Electronic Supporting Information for:

Redox-Active Zinc Thiolates for Low-Cost Aqueous Rechargeable Zn-ion Batteries

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General Experimental Details

All experiments were carried out under nitrogen (or argon) atmosphere using an MBraun glovebox and/or standard Schlenk techniques unless stated otherwise. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 or 600 MHz spectrometer and were externally referenced to the NMR residual solvent peaks. ATR-IR spectra were measured using a Nicolet IR 200 with a diamond ATR accessory. Cyclic voltammetry and potentio-electrochemical impedance spectroscopy experiments were performed with a Biologic SP-150 or SP-50 single-channel potentiostat. Galvanostatic cycling experiments were performed with a LAND CT2001A battery testing system. Raman spectra were measured using a Renishaw Raman IR microprobe with a 514 nm laser beam. X-ray fluorescence (XRF) spectra were measured by an Olympus/Innov-X X-5000 XRF analyzer with a tantalum X-ray tube source and a Silicon Drift Detector. Unless otherwise noted, all solvents were degassed and dried using a Pure Process Technology (PPT) solvent purification system and stored under an atmosphere of nitrogen over 4 Å molecular sieves. DMSO-*d*₆ and C₆D₆ (Cambridge Isotope Labs) were dried over CaH₂ and vacuum transferred onto 4 Å molecular sieves prior to use. All glassware were dried at 175 °C before use. All reagents were purchased from Sigma Aldrich unless otherwise noted.

Preparation and Characterization of Compounds

Scheme S1. Synthesis of 1



Synthesis and Characterization of poly-[zinc-1,3,4-thiadiazole-2,5-dithiolate] (1)

Dipotassium-1,3,4-thiadiazole-2,5-dithiolate (42.86 g, 0.189 mol) was dissolved in DI H₂O (300 mL), and zinc chloride (25.8 g, 0.189 mol) was added. The reaction was stirred at 75 °C for four hours, resulting in an opaque colorless precipitate. The precipitate was filtered, washed with water (3 × 50 mL), and dried in a vacuum oven (80 °C) to yield the pure product as a fine, colorless powder (37.2 g, 0.174 mol). IR: (ATR, cm⁻¹) 3404 (H₂O), 3202 (H₂O), 1612, 1481, 1372, 1088, 1045, 963, 864, 780, 736, 675, 580, 543, 469. Elemental Analysis: Calcd. for $C_2N_2S_3Zn$ (%): C, 11.25; H, 0; N, 11.25. Found: C, 10.45; H, 0.67; N, 11.95.



Figure S1. IR (ATR) spectra of poly-[zinc-1,3,4-thiadiazole-2,5-dithiolate] (1).

Scheme S2. Synthesis of 2



Synthesis and Characterization of zinc-bis-(2-methylthio)-1,3,4-thiadiazole-5-thiolate (2)

5-(methylthio)-1,3,4-thiadiazole-2(3H)-thione was prepared according to a modified literature procedure.¹ KOH (56.1 g, 1.00 mol) and EtOH (900 mL) were added to a 3 L flask, and the mixture was stirred at 50 °C for two hours. The reaction was cooled to 10 °C in an ice water bath, and 2.5-dimercapto-1.3.4-thiadiazole (150.2 g, 0.9998 mol) was added in portions over 20 minutes. The reaction mixture was then stirred at 60 °C for three hours. After cooling to 15 °C, CH₃I (142 g, 1.00 mol) was added to the reaction mixture over 20 minutes, and the mixture was heated at reflux (78 °C) for six hours. The reaction mixture was concentrated to ~50% via distillation, and the remaining solution was cooled to room temperature and extracted with water and toluene (3×75 mL). The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*, affording the crude product. The crude product was recrystallized using reagent grade toluene, resulting in a crude 13:87 mole mixture of 2,5-bis(methylthio)-1,3,4thiadiazole and 5-(methylthio)-1,3,4-thiadiazole-2(3H)-thione (64 g). A portion of the crude mixture (22.8 g) was dissolved in DI H₂O (250 mL), and KOH (7.8 g, 0.14 mol) was added. The reaction was heated (80 °C) under nitrogen for four hours and allowed to cool to room temperature. The reaction mixture was extracted with reagent grade toluene (2×75 mL), and the organic phase was transferred to a 500 mL round bottom flask. ZnCl₂ (9.1 g, 0.067 mol) was added to the flask, and the mixture was heated (75 °C) under nitrogen for four hours, generating an opaque colorless precipitate. After the mixture cooled to room temperature, the precipitate was filtered, washed with DI H₂O, and dried in a vacuum oven (80 $^{\circ}$ C), yielding the final product as a colorless solid (25.7 g, 0.0656 mol). ¹H NMR (DMSO-*d*₆, 400 MHz): δ 2.78 (s, 6H). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 177.70, δ 161.21, δ 16.13. IR: (ATR, cm⁻¹) 2921, 1426, 1408, 1367, 1358, 1312, 1217, 1159, 1097, 1088, 1068, 1058, 1032, 1024, 972, 768, 708, 672, 609, 551. ESI-MS (m/z) calcd. for $[C_3H_3N_2S_3]^-$ ($[M]^-$): 162.95, found: 163.0. Elemental Analysis: Calcd. for C₆H₆N₄S₆Zn (%): C, 18.39; H, 1.54; N, 14.30. Found: C, 18.06; H, 1.56; N, 14.15.



