## **Energy Materials**

## **Supporting Information**

Dendrite-free Zn anodes enabled by interface engineering for non-alkaline Zn-air and Znion batteries

## Tao Fang<sup>#</sup>, Mengxue Wu<sup>#</sup>, Feiyu Lu<sup>#</sup>, Zhengyi Zhou, Yanpeng Fu<sup>\*</sup>, Zhicong Shi<sup>\*</sup>

Institute of Batteries, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, Guangdong, China.

<sup>#</sup>Authors contributed equally and co-first authors.

**Correspondence to:** Yanpeng Fu, School of Materials and Energy, Guangdong University of Technology, No. 100 Waihuan Xi Lu, Guangzhou Higher Education Mega Center, Panyu District, Guangzhou 510006, Guangdong, China. E-mail: fuyanpeng@gdut.edu.cn; Prof. Zhicong Shi, School of Materials and Energy, Guangdong University of Technology, No. 100 Waihuan Xi Lu, Guangzhou Higher Education Mega Center, Panyu District, Guangzhou 510006, Guangdong, China. E-mail: zhicong@gdut.edu.cn



Figure 1. Digital photos of ZSO electrolytes with and without different concentrations of TEAB additives (0, 0.01, 0.05, 0.1 and 0.2 M).



Figure 2. The ignition test of ZSO electrolyte with 0.2 M TEAB additive.



Figure 3. CV curves of Zn||Cu cells in ZSO electrolytes with and without 0.1 M TEAB additive.



Figure 4. Nyquist plots of Zn||Zn symmetric cells in ZSO electrolytes with and without 0.1 M TEAB additive.



Figure 5. Cycling performance of Zn $\|$ Zn symmetrical cells in ZSO electrolytes with and without 0.1 M TEAB additive under a current density and area capacity of 5 mA cm<sup>-2</sup> and 5 mAh cm<sup>-2</sup>.



Figure 6. Rate performance of Zn||Zn symmetrical cell in ZSO electrolytes with and without 0.1

M TEAB additive at different current densities from 1 to 30 mA cm<sup>-2</sup>.



Figure 7. Rate performance of Zn||Zn symmetric cells in ZSO electrolytes with and without 0.1 M TEAB additive at different current densities ranging from 0.1 to 5 mA cm<sup>-2</sup>.

In ZSO, a significant enhancement in the overpotential (from 25.1 mV to 463.4 mV) and

noticeable voltage fluctuations are observed when the current density reaches  $0.3 \text{ mA cm}^{-2}$ . As the current density further increases, dendrite accumulation and side reactions lead to a substantial deterioration and a rapid short-circuit during Zn plating/stripping. In contrast, the symmetric cells with 0.1 M TEAB electrolyte demonstrate sustained stability with reasonable changes in the overpotential (24.8 mV at 0.1 mA cm<sup>-2</sup> and 272.3 mV at 5 mA cm<sup>-2</sup>).



Figure 8. Corresponding voltage profiles at various cycles in the pure ZSO electrolyte.



Figure 9. SEM images of bare Zn foils soaked for a week in ZSO electrolytes with and without 0.1

M TEAB additive.



Figure 10. Nyquist plots of Zn||Zn symmetric cells at different temperatures: (A) ZSO +0.1 M TEAB additive and (B) ZSO. (C) Corresponding Arrhenius curves and comparison of activation energies of ZSO electrolytes with and without 0.1 M TEAB additive.



Figure 11. SEM image of the cathode materials  $\delta$ -MnO<sub>2</sub>.



Figure 12. EIS of Zn||MnO<sub>2</sub> full cells in ZSO electrolytes with and without 0.1 M TEAB additive.



Figure 13. Rate performance of  $Zn||MnO_2$  full cells in ZSO electrolytes with and without 0.1 M

TEAB additive.



Figure 14. The schematic diagram of Zn||air cell.



