Electronic Supplementary Material (ESI) for Nanoscale Advances.


Supporting Information for

# 200 MPa Cold Isostatic Pressing Creates Surface-microcrack Zn Foil for Scalable and Long-life Zinc Anodes

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**Experimental**

**Materials:** Zinc foil (30 μm thick, 99.9%), $ZnSO_4 \cdot 7H_2O$ (AR) and isopropanol (AR) were purchased from Sinopharm Chemical Reagent. Polytetrafluoroethylene (PTFE) dispersion (60 wt% PTFE aqueous solution) was purchased from Li Zhiyuan Technology. Glass fiber filters (GF/C) were purchased from Whatman. $VO_2$ (99%) and conductive carbon (acetylene black) were purchased from Taobao. Ultrapure water was obtained from a Milli-Q water purification system. Cold isostatic pressing machine from SXKYYC.

**Preparation of electrodes: 1) Pure zinc anode.** Zinc foils (30 μm thick, 99.9%) were first ultrasonically cleaned with acetone, and then cut into zinc foils with a diameter of 12 mm and an area of about 1.13 $cm^{-2}$ using a microtome. Finally, these zinc foils were ultrasonically cleaned and dried again using acetone. **2) 50 MPa, 100 MPa, 200 MPa and 300 MPa zinc anodes.** First, ultrasonically clean the zinc foil with acetone, then dry the zinc foil and seal it with a sealed bag, and place it in a cold isostatic pressing container. Set different pressure values (50 MPa, 100 MPa, 200 MPa and 300 MPa) respectively to obtain zinc foils after different cold isostatic pressing. Here, the parameters are set to 150 s for both boost and buck, and the dwell time is 120 s. The zinc foil after cold isostatic pressing was washed with acetone again, and then cut into zinc foils with a diameter of 12 mm and an area of about 1.13 $cm^{-2}$ using a microtome, and ultrasonically cleaned and dried with acetone for battery assembly. **3) $VO_2$ positive electrode.** The mass ratio of $VO_2$, acetylene carbon black and PTFE is 6:2:2, and the rolling method is used to obtain the positive electrode. First, 150 mg $VO_2$ powder and 50 mg acetylene carbon black was placed in a mortar for thorough grinding for 10 minutes, and then 83.3 mg of 60% PTFE solution (the mass of PTFE is 50 mg) was added to continue grinding for 2 minutes, and then an appropriate amount of isopropanol was continuously added in ventilation. Wet grinding was performed in the cabinet for 5 minutes. The milled mixture is then repeatedly pressed into flakes using a roll press. During the rolling process, isopropyl alcohol was continuously added to maintain the cohesiveness of the PTFE. When the thickness of the sheet is 5 mm, it is cut into a circle with a diameter of 11 mm with a microtome under a certain humidity. Finally, the discs were dried in an oven at 80 °C for 12 h, and then weighed and used as positive electrodes. The quality of the positive active material is controlled at about 5.4 mg. **4) Zinc anode and $VO_2$ cathode of soft pack batteries.** The zinc foil was cut into 6 cm×6 cm zinc sheets, ultrasonically cleaned with acetone and dried as anodes. The positive electrode was also prepared by the rolling method, cut into a positive electrode sheet of 6 cm×6 cm, and then dried in an oven at 80 °C for 12 h to be used as a positive electrode.

**Preparation of electrolyte:** Configure 10 mL 1 M $ZnSO_4$ electrolyte. Dissolve 2.87 g $ZnSO_4 \cdot 7H_2O$ in 8.74 g pure water, and stir for 1 h. Thus, 1 M $ZnSO_4$ electrolyte was obtained.

**Characterization:** SEM and EDS images were taken using a Zeiss Auriga SEM/FIB system. Atomic force microscopy (AFM) was used to photograph zinc foil surface flatness tests. Rigaku Miniflex 600 was used to measure zinc electrode XRD patterns. Dendrite growth on the zinc surface was observed in situ using a Scienscope Optical microscope.

**Electrochemical measurement:** The battery was tested with a Lanhe battery test system, the temperature was controlled at 26°C, and the coin cell battery case model was CR2016. The assembly sequence is positive electrode shell, positive electrode sheet, separator, drop 70 μL of electrolyte, negative electrode sheet, gasket, and negative electrode shell. The battery was then sealed and allowed to stand for 2 h before testing. The EIS, Tafel, CA and CV data tests of the batteries were all performed on an electrochemical workstation (Bio-Logic).