Figure S2. (A) ¹H NMR (DMSO-*d*₆, 400 MHz), (B) IR (ATR), and (C) ¹³C NMR (DMSO-*d*₆, 100 MHz) spectra of zinc-bis-(2-methylthio)-1,3,4-thiadiazole-5-thiolate (**2**). Blue dot indicates product; yellow dot indicates NMR solvent (δ 2.51 – DMSO-*d*₆), red dot indicates solvent impurity (δ 3.33 – water).

Scheme S3. Synthesis of 3



Synthesis and characterization of 1,2-bis(5-(methylthio)-1,3,4-thiadiazol-2-yl)disulfane (3)

Potassium 5-(methylthio)-1,3,4-thiadiazole-2-thiolate was isolated as an off-white solid via the addition of KOH to the crude mixture of **4** and **5** according to the previous synthetic procedure.¹ In a scintillation vial, potassium 5-(methylthio)-1,3,4-thiadiazole-2-thiolate (1.8 g, 8.88 mmol) was suspended in a 50:50 biphasic mixture of DI H₂O (40 mL) and EtOAc (40 mL). H₂O₂ (30%, 1.01 g, 8.88 mmol) was added dropwise, and the reaction was stirred for 24 hours. The aqueous phase was extracted with EtOAc ($2 \times 30 \text{ mL}$), and the combined EtOAc phases were dried over MgSO₄ and filtered. All volatiles were evaporated *in vacuo* to give a yellow oil. The hot oil was triturated with Et₂O, causing a yellow solid to precipitate. The yellow oil/solid mixture was washed thoroughly with Et₂O ($3 \times 15 \text{ mL}$) and dried *in vacuo* to afford the crude product. The crude solid was crushed, washed again with Et₂O ($2 \times 5 \text{ mL}$), and recrystallized by vapor diffusion of Et₂O into a DCM solution to yield the pure product as yellow crystals (936 mg, 32%). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an EtOAc solution of the crude product. ¹H NMR (CDCl₃, 400 MHz): δ 2.78 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 171.20, δ 164.10, δ 16.42. IR: (ATR, cm⁻¹) 3008 (C-H), 2927 (C-H), 1423, 1408, 1393, 1383, 1368, 1342, 1302, 1209, 1186, 1157, 1132, 1080, 1048, 1022, 962, 952, 745, 711, 701, 647, 605, 593, 552, 526 (S-S), 516 (S-S), 488. HRMS-ESI (*m/z*) calcd. for C₄H₆N₄S₆ ([M-H]⁺): 326.8989, found: 326.8983.



Figure S3. (A) ¹H NMR (CDCl₃, 400 MHz), (B) IR (ATR), and (C) ¹³C NMR (CDCl₃, 100 MHz) spectra of 1,2-bis(5-(methylthio)-1,3,4-thiadiazol-2-yl)disulfane (**3**). Blue dots indicate product; yellow dot indicates NMR solvent (δ 7.26 – CDCl₃).

XRD Measurements

Powder X-Ray Diffraction

Powder diffraction data of **1** and **2** were collected using a Bruker D8 Powder X-Ray Diffractometer employing Cu $K(\alpha)$ 1 line with a wavelength of 0.4579 Å, step size 0.02°, exposure time of 1 sec per step. We were unable the determine the structure of **1** due to the poor crystallinity of the sample (Figure S4).



