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## **Supporting Information**

#### An All-Aqueous Redox Flow Battery with Unprecedented Energy Density

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#### 1. Experimental Details

**Cell assembly.** In anode half-cell, zinc plate with apparent area of 7 cm<sup>2</sup> served as anode and copper foil as current collector. In cathode half-cell, graphite foil with apparent area of 7 cm<sup>2</sup> served as cathode and stainless-steel mesh as current collector. The commercially available cation exchange membrane (Nafion 117, Dupont, USA) was used as the separator to be sandwiched between two half cells. First, the Nafion 117 membranes were treated with 3% H<sub>2</sub>O<sub>2</sub> under 100°C for 1 h and then washed with deionized water at 100°C for 1 h. Secondly, the Nafion 117 membranes were transferred into 0.5 M H<sub>2</sub>SO<sub>4</sub> at 100°C for 1 h and then washed with deionized water at 100°C for 1 h to change the membrane into K<sup>+</sup> conductive membrane. The original catholytes with different concentrations were prepared by dissolving appropriate potassium iodide (KI,  $\geq$  99%, Aldrich) with iodine (I<sub>2</sub>,  $\geq$  99%, Aldrich) in deionized water. The volume of catholyte was designed to be 10 ml for each cathode half-cell. The original anolytes were prepared with corresponding concentration of potassium hydroxide (KOH,  $\geq$  85%) for balanced osmolarity. The single cell was assembled as shown in Fig. S2.

**Characterization and electrochemical measurements.** The cyclic voltammogram test was conducted in a three-electrode cell using a CHI660C workstation (CH Instruments, USA). A graphite rob, glassy carbon and Ag/AgCl (filled with 3M KCl) electrode were used as the counter, working and reference electrodes, respectively. Testing was performed in 0.1 M zinc acetate (ZnAc) with 3M KOH solution to determine the potentials of the  $Zn(OH)_4^{2-}/Zn$  redox pair, and in 0.1M KI electrolyte to determine the potentials of the  $I_3^-/I^-$  redox pair. Discharge and charge cycling was carried out by a recurrent galvanic pulse method at different current density. The morphology and of the membrane was imaged by scanning electron microscopy (SEM) (LEO FESEM 1530).

**Permeability measurements.** Permeability of ions through Nafion 117 was investigated in a membrane separated diffusion cell. All the membranes were activated to  $K^+$  ion conductor with an effective area of 2.54 cm<sup>2</sup> and a thickness of 170 mm. The solution volume of each half-cell

was 250 mL. The left compartment was filled with saturated Zn<sup>2+</sup> ions in 2M and 4M KOH solution, respectively. The right compartment was filled with 2M and 4M KI solution, respectively. To detect the zincate ions that were diffused during the permeability test, the permeate solution (0.5 mL) was collected every hour and then diluted and acidified with diluted mixed acid solution of 0.45 mol L<sup>-1</sup> HCl and 0.2 mol L<sup>-1</sup> HNO<sub>3</sub>. Zincate ions were transformed into zinc ion during this process. After the volume was fixed at 25 mL, the sample solutions at different diffusion time were ready for the zinc determination via ICP-OES (Perkin Elmer Ltd., USA). According to the standard line created by the commercial standard zinc ion solutions, the zinc ion concentration in each acidic diluted solution was obtained. The permeability coefficient can be calculated by the following equation:

$$V_{\rm R} \frac{{\rm d}c_{\rm R}(t)}{{\rm d}t} = {\rm A}_{L}^{P} [c_{\rm L} - c_{\rm R}(t)]$$

Where P is the ion permeability coefficient ( $cm^2 min^{-1}$ ). L is the membrane thickness (µm), A is the effective area of the membrane ( $cm^2$ ), C<sub>L</sub> and C<sub>R</sub> are the initial concentration of ions in the left and right compartment (mol L<sup>-1</sup>), respectively, and V<sub>R</sub> is the volume of the solution (mL). Assumption is suggested that P is independent of concentration.

#### 2. Theoretical Volumetric Energy Density Calculation

Condition: Zn metal is unlimited. The concentration of  $I_3^-$  solution is 1 mol/L.

Volumetric Energy Density (Wh 
$$L^{-1}$$
) =  $\frac{F \cdot c \cdot n \cdot OCV}{3600}$ 

where F is the Faraday constant 96485 C/mol, n is the number of electrons transferred during reaction per mole reactant, c is the concentration of  $I_3^-$  solution, OCV is the battery's nominal voltage.