## Figures and Tables

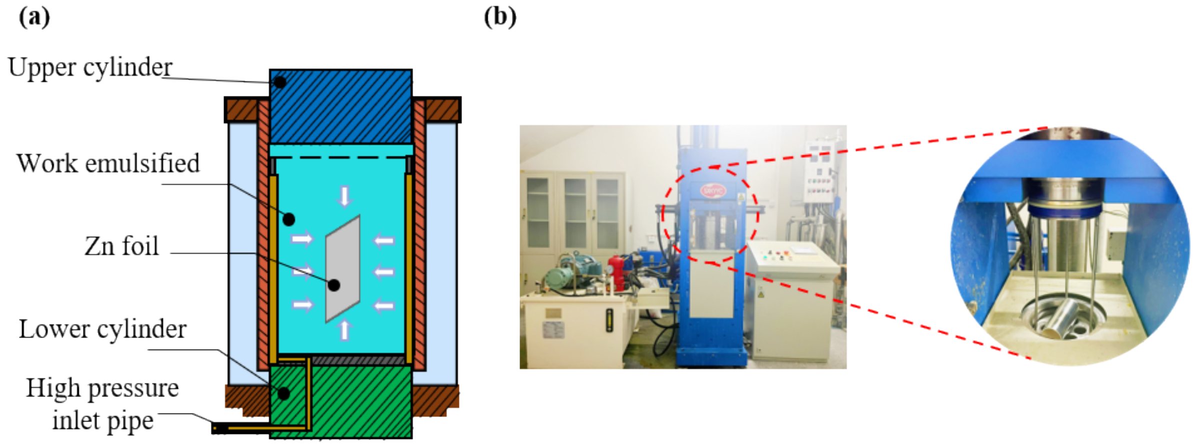


**Figure S1** Schematic of the cold isostatic pressing. a) Schematic of the cross section of the container compartment of the cold isostatic pressing. The object is subjected to isobaric treatment of liquid in all directions in the container compartment. b) Large-scale processing of zinc foil pictures by cold isostatic pressing. Placing a large amount of zinc foil in the container compartment and setting different parameters for batch processing can achieve ideal results.