Figure S4. Powder X-ray diffraction data of 1.



Figure S5. X-ray diffraction pattern of (A) **2** compared with the simulated pattern obtained from the previously reported single-crystal X-ray diffraction data², (B) **3** compared with the simulated pattern obtained from experimental data, and (C) pristine **2** compared with discharged **2** after 60 cycles.

Scanning Electron Microscopy

To prepare the cycled samples for microscopy, the cathode powder was placed on a p50 carbon fiber disk as the current collector. After cycling, the battery was disassembled, and the cathode was washed with 10 drops of DI water and dried under vacuum for one hour. The pristine powder sample and cycled cathode sample were prepared on conductive carbon tape substrate. Micrographs were acquired with a 10 keV beam voltage and 50 pA beam current in OptiPlan mode.



Figure S6. Micrographs of (A) pristine 2 and (A) a cathode of 2 after cycling in 1 M ZnSO₄ for 60 cycles, ending on a discharge. The electrode surface shows light colored particles/crystals of 2 embedded in dark colored Super P. The cycled sample (B) also shows a glassy fiber rod leftover from the separator.

Single Crystal X-Ray Diffraction

Single crystal data was collected on a Bruker D8 Venture instrument and a Photon II detector with Mo K α radiation source ($\lambda = 0.71073$ Å). Single crystals were mounted with Paratone oil on glass fibers and immediately placed under a cold nitrogen stream (Oxford Cryosystems Cryostream) at 100(2) K. The data were integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite³ in the Olex2 program and were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS.⁴ Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included in idealized positions. All crystal structures were rendered in Olex2 using 50% probability ellipsoids. Single crystal diffraction data of **2** has been previously published² and is available on the Cambridge Crystallographic Data Centre website (CCDC: 1828049).



Figure S7. Solid-state structure of 3 (CCDC: 2095600) with thermal ellipsoids represented at the 50% probability level.

 Table S1. Crystal data and structure refinement for 3.

Identification code	DMcTMe2		
Empirical formula	C6 H6 N4 S6		
Formula weight	326.51		
Temperature	100.0 K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group (Z)	P-1 (2)		
Unit cell dimensions	a = 7.7096(5) Å	a= 85.493(2)°	
	b = 8.5742(6) Å	b= 86.271(2)°	
	c = 9.4537(6) Å	$g = 80.637(2)^{\circ}$	
Volume	613.82(7) Å ³		
Density (calculated)	1.767 Mg/m ³		
Absorption coefficient	1.089 mm ⁻¹		
F(000)	332		
Crystal size	0.341 x 0.108 x 0.092 mm	3	
Crystal color, habit	Yellow Rod		
Theta range for data collection	3.129 to 30.532°.		
Index ranges	-11<=h<=11		
	-12<=k<=12		
	-13<=1<=13		
Reflections collected	40620		
Independent reflections	3732 [R(int) = 0.0270, R(s)]	igma) = 0.0122]	
Completeness to $\theta = 25.000^{\circ}$	99.4 %		
Absorption correction	Semi-empirical from equiv	alents	
Max. and min. transmission	0.2657 and 0.2186		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	3732 / 0 / 147		
Goodness-of-fit on F ²	1.086		
Final R indices [I>2σ(I)]	$R_1 = 0.0196$		
	$wR_2 = 0.0465$		
Largest diff. peak and hole (e • Å ⁻³)	0.411 and -0.354		

Table S2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for **3**. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	X	У	Z	U(eq)
S(1)	3309(1)	9889(1)	2391(1)	18(1)
S(2)	5747(1)	8998(1)	3128(1)	18(1)
S(3)	2421(1)	7829(1)	5098(1)	17(1)
S(4)	7144(1)	7067(1)	572(1)	26(1)
S(5)	-473(1)	6298(1)	6658(1)	18(1)
S (6)	7994(1)	3767(1)	-459(1)	26(1)
N(1)	307(1)	8834(1)	3106(1)	19(1)
N(2)	-661(1)	8024(1)	4123(1)	19(1)
N(3)	5997(1)	5853(1)	2936(1)	19(1)
N(4)	6527(1)	4596(1)	2102(1)	19(1)
C(1)	1895(1)	8836(1)	3483(1)	16(1)
C(2)	269(1)	7439(1)	5209(1)	15(1)
C(3)	6236(1)	7200(1)	2290(1)	17(1)
C(4)	7149(1)	5049(1)	840(1)	18(1)
C(5)	-2675(2)	6236(2)	6160(1)	22(1)
C(6)	8137(2)	1900(1)	565(1)	27(1)

