Supporting information

Grid-scale Corrosion-free Zn/Br Flow Batteries Enabled by Multi-electron Transfer Reaction

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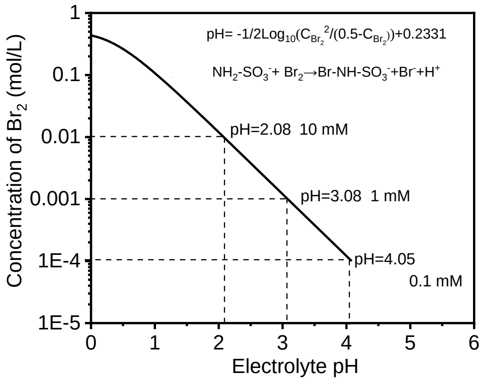


Supplementary Fig. 1. The concentration of free Br_2 in the electrolyte after the reaction with SANa at different pH. The initial electrolyte composition was determined to 0.5 M SANa + 0.5 M Br_2, the Br_2 concentration and SANa after the reaction were same, the concentration of formed Br^- and $Br\text{-}NH\text{-}SO_3^-$ were $0.5\text{-}C_{Br2}$, the proton concentration in the electrolyte was $C_{(H+)}$.

Chemical reaction: $NH_2SO_3^- + Br_2 \Rightarrow BrNHSO_3^- + Br^- + H^+$

Reaction I: $Br_2 + 2e^- \Rightarrow 2Br^-$

$$E_1 = 1.087 + 0.0296 \times \mathrm{Log}\frac{C_{Br_2}}{C_{Br^-}^{\ 2}} = 1.087 + 0.0296 \times \mathrm{Log}\frac{C_{Br_2}}{\left(0.5\text{-}C_{Br_2}\right)^2}$$

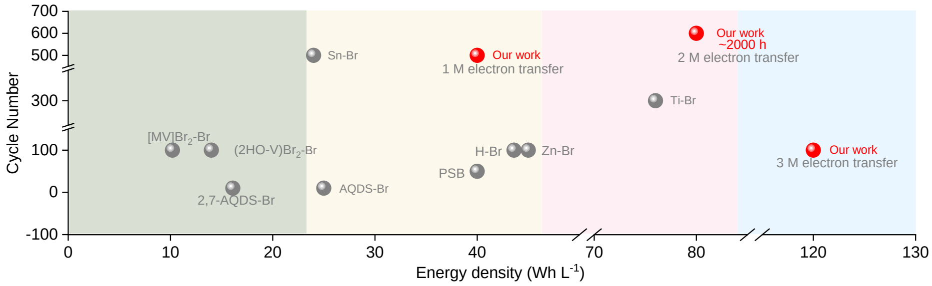
Reaction II: $BrNHSO_3^- + H^+ + e^- \Rightarrow NH_2SO_3^- + \frac{1}{2}Br_2$

$$E_2 = 1.1146 + 0.0592 \times \mathrm{Log}\frac{C_{BrNHSO_3^-} \times C_{H^+}}{C_{NH_2SO_3^-} \times [C_{Br_2}]^{1/2}} = 1.1146 + 0.0592 \times \mathrm{Log}\frac{C_{H^+}^{\ 2}}{[C_{Br_2}]^{3/2}}$$

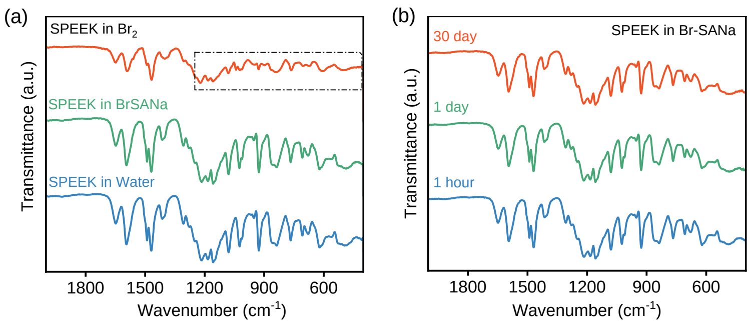
The equilibrium of this chemical reaction means that the redox potentials of reactions I and II are the same, therefore, the relationship between bromine concentration and pH was obtained as follows:

$$pH = -\ 0.5 * \mathrm{Log}\frac{C_{Br_2}^{\ 2}}{(0.5\text{-}C_{Br_2})} + 0.2331$$