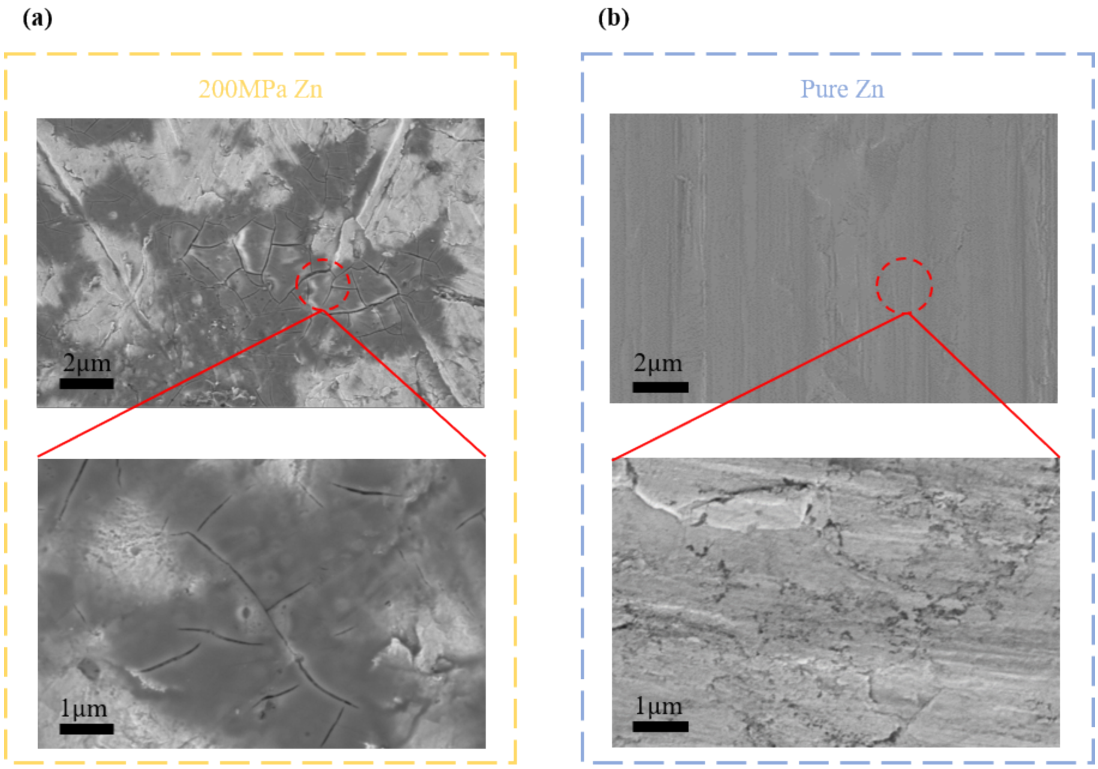


**Figure S2** Surface morphology of zinc foil. a) SEM image of the zinc foil surface treated by cold isostatic pressing at 200 MPa. Various microcracked structures are produced on the surface. b) SEM image of pure zinc surface. The surface is rough and uneven and contains various impurities.

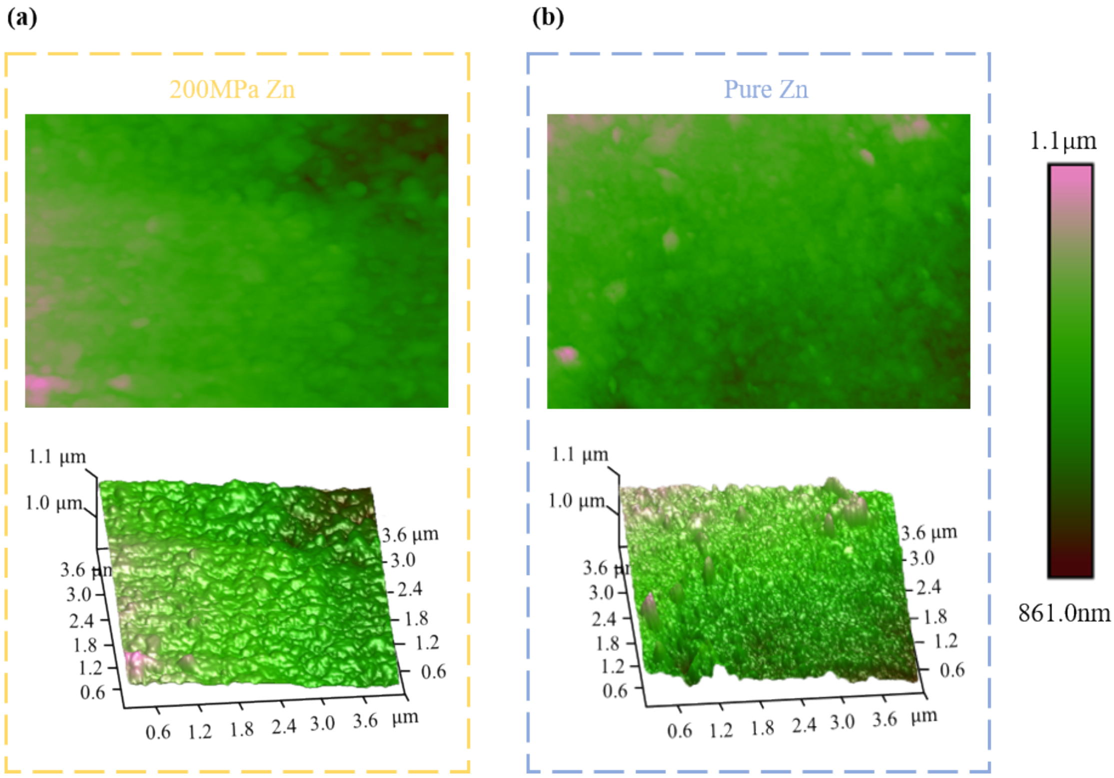


**Figure S3** Surface flatness test image of zinc foil. a) AFM image of 200 MPa Zn surface. The surface is smooth, no large protrusions appear. b) AFM image of pure zinc surface. The surface is rough and uneven, and there are various protrusions.

