Supplementary Materials: Cold sintering as a cost-effective process to manufacture porous zinc electrodes for rechargeable zinc-air batteries

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1. Supplementary Electron Microscopy and X-ray diffraction data

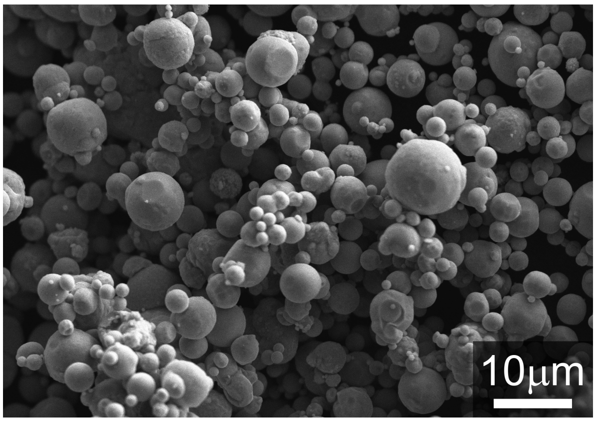

Figure S1. Secondary Electron (SE) image of initial Zn powder

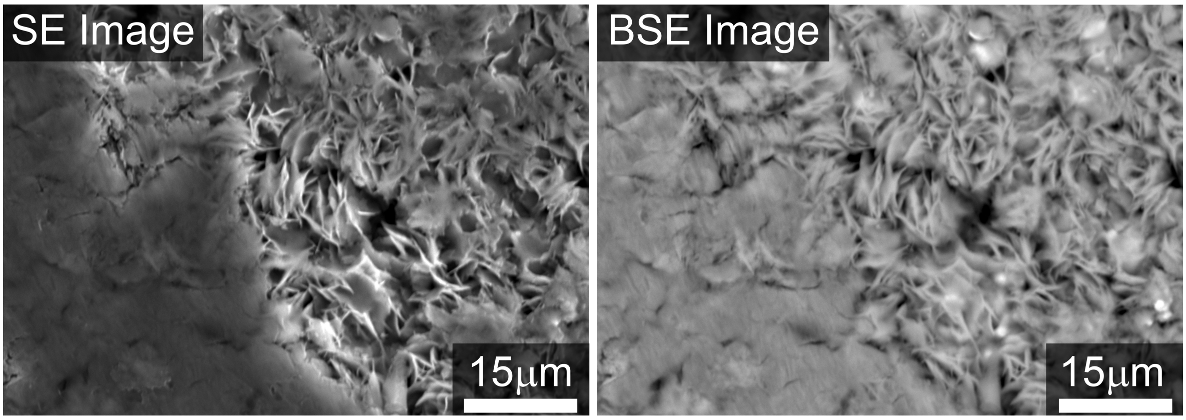

Figure S2. Secondary Electron (SE) and Backscattered Electron (BSE) images of a porous Zn monolith after reaction with acetic acid

2. Thermodynamic Model

The thermodynamic model used to create the Pourbaix diagrams is implemented according to the method described in Ref [1]. The equilibrium stability and solubility product constants used in the model are listed in Table S1.

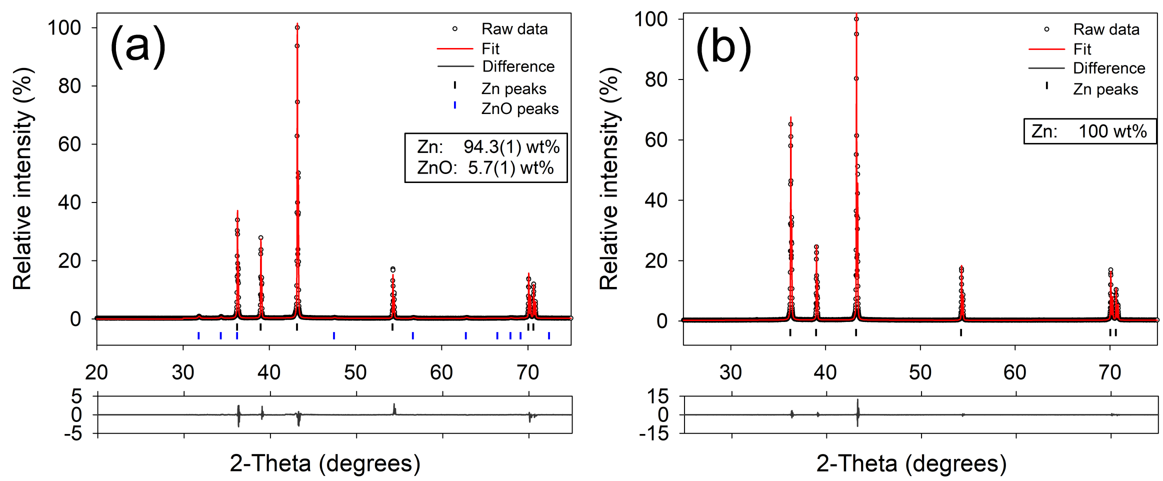

Figure S3. Fitted x-ray diffractograms of as-received (a) Zn powder and (b) Zn foil. A strong degree of preferred orientation was observed for the Zn foil sample, and corrected for using a spherical harmonics type correction function

Table S1. Reactions, equilibrium stability constants, and solubility product constants used in the thermodynamic model. Values are compiled from Refs [2] & [3].