The results showed that when the pH of the electrolyte was 2.08, the concentration of residual Br_2 in the solution was lower than 10 mM and when the pH rose to 4, the residual bromine concentration was less than 1 mM.



Supplementary Fig. 2. Comparison diagram of cycle number and energy density of different bromine-based flow battery systems. Compared with other bromine-based batteries, the battery system we designed demonstrated absolute advantages in terms of cycle stability and energy density due to the two-electron transfer mechanism and Br_2-free environment. (See ***Methods*** for references for all comparisons).



Supplementary Fig. 3. Infrared spectra characterization for SPEEK membrane immersed in different catholytes. (a) Infrared spectra of SPEEK membrane immersed into deionized water, 1 M Br-SANa solution and 1 M Br_2 solution for 1 hour, respectively. **(b)** Infrared spectra of SPEEK membrane immersed into Br-SANa solution for 1 hour, 1 day and 30 days, respectively. The results indicated that in Br-SANa electrolyte, SPEEK membrane could maintain long-term stability, but in Br_2, the membrane exhibited significant degradation.

Table S1. Cost of electrolyte composition of traditional Zn/Br FB electrolyte.

Reagent	$ZnBr_2$[1]	KCl[2]	MEP[3]
Cost ($ Kg^{-1})	7.17	1.43	22.96
Molecular weight (g mol^{-1})	225.19	74.55	194.11

1. Shandong Weitai Fine Chemical Co., Ltd. 2. Dalian Shunxing Chemical Raw Materials Co., Ltd. 3. Israel Chemical Group

Electrolyte composition: 2 M $ZnBr_2$ + 3 M KCl + 0.4 M MEP;

The required electrolyte volume per kWh is 24 L. (**Data based on our experimental data, 2400 L electrolyte for a 100 kWh system**);

Electrolyte cost per kWh is ***$127.96***.

Table S2. Price of electrolyte composition of our designed electrolyte.

Reagent	$ZnBr_2$[1]	KBr[2]	KAc[3]	SANa[4]
Cost ($ Kg^{-1})	7.17	2.48	1.38	3.03
Molecular weight (g mol^{-1})	225.19	119.00	98.14	119.07

1. Shandong Weitai Fine Chemical Co., Ltd. 2. Dalian Shunxing Chemical Raw Materials Co., Ltd. 3. Israel Chemical Group

Electrolyte composition: 1 M $ZnBr_2$ + 2 M KBr + 1.5 M SANa + 2 M KAc;

The required electrolyte volume per kWh is 25 L (15 L for negative electrolyte and 10 L for positive electrolyte).

Electrolyte cost per kWh is ***$78.13***.

Table S3. Price of stack components of model stack for traditional Zn/Br FB.

Components	Bipolar plate[1]	Membrane[2]	Electrode[3]	Endplate[4]	Collector[5]	Gasket[6]	Frame[7]
Cost ($)	$14.34 m^{-2}	$30 m^{-2}	$57.39 m^{-2}	215.21	14.34	4.30	1.43
Number	35.2 m^2	35.2 m^2	43.2 m^2	2	4	120	120

* All system costs are calculated based on a model stack consisting of 60 cells of 3600 cm^2 connected in series, which is a mature stack design in our group.

