Commercially Available Ionic Liquids Enables High-Performance of Aqueous Zinc-Iodine Batteries: Sequestered Nitrogen-sites for Efficient Electrocatalytic Iodine Conversion

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Electrochemical characterization

The DMPII/LiI+I_2 catholyte is fabricated by mixing 1,2-dimethyl-3-propylimidazolium iodide (DMPII, 0.6 M), I_2 (0.1 M) and LiI (1.0 M) in the solution of alcohol. The DMPII come from Shanghai Aladdin Biochemical Technology Co., Ltd, the product number is D119483, purity is 98 %, and price is 1 g/6 USD. The LiI+I_2 catholyte is fabricated by the same method without the additive of DMPII. For the electrolyte of Zn-I_2 battery, the aqueous solution with $ZnSO_4$ (0.5 M) and Li_2SO_4 (0.5 M) is prepared. The current collector is carbon paper, where the nominal thickness is 245 nm, nominal basis weight is 75 g/m^3, break strength machine direction is 6.5 MPa, bulk density is 0.29 g/cm^3, and compressibility is 10.7 %. The area of the electrodes is 1 cm^2, the separator uses glass fiber from Whatman (product code: 1823-047), and Every coin cell is infiltrated by about 100 μL electrolyte. The potential range is 0.6-1.6 V during the long-term cycling and CV test. The electrochemical measurements were carried out using the CR2032-type coin cell that was adopted for the cell test. The C-rate currents and capacities were computed based on active materials-iodide (1 C corresponds to 200 mA/g). The chronoamperometry curves were measured by the pulsed potentials between -0.1 V (20 s) and 0.1 V (20 s). All cells were aged and then activated for several cycles before the cyclic test.

Material characterization

The SmartLab Rigaku X-ray diffractometer is used to detect the X-ray diffraction (XRD) patterns for testing the crystal structure of materials. JSM-7610F Plus scanning electron microscope (SEM) is used to show the morphology of materials in micrometer scale. Park Systems XE-70 atomic force microscope (AFM) is used to detect the surface condition of sample. Shimadzu UV-1780 is used to detect the UV-vis to analyze the ability for absorbing polyiodide. The Zolix Finder Smart FST2-MPL501-405C1 Micro-Raman system is used to detect the Raman spectrum. The CHI600e electrochemical workstation is used to test the cyclic voltammetry (CV) curves. The NEWARE battery test system is used to measure the stability about the long-term cycling. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a Gamry potentiostat by applying a sine wave with the amplitude of 10.0 mV over the frequency range from 100 kHz to 10 mHz.

Computational methods

All the calculations were carried out using the NWChem package [1]. The density functional theory (DFT) calculations were treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP) [2-3]. The calculations for C, N and H ions were performed using polarized split-valence 6-31G(d) basis set, while for I ions, we used the relativistic effective core potential (ECP) basis set of LANL2DZ basis sets in the calculations [4]. The methods and basis sets have been shown to adequately compute the chemical properties of molecular systems [5-6]. We also performed frequency analyses at the same levels to show that the relaxed structures were local minima.

References:

[1] Comput. Phys. Commun., 2010, 181, 1477-1489.

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[4] J. Phys. Chem. A, 2001, 105, 34, 8111-8116.

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Table S1 Electrochemical performance of the DMPII-based Zn-I$_2$ cells and other reported improved zinc batteries.