Homogeneous Reactions	$\log_{10} K_{eq}$
$H^+ + OAc^- \rightleftharpoons HOAc$	5.015
$Zn^{2+} + OAc^- \rightleftharpoons Zn(OAc)^+$	0.91
$Zn^{2+} + 2\,OAc^- \rightleftharpoons Zn(OAc)_2$	1.36
$Zn^{2+} + 3\,OAc^- \rightleftharpoons Zn(OAc)_3{}^-$	1.57
$Zn^{2+} + OH^- \rightleftharpoons Zn(OH)^+$	6.5
$Zn^{2+} + 2\,OH^- \rightleftharpoons Zn(OH)_2$	11.6
$Zn^{2+} + 3\,OH^- \rightleftharpoons Zn(OH)_3{}^-$	13.8
$Zn^{2+} + 4\,OH^- \rightleftharpoons Zn(OH)_4{}^{2-}$	14.7
Precipitation Reactions	$\log_{10} K_{sp}$
$Zn^{2+} + 2\,OH^- \rightleftharpoons ZnO(s)$	16.66
$Zn^{2+} + 2\,OH^- \rightleftharpoons Zn(OH)_2(s)$	16.48

3. Techno-Economic Analysis

To determine the power required to mix the zinc slurry, it is first necessary to calculate the Reynolds number for the flow in the mixer:

$$Re = \frac{d^2 \omega \rho}{\mu} \tag{1}$$

where d is the diameter of the impeller, ω is the speed of rotation, ρ is the slurry density, and μ is the viscosity of the zinc slurry, estimated as 1 Pa s [4]. Mixing power is then calculated as:

$$P_{\text{mixing}} = N_p \rho N^3 d^5 \tag{2}$$

The power number for the impeller, N_p, depends on the Reynolds number and impeller design. N_p for a generic impeller with a Reynolds number in the transition region is estimated as 2.5 [5].

The thermal sintering process takes place under a reduced pressure of 20 mbar. The energy required to reduce the pressure is calculated as:

$$W = V\Delta p \tag{3}$$

where V is the volume of the chamber (assumed to be 5 L) and Δp is the change in pressure. The heating and cooling energy are calculated under ideal conditions as:

$$\Delta Q = mc\Delta T \tag{4}$$

where ΔQ is the energy that goes into the system of mass m and specific heat capacity c to change the temperature by ΔT degrees. The heat capacity of Zn slurry is calculated as:

$$\sum_i c_i X_i \tag{5}$$

where c_i is the heat capacity of slurry component i with mass fraction X_i. Heat capacities for materials used in this study are listed in Table S2. Heating and cooling power are calculated using the time-derivative of equation 4:

$$P_{\text{thermal}} = \dot{Q} = mc\dot{T} \tag{6}$$

where $\dot{T}$ is the heating rate. To remove the influence of equipment variations, it is assumed that the process takes place under ideal conditions and that no power is required to maintain a constant temperature.

Table S2. Material parameters used in this work.

Material	Density, kg L^{-1}	Specific Heat Capacity, J kg^{-1} K
Zinc	7.14	390
Water	1.00	4200
Decane	0.73	2218
80wt% Aqueous Acetic Acid	1.05	3105

Table S3. Assumed mixer parameters.

Volume, L	1.0
Container Diameter, cm	9.0
Impeller Diameter, cm	3.0
ω, s^{-1}	41

Table S4. Material prices used in this work.

Material	CAS	Details	Price per Unit
Zinc Powder	7440-66-6	99.99% Purity	\$39 kg^{-1}
Ethanol	64-17-5	Absolute	\$11 L^{-1}
Acetic Acid	64-19-7	≥99% Reagent plus	\$47 kg^{-1}
Decane	124-18-5	≥95% Purity	\$60 L^{-1}
Sodium lauryl sulfate	151-21-3		\$50 kg^{-1}
CMC	9004-32-4	Medium viscosity	\$145 kg^{-1}
Aluminum Foil	Z185140		\$1.19 m^{-2}
Copper Mesh	7440-50-8		\$505.44 m^{-2}

3.1. Thermal Sintering

The recipe for the zinc-water slurry and the emulsified zinc-water slurry called for in the preparation of the thermal sinteted Zn electrodes are given in Table S5. The Reynolds numbers for mixing the Zn-water slurry and emulsified Zn-water slurry under the conditions described in Table S3 are 139 and 99, respectively. The flow is in the transition region between laminar and turbulent flow.

Table S5. Slurry preparation for thermal sintered Zn electrodes.

Material	**Density,** kg L^{-1}	**vol%**	**Material Volume,** L	**wt%**	**Material Mass,** kg
Zinc	7.14	45%	0.14	85.38%	1.00
DI Water	1.00	55%	0.17	14.62%	0.17
Zn-water slurry	***3.76***	***100%***	***0.31***	***100%***	***1.17***
Zn-water slurry	3.76	63.39%	0.31	89.47%	1.17
Decane	0.73	35%	0.17	9.58%	0.13
Sodium lauryl sulfate	1.01	0.11%	5.40×10^{-4}	0.04%	5.45×10^{-4}
CMC	1.60	1.50%	7.36×10^{-3}	0.90%	1.18×10^{-2}
Emulsified Zn-water slurry	***2.67***	***100%***	***0.49***	***100%***	***1.31***

3.2. Cold Sintering

The recipe for the zinc-ethanol slurry and the emulsified zinc-water slurry called for in the preparation of the cold sinteted Zn electrodes are given in Table S6. The Reynolds number for mixing the Zn-ethanol slurry under the conditions described in Table S3 is 158. The flow is in the transition region between laminar and turbulent flow.

Table S6. Slurry preparation for cold sintered Zn electrodes.

Material	**Density,** kg L^{-1}	**vol%**	**Material Volume,** L	**wt%**	**Material Mass,** kg
Zinc	7.14	55%	0.14	91.70%	1.00
Ethanol	0.79	45%	0.11	8.30%	0.09
Zn-ethanol slurry	***4.28***	***100%***	***0.25***	***100%***	***1.09***

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