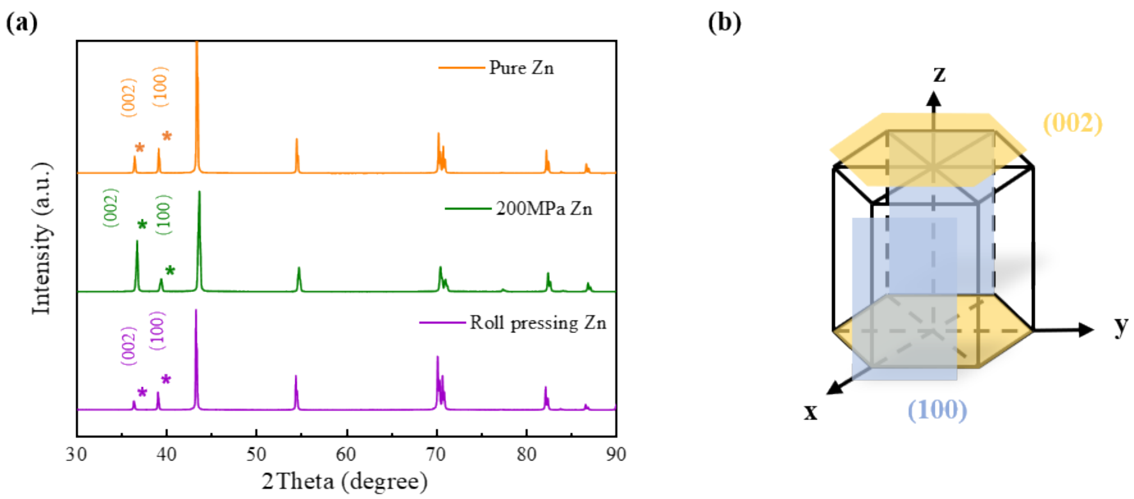

**Figure S4** Zinc plane structure. a) XRD image with (002) plane and (100) plane peaks. It can be seen that the 200MPa treatment changes the internal structure of zinc and increases the (002) crystal plane. b) Schematic of the zinc structure.

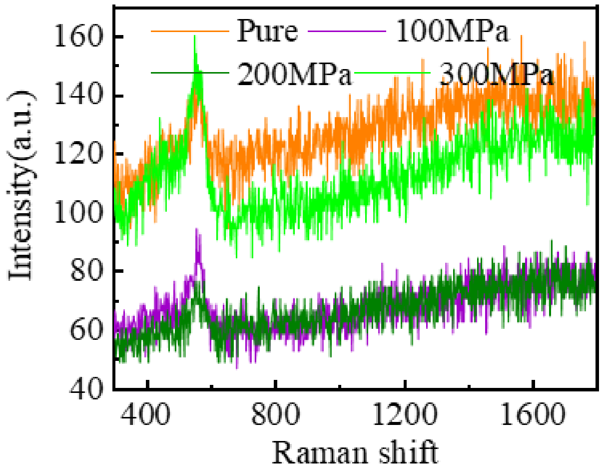


**Figure S5** Pure, 100 MPa, 200 MPa and 300 MPa surface Raman images of zinc foil. The zinc surface contains oxide peaks, and the 200 MPa Zn oxidation peak intensity is lower. The treatment effect is the best.

