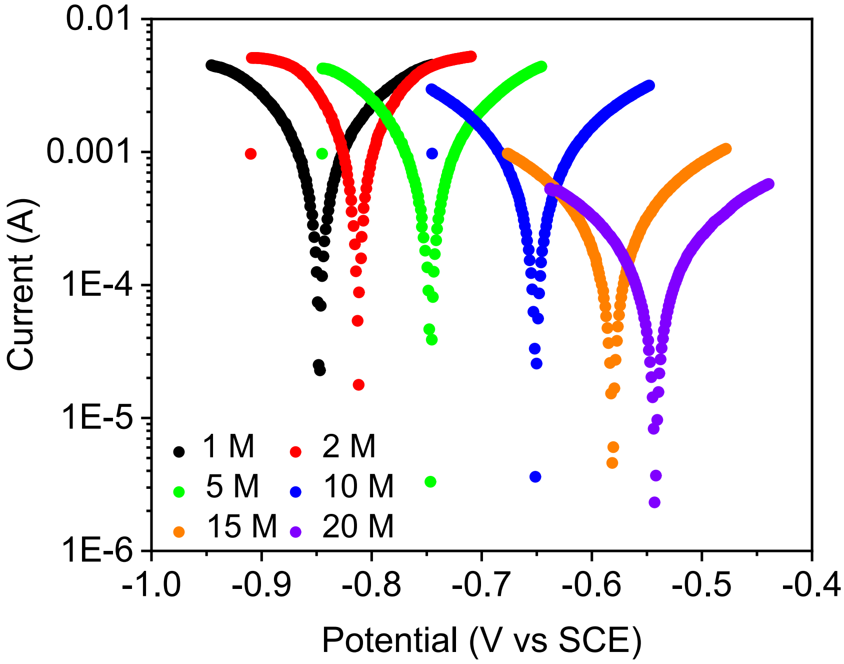

Figure S3. Linear polarization curve of zinc anode in different concentration of $ZnBr_2$ solution.

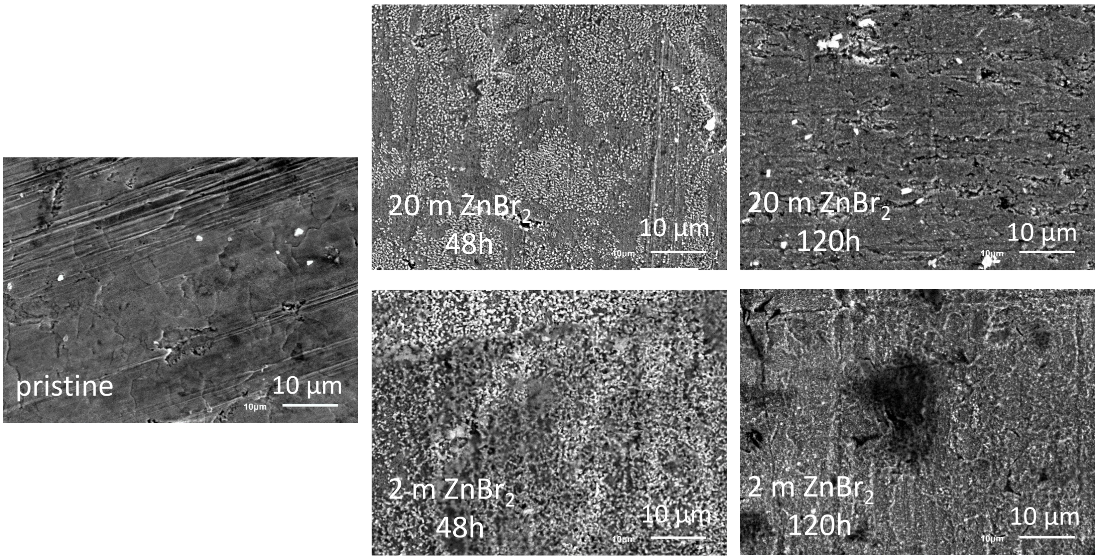

Figure S4. SEM image of the surface of zinc foil immersed in 2 M and 20 M $ZnBr_2$ solutions for different hours.