1, 7. Produced by the research team itself; 2. Daramic company; 3. Liaoyang Jingu Carbon Materials Co., Ltd. 4, 5. Dalian Youlian High-tech Co., Ltd. 6. Dalian Ziyun Rubber Products Co., Ltd.

Cost of model stack: ***$5215.40.***

*See **"Cost calculation"** in Methode for detail.

Table S4. Price of stack components of model stack for our designed system.

Components	Bipolar plate[1]	Membrane[2]	Electrode[3]	Endplate[4]	Collector[5]	Gasket[6]	Frame[7]
Cost ($)	$14.34 m^{-2}	$12.3 m^{-2}	$57.39 m^{-2}	215.21	14.34	4.30	1.43

Number	35.2 m^2	35.2 m^2	43.2 m^2	2	4	120	120

*All system costs are calculated based on a model stack consisting of 60 cells of 3600 cm^2 connected in series, hich is a mature stack design in our group.

1,2,7. Produced by the research team itself; 3. Liaoyang Jingu Carbon Materials Co., Ltd. 4, 5. Dalian Youlian High-tech Co., Ltd. 6. Dalian Ziyun Rubber Products Co., Ltd.

Cost of model stack: ***$4592.36***

*See **"Cost calculation"** in Methods for detail.

Table S5. Cost of different components of the system for 1 MW traditional Zn/Br FB.

Device	BMS[1]	PCS[2]	HES[3]	Pump[4]	Pipe[5]
Cost ($ MW^{-1})	129124.82	63127.69	37302.73	37302.73	21520.80

*BMS is battery management system; HES is heat exchange system; PCS is power conversion system.

1. Nanjing Nanrui Electrical Co., Ltd. 2. Dalian Dongfang Puside Electrical Appliance Manufacturing Co., Ltd. 3. Hangzhou Lide Machinery Equipment Co., Ltd. 4. Xie Ci Co., Ltd. 5. Qingdao wode Pipe Fittings Co., Ltd.

***The selection of the above component specifications is closely related to the output power of the system.**

Table S6. Cost of different components of the 1 MW system we designed.

Device	BMS[1]	PCS[2]	HES[3]	Pump[4]	Pipe[5]
Cost ($ MW^{-1})	129124.82	63127.69	37302.73	18364.42	6456.24

1. Nanjing Nanrui Electrical Co., Ltd. 2. Dalian Dongfang Puside Electrical Appliance Manufacturing Co., Ltd. 3. Hangzhou Lide Machinery Equipment Co., Ltd. 4. Xie Ci Co., Ltd. 5. Qingdao wode Pipe Fittings Co., Ltd.

*The selection of the above component specifications is closely related to the output power of the system.

***Since the electrolyte is milder, the cost of related equipment such as pumps or pipes is reduced.**

Table S7. Cost of electrolyte tank for traditional Zn/Br FB with various volume.

Volume	20 m^3	40 m^3	60 m^3	80 m^3	120 m^3
Cost ($)	22955.52	34433.28	40172.16	43041.60	51649.93

*The material of the tank is chlorinated polyvinyl chloride (CPVC).

Table S8. Cost of electrolyte tank for our designed system with various volume.

Volume	20 m^3	40 m^3	60 m^3	80 m^3	120 m^3
Cost ($)	11477.76	16499.28	18651.36	21520.80	25824.96

*The material of the tank is polyproplyene-Homo (PPH).

Table S9. The cost of traditional Zn/Br FB at a power density of 60 mW cm^{-2}.