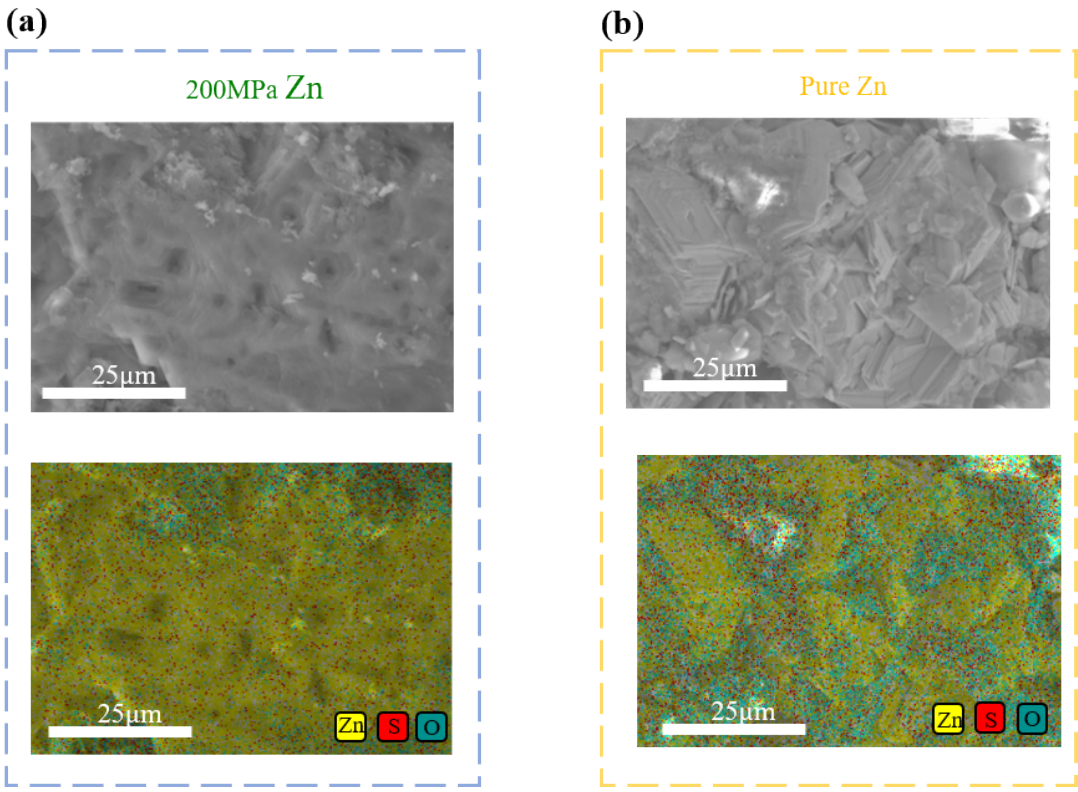

**Figure S6** Morphology and EDS image of dendrite growth on Zn surface after symmetric battery cycling.

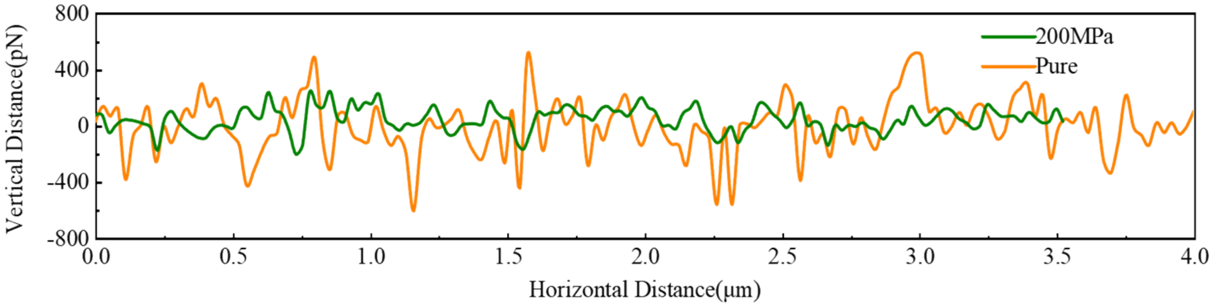


**Figure S7** Surface flatness curve of zinc foil.

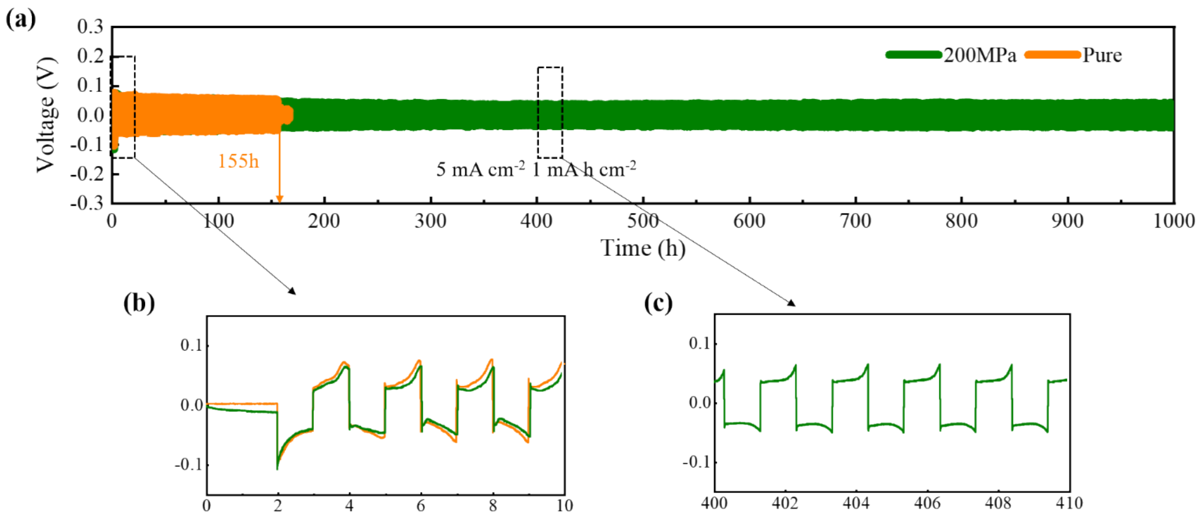