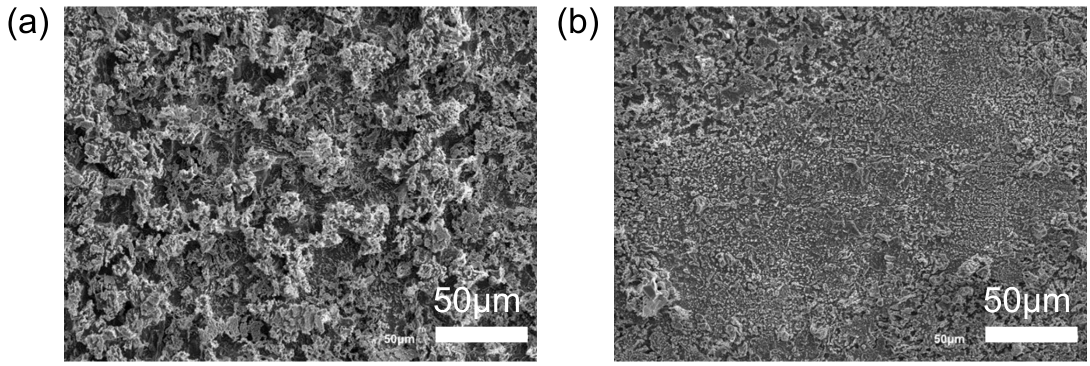

Figure S5. The SEM images of the surface of zinc foil charge/discharged at 1 mA·cm^{-2} and 0.5 mAh·cm^{-2} in (a) 20 M $ZnBr_2$ and (b) 20 M $ZnBr_2$ + 10 M LiCl for 100 cycles.

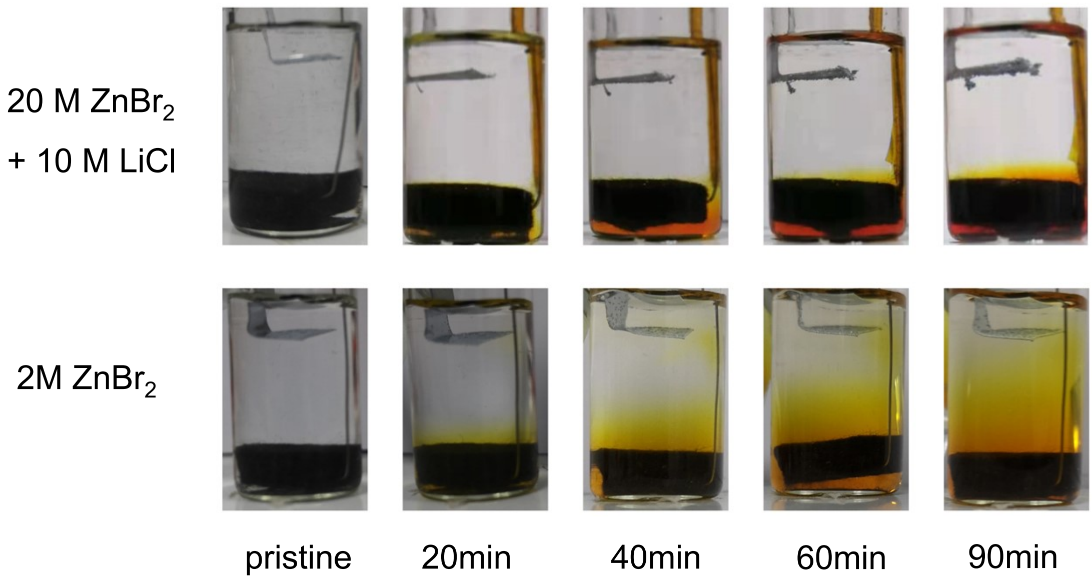

Figure S6. Photograph of different electrolyte during charging process under a current of 5 mA.