Electrochemical Measurements

Two-Electrode Solid State Cyclic Voltammetry

Solid-state CV experiments were carried out using a two-electrode coin-type cell, consisting of a cathode of 1 or 2 and Zn metal as the anode (see Coin Cell Assembly). The coin cells were allowed to rest for one hour and then submitted to a single galvanostatic charge-discharge cycle at 0.5C to ensure consistency between cells. Subsequent CV scans were performed at a scan rate of 0.1 mV s^{-1} .

Three-Electrode Solid State Cyclic Voltammetry

Solid-state CV experiments were carried out using a three-electrode cell, consisting of a reticulated vitreous carbon (RVC) working electrode (Duocell Foam, 3% rel. density, 60 ppi) coated with redox-active material, a Ag^+/Ag reference electrode (BASi) soaked in aqueous 3 M NaCl, and an RVC counter electrode. CV scans were performed in varying concentrations of ZnSO₄ and H₂SO₄ electrolytes at a scan rate of 0.1 mV s⁻¹ after an initial rest period of one hour.

To create the RVC electrodes, RVC was cut from a small block using a borer. Copper wire was pushed into the top of the RVC electrode and sealed with a paste consisting of Super P and EtOH. The bottom of the RVC working electrode was dipped into a slurry mixture consisting of approximately 5 mg of electrode powder (70% redox-active material, 20% Super P, 10% binder) and EtOH (~5 drops). The electrodes were allowed to dry for 10 minutes in an 80 °C oven prior to use.



Figure S8. Depiction of adjustment made to solid-state CV curves of **3** in 1 M H₂SO₄ electrolyte. The position of the 1 M H₂SO₄ curve (pH \approx 0, dotted line) is adjusted to represent a dilute H₂SO₄ solution (pH \approx 4, solid line), calculated based on the Nernst equation. The solid-state CV curve of **3** in 1 M ZnSO4 is included for reference.

Battery Testing

Electrode Powder Fabrication

Conductive electrode powder mixtures were prepared by combining **1** or **2** with conductive carbon (Super P) and polyvinylidene fluoride (PVDF) binder in a 70:20:10 weight ratio using a mortar and pestle to mill mixtures until homogeneous. The electrode powders were used directly in coin cell assembly.

Nafion Preparation

Prior to use, Nafion separators were pretreated sequentially in (1) 4% H_2O_2 , (2) DI water, (3) 0.8M H_2SO_4 , and (4) DI water at 80 °C for 30 min each, with numbers corresponding to the order of treatment. The pretreated Nafion membranes were then soaked in fresh 1 M or 3 M ZnSO₄ for 24 hours prior to use in coin cells. After soaking, the ZnSO₄ solution became highly acidic and was discarded after use.

Coin Cell Assembly

Coin-type cells were assembled in open air with powder mixtures of **1** or **2** as the cathode, 1 M ZnSO₄ (Zinc Sulfate) or 3 M ZnSO₄ as the aqueous electrolyte, GF/A only or GF/A and Nafion as the separator(s), and Zn foil as the anode. Coin cells were assembled bottom to top: coin cell bottom, cathode powder, separator(s), 150 µL electrolyte, Zn anode, stainless steel current collector, wave/conical washer, coin cell top with gasket. Coin cells were crimped in a Gelon GN-CCM20 coin cell crimper at 900 psi and used for battery testing after a rest period of one hour.

Galvanostatic Charge-Discharge Cycling

Galvanostatic charge-discharge cycling was performed with coin-type cells containing cathode of 1 or 2 with a voltage window of 0.2-1.6 V (*vs.* Zn^{2+}/Zn) for 1 or 0.6-1.6 V for 2. The current applied during battery cycling experiments was calculated based on the theoretical capacity of each compound (assuming a two-electron input) and the weight of the active cathode material used in each cell.



Figure S9. (A) Charge-discharge curves and (B) galvanostatic cycling data of **1** in 1 M ZnSO₄ at a rate of 0.5C (125 mA g⁻¹).