**Figure S8** Cycling curves and overpotentials of symmetric cells at 5 mA $cm^{-2}$ and 1mA h $cm^{-2}$.

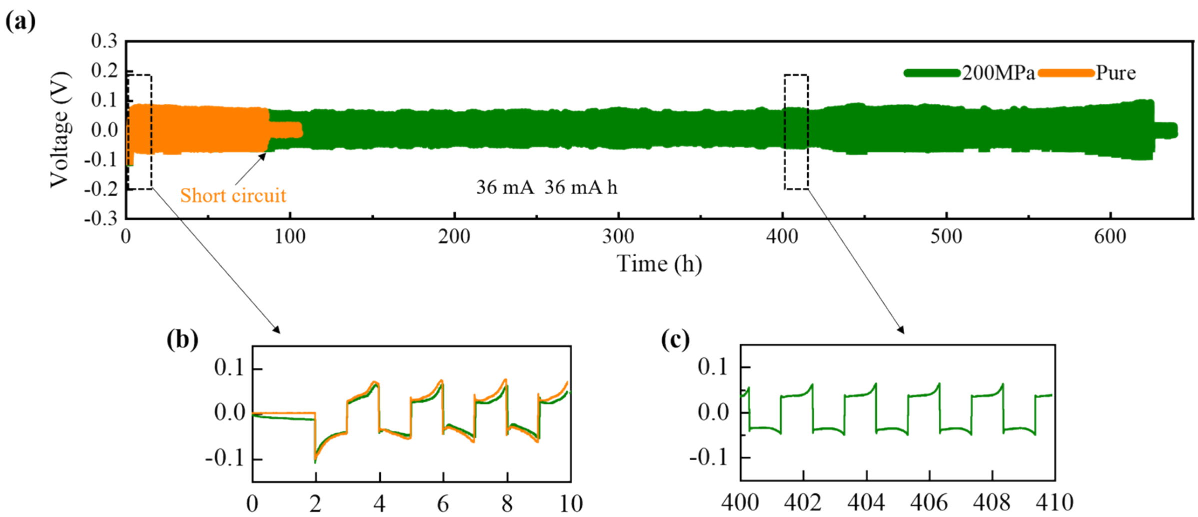

**Figure S9** Cyclic test curve and overpotential of a soft-pack symmetrical battery at 36 mA 36 mA h.

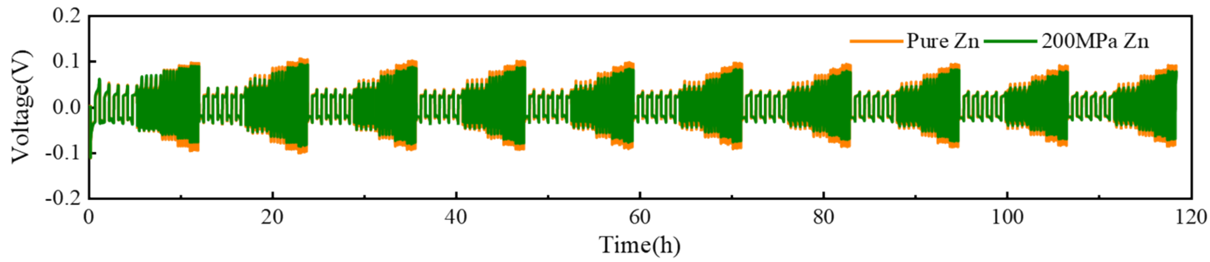


