batteries

MDPI

S1. Rection mechanisms in literature

Table S1. Overview of the reaction mechanisms during charging (CH)/discharging (DCH) mentioned in the literature. The reaction equations are normalized to a transfer of 6 e^- for better comparability. (based on [1].)

	#	Chemical Reaction Equation	Source
Anode	1	***Zn/Zn^{2+} Dissolution (DCH)/Deposition (CH):*** $3\ Zn \rightleftharpoons 3\ Zn^{2+} + \mathbf{6\ e^-}$ ($E_0 = 0$ V vs. Zn/Zn^{2+})	[2–7]
	2	***Hydrogen Evolution Reaction (HER, CH):*** $6\ H^+ + \mathbf{6\ e^-} \rightarrow 3\ H_2\uparrow$ ($E_0 = +0.52$ V vs. Zn/Zn^{2+}, pH ~4)	[2,8–10]
Cathode	3	***MnO$_2$ /Mn^{2+} Dissolution/Deposition:*** $3\ MnO_2 + \mathbf{6\ e^-} + 12\ H^+ \rightleftharpoons 3\ Mn^{2+} + 6\ H_2O$ ($E_0 = +1.54$ V vs. Zn/Zn^{2+}, pH ~4) *proton source: H_2O*	[2,7,8,10–16]
	4	***Alternative mechanism:*** $3\ MnO_2 + 12\ [M(H_2O)_6]^{2+} + \mathbf{6\ e^-} \rightleftharpoons 3\ Mn^{2+} + 12\ [M(H_2O)_5OH]^+ + 6\ H_2O$ *proton source: $[M(H_2O)_6]^{2+}$, here: M = Zn or Mn*	[17–20]
	5	***Zinc hydroxide sulfate (ZHS) precipitation/dissolution:*** $12\ OH^- + 2\ SO_4^{2-} + 8\ Zn^{2+} + 2n\ H_2O \rightleftharpoons 2\ Zn_4(OH)_6SO_4 \cdot n\ H_2O$ *with n = [4, 5]* ***MHO precipitation/dissolution (universal):*** $[M(H_2O)_6]^{2+} + 2\ OH^- \rightleftharpoons M(OH)_2 + 6\ H_2O$ *with M = Zn or Mn*	[8,12,21]
	6	***Zn^{2+} intercalation (DCH)/deintercalation (CH):*** $x\ Zn^{2+} + 2x\ e^- + MnO_2 \rightleftharpoons Zn_xMnO_2$	[3,5,11,22–39]
	7	***H$^+$ intercalation (DCH)/deintercalation (CH):*** $6\ MnO_2 + 6\ H^+ + \mathbf{6\ e^-} \rightleftharpoons 6\ HMnO_2$	[8]
	8	***O$_2$-reduction (ORR, DCH)/O$_2$-formation (OER, CH):*** $1{,}5\ O_2 + 6\ H^+ + \mathbf{6\ e^-} \rightleftharpoons 3\ H_2O$ ($E_0 = +1.75$ V vs. Zn/Zn^{2+}, pH ~4)	[2,8,10,40]
	9	***Formation of (inert) ZnMn$_2$O$_4$ (CH):*** $3\ Zn^{2+} + 6\ Mn^{2+} + 24\ OH^- \rightarrow 3\ ZnMn_2O_4 + 12\ H_2O + \mathbf{6\ e^-}$	[8,11]

S2. Energy density estimates

- substance concentration $c(Zn^{2+}) = c(Mn^{2+}) = 1\ mol.l^{-1}$,
- **volumetric energy density** in $Wh.l^{-1}$, based on ***Faraday's* law** (z = 2 for the chemical reaction 3 (s. **Error! Reference source not found.**), nominal discharge voltage approx. 1,65 V at pH 4):
  $\frac{E}{V} = UczF = 1{,}65\ \mathrm{V} \cdot 1\ \mathrm{mol.l^{-1}} \cdot 2 \cdot 96.485\ \mathrm{As.mol^{-1}} = 192.970\ \mathrm{As.l^{-1}} = \mathbf{88{,}4\ Wh.l^{-1}}$,
- **electrolyte volume 11,3 l.kWh^{-1}**,
- **specific weight for 1 l electrolyte** (based on a reference electrolyte composition with 1 M $Zn(CH_3COO)_2$, 1 M $Mn(CH_3COO)_2$):
  - assumption 50 ml equal to 58,86 g,
  - equal to 1,177 g/ml,
  - equal to 1,177 kg/l electrolyte.
- **gravimetric energy density** in $Wh.kg^{-1}$
  $\frac{E}{m} = \frac{UczF}{m_{\mathrm{Elektrolyt}}} = \frac{1{,}65\ \mathrm{V} \cdot 1\ \mathrm{mol.l^{-1}} \cdot 2 \cdot 96.485\ \mathrm{As.mol^{-1}}}{1{,}18\ \mathrm{kg}} = \mathbf{75{,}0\ Wh.kg^{-1}}.$