Figure S10. (A) Charge-discharge curves and (B) galvanostatic cycling data of **2** in 1 M ZnSO₄ at a rate of 0.5C (68 mA g⁻¹).

pH-dependent Galvanostatic Charge-Discharge Cycling

Galvanostatic charge-discharge cycling was performed with coin-type cells containing cathodes of 2 in a 1 M ZnSO₄ electrolyte. The pH of the electrolyte was adjusted with 1 M H₂SO₄ to obtain the desired pH as indicated by pH paper.

Figure S11. pH-dependent charge-discharge curves for **2** at (A) cycle 2 and (B) cycle 25 in 1 M ZnSO₄. Inset shows a close-up of the H⁺ insertion region.

Figure S12. pH-dependent galvanostatic cycling data for 2 in 1 M ZnSO₄.

Galvanostatic intermittent titration technique (GITT) experiment of Zn-2 cell

Ion diffusion coefficient can be determined by GITT analysis based on the following equation:

$$D = \frac{4}{\pi * \tau} (\frac{n_m V_m}{S})^2 (\frac{\Delta E_s}{\Delta E_t})^2$$

Where τ (3600 s) is the duration of the current pulse, n_m is the number of mols, V_m is the molar volume of **2**, S is the electrode area, ΔE_s is steady-state voltage change, and ΔE_t is the voltage change during constant current pulse.

Figure S13. Discharge GITT profile of 2 in 1 M ZnSO₄.

Optimization of Zn-2 Cell Performance

To hinder the potential proton insertion pathway, we investigated the effect of increasing the Zn^{2+} concentration. As ZnSO₄ is mildly acidic, the relationship between increasing Zn²⁺ concentration and the resulting change in H⁺ should be considered. Therefore, we analyzed the pH of 1 and 3 M ZnSO₄ and compared the concentration of Zn²⁺ and H⁺ to the respective electrolytes. When 3 M ZnSO₄ is used, the overall ratio of Zn²⁺:H⁺ is 1.89 times higher compared to 1 M ZnSO₄.

Electrolyte	[Zn ²⁺]	pН	[H+]	[Zn ²⁺]:[H ⁺]	3 M:1 M
1 M ZnSO ₄	1	4.39	4.07 x 10^-5	24547:1	1 80
3 M ZnSO4	3	4.19	6.46 x 10^-5	46464:1	1.09

Table S3. Quantitative analysis of Zn²⁺ concentration and pH of freshly prepared 5 mL electrolyte solutions

Figure S14. (A) Charge-discharge curves and (B) galvanostatic cycling data of **2** in 1 M ZnSO₄ at a rate of 1C (136 mA g⁻¹).

Figure S15. (A) Charge-discharge curves and (B) galvanostatic cycling data of **2** in 3 M ZnSO₄ at a rate of 1C (136 mA g^{-1}).

Figure S16. (A) Charge-discharge curves, (B) galvanostatic cycling data, and (C) rate-dependent cycling data of 2 in 3 M ZnSO₄ with Nafion (cycled at a rate of 1C (136 mA g^{-1}) for A and B).

Figure S17. Galvanostatic charge-discharge comparison of cycle 10 from cells of **2** in 1 M ZnSO₄ (purple), 3 M ZnSO₄ (green), and 3 M ZnSO₄ with Nafion (blue) at a rate of 1C (136 mA g⁻¹). Inset shows a close-up of the H⁺ insertion region.

X-ray Fluorescence Spectroscopy

X-ray fluorescence spectra were obtained from 10 mg samples of 2 (pristine, charged, and discharged cathode powders). Samples were scanned with a Tantalum anode at 35 keV with a 26 μ A tube for 15 seconds. Each sample was evenly distributed in a plastic bag that covered the entire detector window. Each sample was scanned three times, and the counts per second values were averaged.

Figure S18. XRF spectra of (A) pristine 2, (B) charged 2, and (C) discharged 2 cathode powders.

Raman Spectroscopy

Raman spectra of samples of **2** (pristine, charged, and discharged cathode powders), pristine **3**, and ZnSO₄·7H₂O were measured under an inert atmosphere using a $50 \times$ or $10 \times$ microscope lens and a 514 nm laser beam at 10% laser power. Spectra were measured from 200 to 1200 cm⁻¹ at 3-5 different spots on each cathode to ensure uniformity.