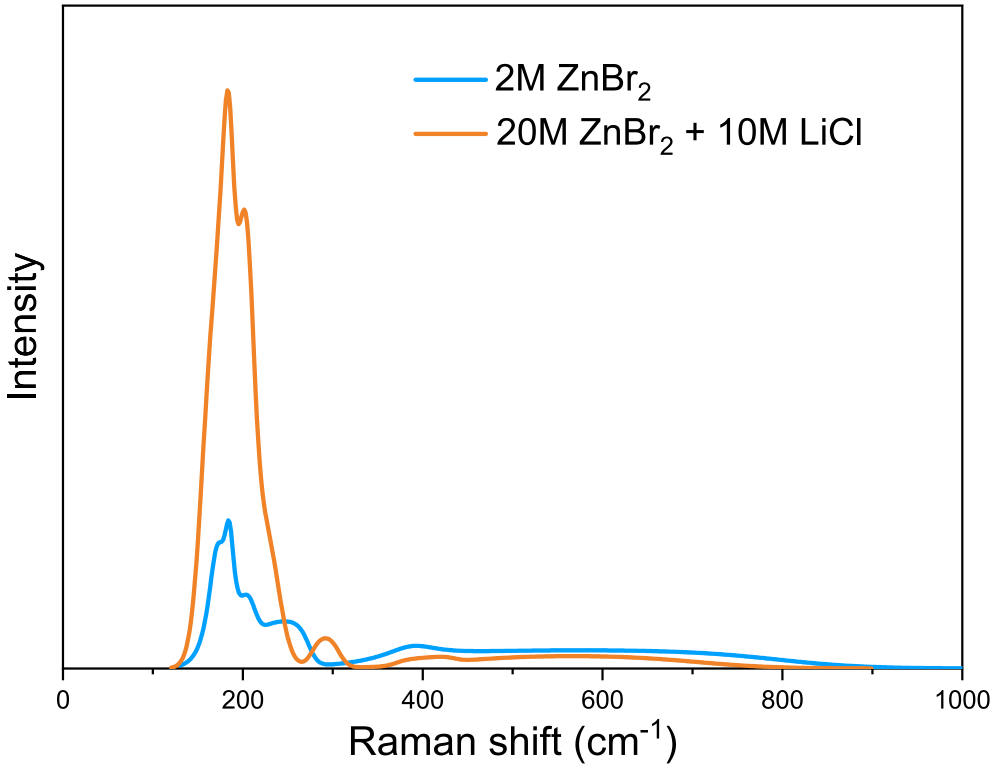

Figure S7. Raman spectra of different electrolyte after charging process of a capacity of 10 mAh.

Calculation of concentration of HBrO ([HBrO])

In an aqueous solution, the electrogenerated bromine species include Br_2, Br_3^-, HBrO and BrO^-, which mutually transform according to the following equations:

$$Br^- + Br_2 \leftrightarrow Br_3^-, K_1 = 16.9\ M^{-1}$$

$$Br_2 + H_2O \leftrightarrow HBrO + H^+ + Br^-, K_2 = 7.2 \times 10^{-9}\ M^2$$

$$HBrO \leftrightarrow BrO^- + H^+, K_3 = 2.3 \times 10^{-9}\ M$$

By rearranging these equations to solve the [HBrO], the mole fraction of HBrO can be expressed as follow[1]:

$$\alpha_{HBrO} = \frac{K_2[H^+]}{[Br^-][H^+]^2 + K_1[Br^-]^2[H^+]^2 + K_2[H^+] + K_2K_3}$$

According to the calculation, in an acidic solution, the fraction of HBrO decreases with increasing $[H^+]$ and $[Br^-]$, as is shown in Fig. S8. Therefore, due to the ultrahigh concentration of $[Br^-]$ and low pH (namely the high concentration of $[H^+]$) of the concentrated electrolyte, the content of HBrO in 20 M $ZnBr_2$ + 10 M LiCl was considerably much lower than that of the common Br_2-containing electrolytes.