(1) For conventional Zn-I<sub>2</sub> flow battery

 $Zn + I_3^- \leftrightarrow Zn^{2+} + 3I^-$  E=1.299 V

*Volumetric Energy Density* (*Wh*  $L^{-1}$ ) =  $\frac{96485 \times 1 \times 2 \times 1.299}{3600}$  = 69.63 (*Wh*  $L^{-1}$ )

(2) For alkaline Zn-I<sub>2</sub> flow battery

 $Zn + I_3^- + 4OH^- \leftrightarrow Zn(OH)_4^{2-} + 3I^- \quad E=1.796 \text{ V}$ 

*Volumetric Energy Density* (*Wh*  $L^{-1}$ ) =  $\frac{96485 \times 1 \times 2 \times 1.796}{3600}$  = 96.27 (*Wh*  $L^{-1}$ )

Therefore, according to the calculation, by converting conventional Zn-I2 flow battery to

alkaline Zn-I<sub>2</sub> flow battery, the theoretical volumetric energy density increases by 38.26%.

*Volumetric Energy enhancement* (%) =  $\frac{96.27 - 69.63}{69.63} \times 100\% = 38.26\%$ 

#### 3. Theoretical Specific Capacity Calculation

Specific Capacity (Ah  $L^{-1}$ ) =  $\frac{F \cdot c \cdot n}{3600}$ 

where F is the Faraday constant 96485 C/mol, n is the number of electrons transferred during reaction per mole reactant, c is the concentration of  $I_3^-$  solution. (1Ah = 3600C)

2M I<sub>3</sub><sup>-</sup> concentration: Specific Capacity (Ah  $L^{-1}$ ) =  $\frac{96485 \times 2 \times 2}{3600}$  = 107.2 (Ah  $L^{-1}$ ) 4M I<sub>3</sub><sup>-</sup> concentration: Specific Capacity (Ah  $L^{-1}$ ) =  $\frac{96485 \times 2 \times 4}{3600}$  = 214.4(Ah  $L^{-1}$ ) 6M I<sub>3</sub><sup>-</sup> concentration: Specific Capacity (Ah  $L^{-1}$ ) =  $\frac{96485 \times 2 \times 6}{3600}$  = 321.6 (Ah  $L^{-1}$ )

#### 4. Zincate ion concentration evaluation

In this work, in order to get the highest energy density, 6M anolyte and catholyte solutions are chosen for the battery cycling test. 10 h charge and discharge times are used for each cycle. The anolyte (KOH solution) volume is 200 mL and the concentration of KOH solution is 6M. The catholyte (KI-I<sub>2</sub> solution) volume is 10 mL and the concentration of KI and I<sub>2</sub> solution is 6M. The discharge current density is 20mA cm-2, and the electrode area is 7 cm<sup>2</sup>. Here, we make an assumption to calculate the concentration of zincate ion for the state of charge (SOC) aspect:

What is the concentration of zincate ion when the battery discharge for 10 h?

The following is the calculation procedure:

(1) The theoretical capacity calculation of the battery

Specific Capacity (Ah  $L^{-1}$ ) =  $\frac{F \cdot c \cdot n}{3600}$ 

where F is the Faraday constant 96485 C/mol, n is the number of electrons transferred during reaction per mole reactant, c is the concentration of I3– solution. (1Ah = 3600C)

Specific Capacity (Ah 
$$L^{-1}$$
) =  $\frac{-96485 \times 2 \times 6}{3600}$  = 321.6 (Ah  $L^{-1}$ )

6M I<sub>3</sub><sup>-</sup> concentration:

The analyte and zinc reactant are abundent, so the capacity limitation of the battery is the catholyte reactant. The volume of KI-I<sub>2</sub> solution is 10 mL. Therefore, the theoretical capacity of the battery is 3.216 Ah.

(2) The number of electrons produced after 10 h discharge

When the battery discharges for 10h, then 20mA cm<sup>-2</sup>  $\times$  7 cm<sup>2</sup>  $\times$  10h = 1.4 Ah electricity released. Because 1Ah = 3600C and 96485C/mol e<sup>-</sup>, the amount of e<sup>-</sup> produced is 0.0522 mol after 10 h discharge.