| Improve strategy	Specific capacities (mAh/g)	Current density	Cycling Stability (cycles)	Reference
DMPII	100	50 C(10 A/g)	20000	This work
ZnS@Zn	105	5 C	2500	*Adv. Mater.* 2020, 32, 2003021
Sac.	100	2.4 C	7500	*Adv. Mater.* 2021, 33, 2100445
Zn@ZIF-8-500	~110	2 A/g	1600	*Joule 3,* 1289–1300
MnSO$_4$	~92	5 C	5000	*Nat Energy 1,* 16039 (2016)
HCZE	~50	0.2 C	500	*Nature Mater 17,* 543–549 (2018)
Zn-BTC	85.1	1.9 A/g	6000	*Adv.Mater.* 2020, 32, 2004240
GBL	~120	2 A/g	2000	*Angew. Chem. Int. Ed.* 2023, e202301570
Gly	86.8	5 A/g	7000	*Chemical Engineering Journal 480 (2024) 148040*
TXA	92.5	3 A/g	1000	*Energy Storage Materials 59 (2023) 102800*
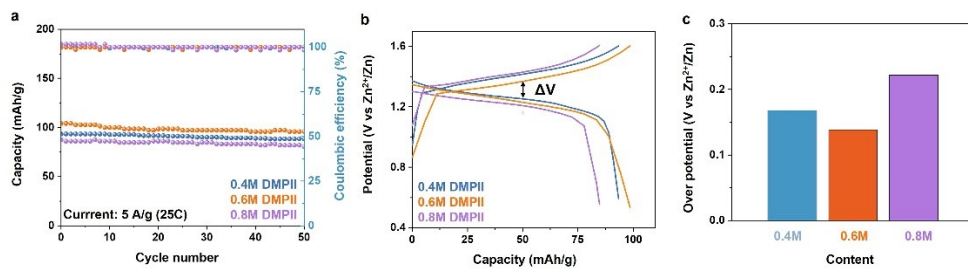
Fig. S1. Cycle stability of DMPII-based Zn-I$_2$ cells using 0.4, 0.6, and 0.8 M DMPII, respectively (a), the corresponding charge-discharge curves (b) and over potential (c).
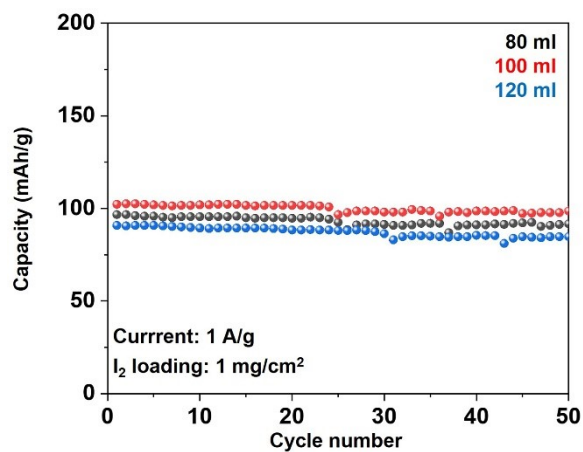
Fig. S2. Cycle stability of DMPII-based Zn-I$_2$ cells using 80, 100, and 120 mL of ZnSO$_4$ + Li$_2$SO$_4$ electrolyte, respectively.