Figure 15. The cycling curves at different times in ZSO electrolyte with 0.1 M TEAB additive.



Figure 16. The Reversible capacity of Zn||air cell in ZSO electrolyte with 0.1 M TEAB additive.



Figure 17. XRD images of anode in ZSO electrolytes with and without 0.1 M TEAB additive.

Table 1. Symmetric Zn||Zn cells cycling performance comparison between this work and other recent reports.

	Current	Cycling	I ;fo	
Strategy/Zn Salt	density	capacity		Ref.
	(mA cm <sup>-2</sup> )	(mAh cm <sup>-2</sup> )	(n)	
β-CD/Zn(ClO <sub>4</sub> ) <sub>2</sub>	1	1	1000	Angew. Chem. Int. Ed. 2022, 61,
	5	5	350	e202210979
PC-sat/Zn(OTf) <sub>2</sub>	1	1	1600	J. Am. Chem. Soc. 2022, 144, 16, 7160– 7170
Zn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> /Zn	1	1	1200	Adv. Mater 2021, 33, 2007416
(OTf) <sub>2</sub>	5	5	200	
BIS-TRIS/ZnSO <sub>4</sub>	1	1	1200	Energy Storage Mater 2021, 41, 515-521
	5	5	600	
Bet/ZnSO <sub>4</sub>	2	2	800	Adv. Mater 2023, 35, 2208237
	5	1	150	
DMSO/ZnCl <sub>2</sub>	0.5	0.5	1000	J. Am. Chem. Soc. 2020, 142, 51, 21404– 21409
Na4EDTA/ZnSO4	2	2	450	Adv. Energy Mater. 2021, 11, 2102010
	5	2	2000	
Glucose/ZnSO <sub>4</sub>	1	1	2000	Rare Metals. 2022, 41, 356-360
15-CE-5/ZnSO <sub>4</sub>	2	2	720	ChemEur. J. 2023, 452: 139572
PAA/ZnSO <sub>4</sub>	0.5	0.5	3000	eScience. 2023, 3, 100153
	1	1	1400	
TC/ZnSO <sub>4</sub>	1	0.5	2000	Adv. Energy Mater. 2022, 12, 2102780
	5	2.5	500	
TEAB/ZnSO <sub>4</sub>	1	1	3950	This work
	5	1	2950	

Strategy/Zn Salt	Full cell	Current density A	Life	Ref.
	system	g-1	(h)	
TBA <sub>2</sub> SO <sub>4</sub> /ZnSO <sub>4</sub>	$Zn \  MnO_2$	1	300	ACS Energy Lett. 2020, 5, 9, 3012-3020
TMA <sub>2</sub> SO <sub>4</sub> /ZnSO <sub>4</sub>	$Zn \  MnO_2$	0.2	200	J. Colloid Interface Sci. 2022, 627, 367- 374
β-CD/Zn(ClO <sub>4</sub> ) <sub>2</sub>	Zn  MnO <sub>2</sub>	1	1000	Angew. Chem. Int. Ed. 2022, 61, e202210979
PC-sat/Zn(OTf) <sub>2</sub>	Zn-ZnMn <sub>2</sub> O <sub>4</sub>	0.5	300	J. Am. Chem. Soc. 2022, 144, 16, 7160– 7170
BIS-TRIS/ZnSO <sub>4</sub>	Zn  MnO <sub>2</sub>	0.5	600	Energy Storage Mater 2021, 41, 515- 521
Na <sub>4</sub> EDTA/ZnSO <sub>4</sub>	$Zn \  VO_2$	4	2000	Adv. Energy Mater. 2021, 11, 2102010
SF/ZnSO <sub>4</sub>	Zn  KVO	3	1000	ACS Nano 2022, 16, 7, 11392–11404
TEAB/ZnSO4	Zn  MnO <sub>2</sub>	1 3	1000 2000	This work

Table 2. Full cells cycling performance comparison between this work and other recent reports.