(3) The concentration of zincate ions after 10 h discharge

The ratio of zincate and electrons produced in this system is 1:2  $(Zn + 4OH^- \rightarrow Zn(OH)_4^{2^-} + 2e^-)$ , so the amount of zincate ions is 0.0261 mol. The volume of anolyte solution is 200 ml. therefore, the concentration of zincate ion after 10 h discharge is 0.1305 mol/L.

Based on the calculation above, we make a table in Table S2.



## (a) Conventional Zn-I<sub>2</sub> flow battery

### **Discharge reaction**

Anode side: Zn  $\rightarrow$  Zn<sup>2+</sup> + 2e<sup>-</sup> Cathode side: I<sub>3</sub> + 2e<sup>-</sup>  $\rightarrow$  3I<sup>-</sup>

### **Charge reaction**

Anode side:  $Zn^{2+} + 2e^- \rightarrow Zn$ Cathode side:  $3I^- \rightarrow I_3 + 2e^-$ 

## (b) Hybrid Alkaline Zn-I<sub>2</sub> flow battery



### **Discharge reaction**

Anode side:  $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$ Cathode side:  $I_3^- + 2e^- \rightarrow 3I^-$ 

## **Charge reaction**

Anode side:  $Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$ Cathode side:  $3I^- \rightarrow I_3^- + 2e^-$ 

Figure S1. Schematic illustration of the working principle of (a) conventional  $Zn-I_2$  flow battery. (b) Hybrid alkaline  $Zn-I_2$  flow battery designed in this work.



Figure S2. Photographs of the hybrid alkaline Zn-I2 flow battery cell configuration.



Figure S3. Zinc pourbaix diagram.



Figure S4. Coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE), and energy density of the experimental  $Zn-I_2$  flow battery of each cycle in different electrolyte concentration.



Figure S5. The open-circuit-voltage and discharge/charge onset voltage of  $Zn-I_2$  flow battery as a function of current density.



Figure S6. SEM images of the cycled Nafion 117 membrane facing to the (a) anode side and (b) cathode side.



Figure S7. (a) The photograph of diffusion cell in simulation of actual battery testing condition. (b) The zincate ion concentration in permeate side with Nafion 117 membrane as a function of time (insert figure: zincate ion permeability coefficients with Nafion 117 membrane in 2M and 6M solution).



Figure S8. (a) Photographs of fresh and cycled zinc plates. SEM images of the (b) fresh zinc electrode, (c) cycled zinc electrode with passivation and (d) cycled zinc electrode with zinc dendrite.

The morphology of the cycled zinc electrode was characterized by SEM. SEM image of a zinc electrode (zinc plate) prior to the cycling shows a flat and uniform structure in nature (Fig. S8a and S8b). Fig. S8c and S8d exhibit the morphology of the cycled zinc electrode in different regions. In Fig. S8c, it shows rod-shaped nanograins are partially deposited on the surface of zinc particles.<sup>1</sup> This observation is the well-known compact passivation layer of zinc oxide species, which will prevent direct contact of hydroxide ions with remaining active zinc species. In Fig. S8d, the needle-sharped nanograins are caused by zinc dendrite formation.<sup>2</sup> During charge, zinc will be deposited back onto the electrode but at a different position, resulting in the shape change of the zinc electrode and formation of zinc dendrite. Further analysis of the zinc electrode with higher depths of charge and discharge of the battery is crucial for improving the battery performance at high rates, hence is a topic of our continuous research.



Figure S9. (a) Polarization curves for  $I_3^-$  reduction to  $I^-$  at different rotation speeds (Solution: 0.02 M KI with 0.01 M I<sub>2</sub> in DDI) (b) Polarization curves for  $I^-$  oxidation to  $I_3^-$  at different rotation speeds (Solution: 0.02 M KI with 0.01 M I<sub>2</sub> in DDI). (c) Polarization curves for Zn<sup>2+</sup> reduction to Zn at different rotation speeds (Solution: 0.01 M ZnAc with 0.3 M KOH in DDI).

	С	0	F	S	Κ	Zn	Ι	Au	Total
Anode side	17.51	7.10	61.89	2.87	3.69	1.60	1.52	3.81	100
Cathode side	14.53	7.02	47.65	1.53	4.37	12.34	8.73	3.85	100

Table S1. The elemental analysis of cycled Nafion 117 membrane on anode and cathode sides obtained from EDX.

Units: wt%

Table s2. Zincate ion concentration as a function of discharge time in 6M anolyte solution.