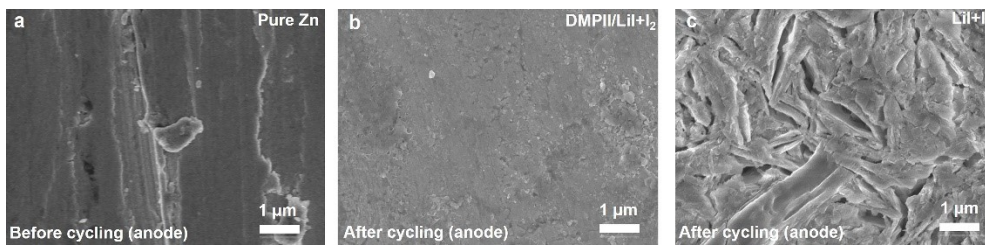
Fig. S3. SEM images of pure Zn (a) before cell cycling, DMPII-modified LiI+I$_2$ (b), and pure LiI+I$_2$ (c) electrode-based Zn anodes after cell cycling.
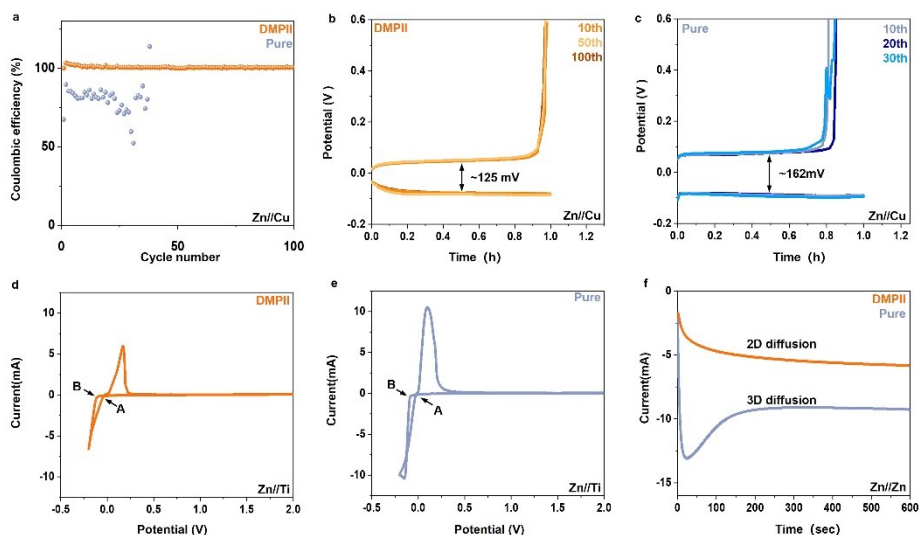
Fig. S4. Coulombic efficiency (a) of Zn//Cu cells at 2 mA/cm² with Zn with DMPII modification and pure Zn foil, and the corresponding 10, 50, and 100th voltage profiles of Zn with DMPII modification (b), and the corresponding 10, 20, and 30th voltage profiles of pure Zn foil (c), respectively. The CV curves of Zn//Ti cells with Zn with DMPII modification (d) and pure Zn foil (e) under 0.5 mV/s, respectively. Chronoamperometry (f) of Zn//Zn cells in the DMPII modification electrolyte at a -150 mV overpotential.
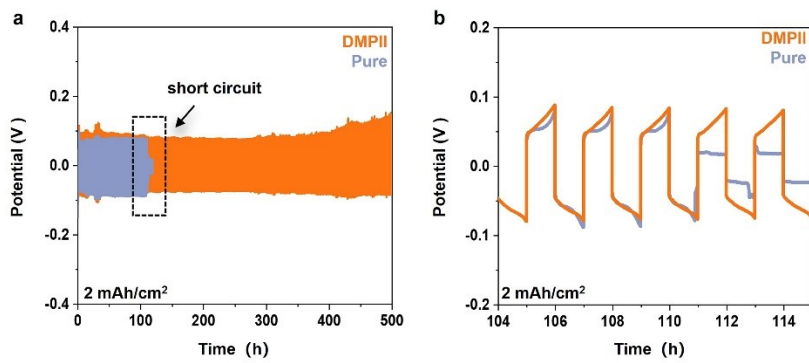
Fig. S5. The stability (a-b) of Zn//Zn symmetric cells in different electrolytes at 2 mAh/cm² and 2 mA/cm².
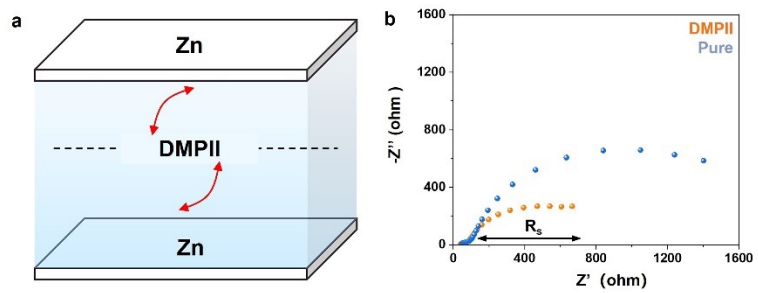
Fig. S6. Schematic illustration of the symmetric cell (a), and the corresponding Nyquist plots (b).