Figure S19. Overlay of Raman spectra of isolated charged 2 cathode powder (green), pristine 3 (brown), and ZnSO₄·7H₂O (gray).

Figure S20. Overlay of Raman spectra of pristine **2** cathode powder (blue), isolated discharged **2** cathode powder (red), and ZnSO₄·7H₂O (gray).

UV-vis Spectroscopy

Beer's Law plots

A solution of **3** or **4** (2.5 mL, 0.1 mM) in 1 M Zn(OTf)₂/MeOH was placed in a quartz cuvette under ambient air at room temperature, and a UV-vis spectrum was taken. Then, five 0.5 mL allotments of 1 M Zn(OTf)₂/MeOH were added to the cuvette to serially dilute the solution. A UV-vis spectrum was taken after each addition. Absorbance values at λ_{max} were plotted against their corresponding concentrations to obtain a Beer's Law plot and corresponding molar extinction coefficient. Beer's Law plots could not be obtained in aqueous electrolyte solutions due to the low solubility of the compounds in aqueous media. Therefore, 1 M Zn(OTf)₂/MeOH was chosen as the solvent because it incorporates both Zn²⁺ ions and a protic solvent, similar to the aqueous electrolyte used in our batteries. A Beer's Law plot for **2** in aqueous electrolyte could not be obtained due to the insolubility of the sample in all relevant solvents.

Figure S21. UV-vis spectra and Beer's Law plots of (A, B) 3 and (C, D) 4.

Solubility Studies in ZnSO₄ Electrolytes

Compounds **3** and **4** (~10 mg) were each allowed to stir in either 1 M ZnSO₄/H₂O (3 mL) or 3 M ZnSO₄/H₂O (3 mL) for 30 min. The mixtures were filtered through glassy fiber filter paper, and the resulting solutions were either diluted or used directly for UV-vis analysis. To obtain the concentrations of each compound in the stock solutions, the extinction coefficient of each DMcT species in aqueous solution was assumed to be the same as that in 1 M $Zn(OTf)_2/MeOH$ solution.

Figure S22. UV-vis spectra comparison of (A) **3** and (B) **4** in 1 M and 3 M $ZnSO_4/H_2O$. (D) Calculated concentrations of **3** and **4** in 1 M and 3 M $ZnSO_4/H_2O$ based on UV-vis absorbance in aqueous $ZnSO_4$ and extinction coefficients in 1 M $Zn(OTf)_2/MeOH$.

Comparison of λ_{max} in different solvents

To determine the effect of solvent and Zn^{2+} concentration on the λ_{max} of compounds **3** and **4**, we performed UV-vis in MeOH and H₂O without added Zn-based electrolytes. We find that shifts in the λ_{max} of **3** and **4** are likely due to solvent effects (MeOH vs. H₂O).

Figure S23. UV-vis spectra comparison of 3 (A, B) and 4 (C, D) in various solvents. Graphs are intended for comparison of λ_{max} only. Absorbance is arbitrary. (E) Summary of λ_{max} found for 3 and 4 in various solvents.

Post-Mortem Analysis of Zn-2 Cells

Coin Cell Disassembly

The cycled coin cells were opened in air after 24 hours of galvanostatic cycling, and disassembled with a Gelon GN-CCM20 coin cell crimping machine employing a disassembly die set. Pictures of the electrodes and separators were taken upon disassembly. To prepare the cathodes for post-mortem analysis, they were washed with DI water $(3 \times 10 \text{ mL})$ and dried at 80 °C under vacuum for 24 hours before being used, unless otherwise noted.

Figure S24. Digital pictures of disassembled coin cells of (A) **3** in 3 M ZnSO₄ with Nafion membrane (from left to right: coin cell top, Zn anode, Nafion membrane, GF/A glass microfiber filter paper, active material cathode), (B) **3** in 1 M ZnSO₄ without Nafion membrane (from left to right: coin cell top, Zn anode, GF/A glass microfiber filter, active material cathode).

GC-MS

After disassembly of the dead cell, the cathode and anode were placed in separate vials and extracted with DCM (~15 mL) for several minutes. Each vial was vortexed thoroughly, and the resulting mixtures were filtered through GFA/pipette filters. Excess solvent was removed via rotary evaporator, and the remaining samples were diluted with a small amount of DCM for GC-MS analysis.

Figure S25. (A) Gas chromatogram and (B) mass spectrum of discharged 2 cathode powder.

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