	Stack	Electrolyte	BMS	PSC	HES	Pump	Pipe	Tank	**Cost ($ kWh^{-1})**
1MW/2MWh E/P=2	406801.2	255920	129124.82	63127.69	37302.73	37302.73	21520.80	68866.56	**509.98**
1MW/4MWh E/P=4	406801.2	511840	129124.82	63127.69	37302.73	37302.73	21520.80	80344.32	**321.84**
1MW/6MWh E/P=6	406801.2	767760	129124.82	63127.69	37302.73	37302.73	21520.80	86083.20	**258.17**
1MW/8MWh E/P=8	406801.2	1023680	129124.82	63127.69	37302.73	37302.73	21520.80	103299.86	**227.77**

At 60 mW cm^{-2}, with the output voltage is 1.7 V, the stack area is 21.6 m^2, the output power of a single stack is:

$$P=60*21.6*10000/1000/1000=12.96\ kW$$

The number of model stacks required for a 1 MW system is:

$$N=1000/12.96\approx 78$$

The stack cost per MWh is:

$$C=78*5215.40=\$406,801.20$$

Table S10. The cost of our designed system at a power density of 60 mW cm^{-2}.

	Stack	Electrolyte	BMS	PSC	HES	Pump	Pipe	Tank	**Cost ($ kWh^{-1})**
1MW/2MWh E/P=2	358204.08	156260	129124.82	63127.69	37302.73	18364.42	6456.24	32998.56	**400.92**
1MW/4MWh E/P=4	358204.08	312520	129124.82	63127.69	37302.73	18364.42	6456.24	40172.16	**241.32**
1MW/6MWh E/P=6	358204.08	468780	129124.82	63127.69	37302.73	18364.42	6456.24	47345.76	**188.12**
1MW/8MWh E/P=8	358204.08	625040	129124.82	63127.69	37302.73	18364.42	6456.24	68149.2	**163.22**

At 60 mW cm^{-2}, with the output voltage is 1.7 V, the stack area is 21.6 m^2, the output power of a single stack is:

$$P=21.6*10000/1000*60=12.96\ kW$$

The number of model stacks required for a 1 MW system is:

$$N=1000/12.96=78$$

The stack cost per MWh is:

$$C=78*4592.36=\$358204.08$$

Table S11. The cost of traditional Zn/Br FB of 1MW/8MWh (E/P=8) at different power density.

	Stack	Electrolyte	BMS	PSC	HES	Pump	Pipe	Tank	**Cost ($ kWh^{-1})**
20 mW cm^{-2}	1209973	1023680	129124.82	63127.69	37302.73	37302.73	21520.80	103299.86	**328.17**
40 mW cm^{-2}	604986.4	1023680	129124.82	63127.69	37302.73	37302.73	21520.80	103299.86	**252.54**
60 mW cm^{-2}	406801.2	1023680	129124.82	63127.69	37302.73	37302.73	21520.80	103299.86	**227.77**

80 mW cm^{-2}	302493.2	1023680	129124.82	63127.69	37302.73	37302.73	21520.80	103299.86	**214.73**

For designs with different power densities (20 mW cm^{-2}, 40 mW cm^{-2}, 60 mW cm^{-2}, 80 mW cm^{-2}), the required number of model stacks are 232, 116, 78, 58 respectively.

Table S12. The cost of our design of 1MW/8MWh (E/P=8) at different power density.

	Stack	Electrolyte	BMS	PSC	HES	Pump	Pipe	Tank	**Cost ($ kWh^{-1})**
20 mW cm^{-2}	1065427.52	625040	129124.82	63127.69	37302.73	18364.42	6456.24	68149.2	**251.62**
40 mW cm^{-2}	532713.76	625040	129124.82	63127.69	37302.73	18364.42	6456.24	68149.2	**185.03**
60 mW cm^{-2}	358204.08	625040	129124.82	63127.69	37302.73	18364.42	6456.24	68149.2	**163.22**
80 mW cm^{-2}	266356.88	625040	129124.82	63127.69	37302.73	18364.42	6456.24	68149.2*	**151.74**

For designs with different power densities (20 mW cm^{-2}, 40 mW cm^{-2}, 60 mW cm^{-2}, 80 mW cm^{-2}), the required number of model stacks are 232, 116, 78, 58 respectively.

* In this design, the negative side consists of a 120 m^2 and a 40 m^3 tanks.