- **material values**: $\varrho(H_2O)$ = 0,997 kg.l^{-1}, $\varrho(Zn(CH_3COO)_2 \cdot 2\ H_2O)$ = 1,74 kg.l^{-1}, $\varrho(Mn(CH_3COO)_2 \cdot 4\ H_2O)$ = 1,59 kg.l^{-1}, $M(Zn(CH_3COO)_2 \cdot 2\ H_2O)$ = 219,50 g.mol^{-1}, $M(Mn(CH_3COO)_2 \cdot 4\ H_2O)$ = 245,09 g.mol^{-1} [41]
- **specific cost:** $g(Zn(CH_3COO)_2)$ = 1.00 \$.kg^{-1} , $g(Mn(CH_3COO)_2 \cdot 4\ H_2O)$ = 1.00 \$.kg^{-1}
- **total cost electrolyte:** $m_{tot} = \sum_i c_i M_i g_i = 0.40$ \$.l^{-1} → 4.46 \$.kWh^{-1}

Note: The specific cost calculations are based on price estimates from alibaba.com. This is for sure not a reliable and absolute price quotation, but at least reflects the price range and the cost potential.

S3. C-rate calculations & transformations

Source	Current Rate	Transformation	C-Rate / C or 1.h^{-1}
[18]	20.6 A.g^{-1}	in paper: 1 C = 0.574 A.g^{-1}	~36
[42]	1 A.g^{-1}	initial capacity approx. 100 mAh.g^{-1} (s. Figure 8 in paper)	~10
[43]	10 mA.cm^{-2}	charge capacity 0.8 mAh.cm^{-2}	12.5
[44]	7000 mA.g^{-1}	specific capacity 374 mAh.g^{-1}	18.7

S4. Ionic conductivity for ZMB electrolytes

Table S2. Overview of selected electrolyte compositions with the respective pH and ionic conductivity values. [1.]

Electrolyte Composition	pH	Ionic Conductivity/mS.cm^{-1}
0.5 M $MnSO_4$	3.5	30.3
2.0 M $ZnSO_4$	3.6	55.4
2.0 M $ZnSO_4$ + 0.5 M $MnSO_4$	3.1	48.6
2.0 M $Zn(CF_3SO_3)_2$	4.0	60.5

S5. Industrial approaches for ZIB.

Table S3. Overview of a selection of relevant industrial approaches to zinc-based battery cell chemistry (as of 2022).

Name Country CEO/CTO	Founding	Battery Cell Technology	State of Research	Source
Urban Electric Power USA Sanjoy Banerjee/ Jinchao Huang	Spin-off (CUNY Energy Institute[1]) 2012	$Zn//MnO_2$, alkaline electrolyte	• Pilot projects (20-1000 kWh) • 300-1000 cycles (at DOD 50-10%), C-rate 1/2-1/24, 380-600 V output voltage • Cost: \$50/kWh per battery	[45–47]
Enerpoly AB Sweden Eloisa de Castro/ Dr. Mylad Chamoun	2018	$Zn//MnO_2$ acid electrolyte ($ZnSO_4$/ $MnSO_4$)	• Cell chemistry is based on published literature • Patent for nanoporous zinc foam anodes, [48] • Current status: Cell concept	[11,49,50]

[1] The City College of New York CUNY Energy Institute

Eos Energy Enterprises USA Joe Mastrangelo/ Carlos Restrepo	2008	Znyth ® Zn//X (with Halide X = Br, Cl, I) neutral electrolyte ($ZnBr_2$, KBr, KCl, additive)	• Carbon fleece cathode with ceramic-coated titanium current arrester • 98.2% annual capacity retention after 20+ years of operation, 100% DOD, C-rate 1/3-1/12 • Cost estimation up to \$95/kWh (system level)	[51,52]
Salient Energy Canada Brian Adams	2016	Zn//V_xO_y- bzw. Mo_xO_y-based cathode zinc salt electrolyte (pH 1-9)	• capacity 60 Ah, cell voltage 1,3 V, energy density 100 Wh.l^{-1} and 60 Wh.kg^{-1}, self discharge 0 % (2 weeks) and 5 % (6 months) • cell fabrication with 100 pieces/month	[53–56]

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