Discharge hours	0 h	1 h	2 h	4 h	6 h	8 h	10 h
Zincate ion concentration	0	0.01305	0.0261	0.0522	0.0783	0.1044	0.1305

Units: mol/L

Systems	Solvent	Theoretical	Demonstrated maximum	Demonstrated maximum	Ref.
	environment	E <sup>o</sup> cell / V	Discharge Specific Capacity	volumetric energy density	
BTMAP-Vi/BTMAP-Fc	All-Aqueous	0.745	16.8 Ah L <sup>-1</sup>	13.0 Wh L <sup>-1</sup>	3
Zn/Fe	All-Aqueous	1.99	12 Ah L <sup>-1</sup>	\	4
All-Fe	All-Aqueous	1.22	4.5 Ah L <sup>-1</sup>	\	5
TEMPTMA/MV	All-Aqueous	1.4	54 Ah L <sup>-1</sup>	38 Wh L <sup>-1</sup>	6
TEMPO/Viologen	All-Aqueous	1.1	\	10 Wh L <sup>-1</sup>	7
Zinc/Polyiodide	All-Aqueous	1.2986	\	167 Wh L <sup>-1</sup> (catholyte)	8
Polysulfide/Iodine	All-Aqueous	1.05	92.03Ah L <sup>-1</sup> (catholyte)	43.1 Wh L <sup>-1</sup>	9
FMN-Na/Ferrocyanide	All-Aqueous	1.30	5.36 Ah L <sup>-1</sup>	4.83 Wh L <sup>-1</sup>	10
Znic/Iodine-bromide	All-Aqueous	1.354	\	101,202 Wh L <sup>-1</sup> (catholyte)	11
Poly(TEMPO)/Zinc	All-Aqueous	1.70	\	8.1 Wh L <sup>-1</sup>	12
VFB	All-Aqueous	1.26	\	50.6 Wh L <sup>-1</sup>	13
Alkaline Zinc/Iodine	All-Aqueous	1.796	193.51 Ah L <sup>-1</sup> (catholyte)	312.22 Wh L <sup>-1</sup> (catholyte)	This work

Table S3. The performance comparison of recent developed redox flow battery.

# **References:**

- 1. M. Bockelmann, L. Reining, U. Kunz and T. Turek, *Electrochimica Acta*, 2017, 237, 276-298.
- 2. K. Wang, P. Pei, Z. Ma, H. Chen, H. Xu, D. Chen and X. Wang, *Journal of Materials Chemistry A*, 2015, 3, 22648-22655.
- 3. E. S. Beh, D. De Porcellinis, R. L. Gracia, K. T. Xia, R. G. Gordon and M. J. Aziz, *ACS Energy Letters*, 2017, 2, 639-644.
- 4. K. Gong, X. Ma, K. M. Conforti, K. J. Kuttler, J. B. Grunewald, K. L. Yeager, M. Z. Bazant, S. Gu and Y. Yan, *Energy Environ. Sci.*, 2015, 8, 2941-2945.
- 5. K. Gong, F. Xu, J. B. Grunewald, X. Ma, Y. Zhao, S. Gu and Y. Yan, *ACS Energy Letters*, 2016, 1, 89-93.
- 6. T. Janoschka, N. Martin, M. D. Hager and U. S. Schubert, *Angewandte Chemie*, 2016, 55, 14427-14430.
- 7. T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager and U. S. Schubert, *Nature*, 2015, 527, 78-81.
- B. Li, Z. Nie, M. Vijayakumar, G. Li, J. Liu, V. Sprenkle and W. Wang, Nat Commun, 2015, 6, 6303.
- 9. Z. Li, G. Weng, Q. Zou, G. Cong and Y.-C. Lu, *Nano Energy*, 2016, 30, 283-292.
- 10. A. Orita, M. G. Verde, M. Sakai and Y. S. Meng, *Nat Commun*, 2016, 7, 13230.
- 11. G.-M. Weng, Z. Li, G. Cong, Y. Zhou and Y.-C. Lu, *Energy Environ. Sci.*, 2017, DOI: 10.1039/c6ee03554j.
- 12. J. Winsberg, T. Janoschka, S. Morgenstern, T. Hagemann, S. Muench, G. Hauffman, J. F. Gohy, M. D. Hager and U. S. Schubert, *Advanced materials*, 2016, 28, 2238-2243.
- 13. S. Roe, C. Menictas and M. Skyllas-Kazacos, *Journal of The Electrochemical Society*, 2015, 163, A5023-A5028.