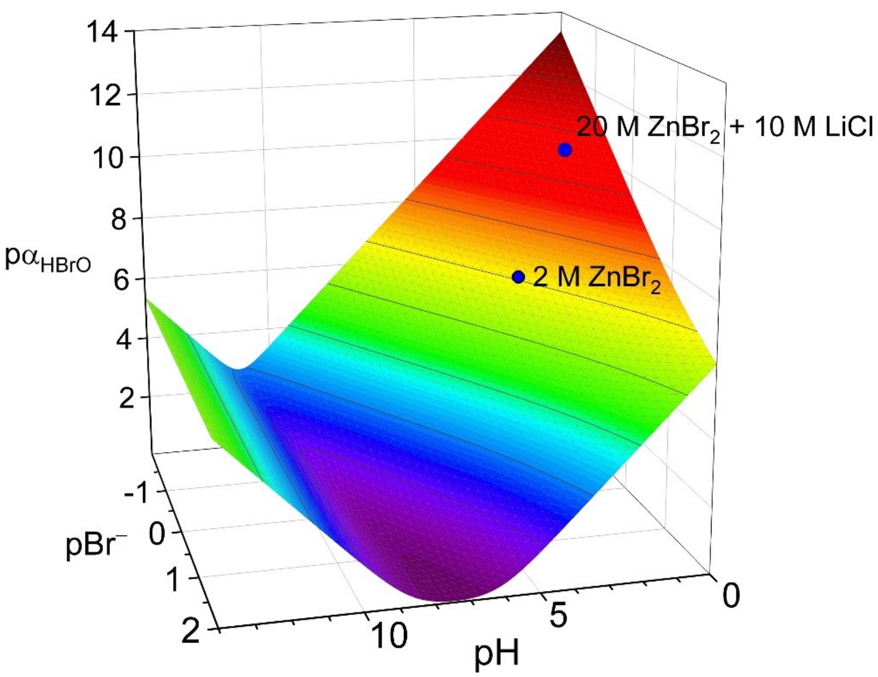

Figure S8. The relationship of the fraction of HBrO as a function of the concentration of Br^- and the pH value of solution.

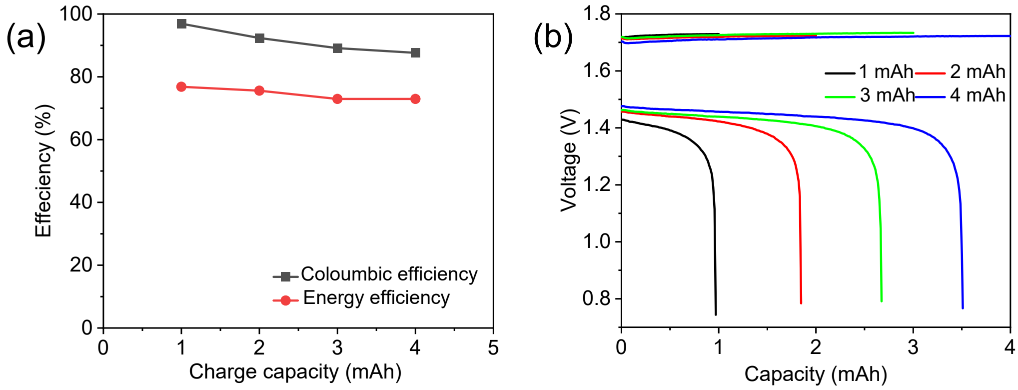

Figure S9. (a) Coloumbic efficiency under different charge capacity; (b) Capacity-voltage curve in the process of charge and discharge under different capacity. The utilization rates of the electrolyte is c.a. 1.8%.

Table S1. Currently reported static membrane-free zinc bromine battery systems and the system developed in this work.

System	CE	EE	Cycle number	Cycle life (h)
Density separation[2]	90%	60%	1000	4000
Protonated N-doped electrodes[3]	90%	80%	1000	2000
Interfacial battery [4]	96%	81%	200	200
This work	**98%**	**88%**	**2500**	**1000**

References

1. M. Takahashi, K. Nakamura and J. Jin, *Electroanalysis*, 2008, **20**, 2205–2211.
2. S. Biswas, A. Senju, R. Mohr, T. Hodson, N. Karthikeyan, K. W. Knehr, A. G. Hsieh, X. Yang, B. E. Koel and D. A. Steingart, *Energy Environ. Sci.*, 2017, **10**, 114–120.
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4. P. Xu, C. Xie, C. Wang, Q. Lai, W. Wang, H. Zhang and X. Li, *Chem. Commun.*, 2018, **54**, 11626–11629.