**Figure S10** Symmetrical cell rate curve.

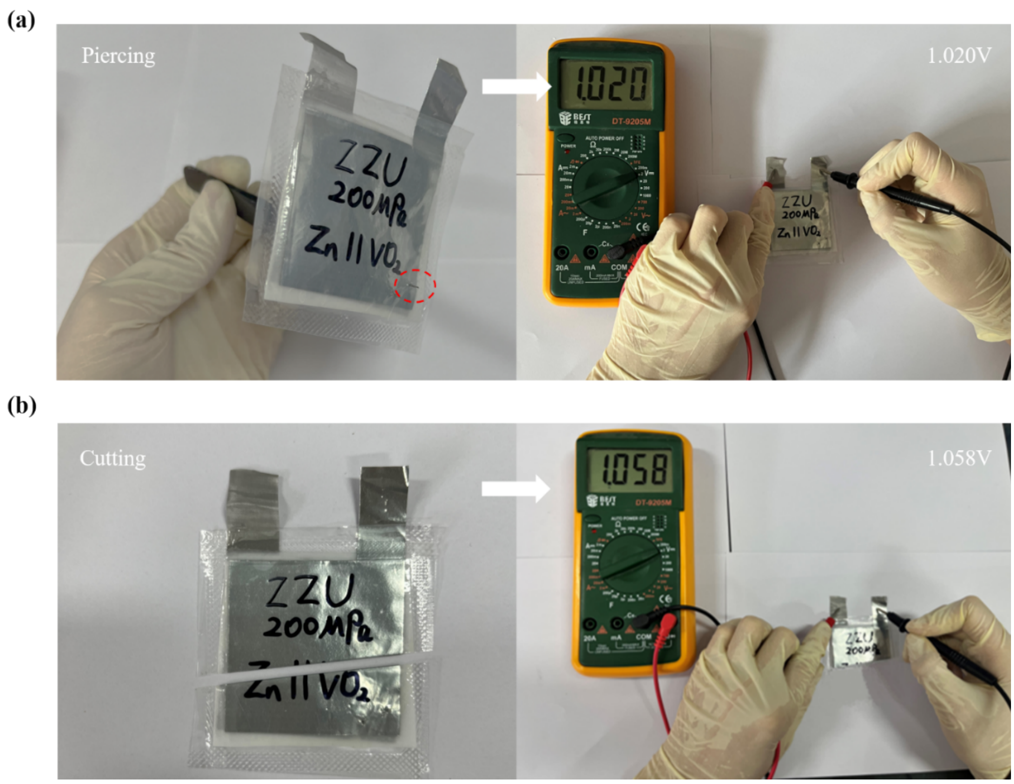


**Figure S11** Piercing and cutting experiments

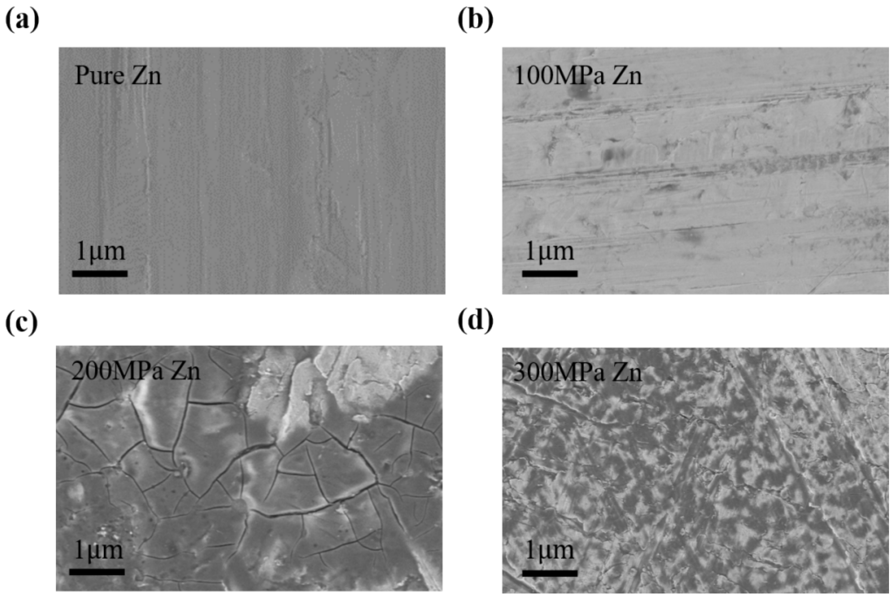


**Figure S12** Comparison of pure zinc, 100MPa, 200MPa and 300MPa zinc foil surface morphology

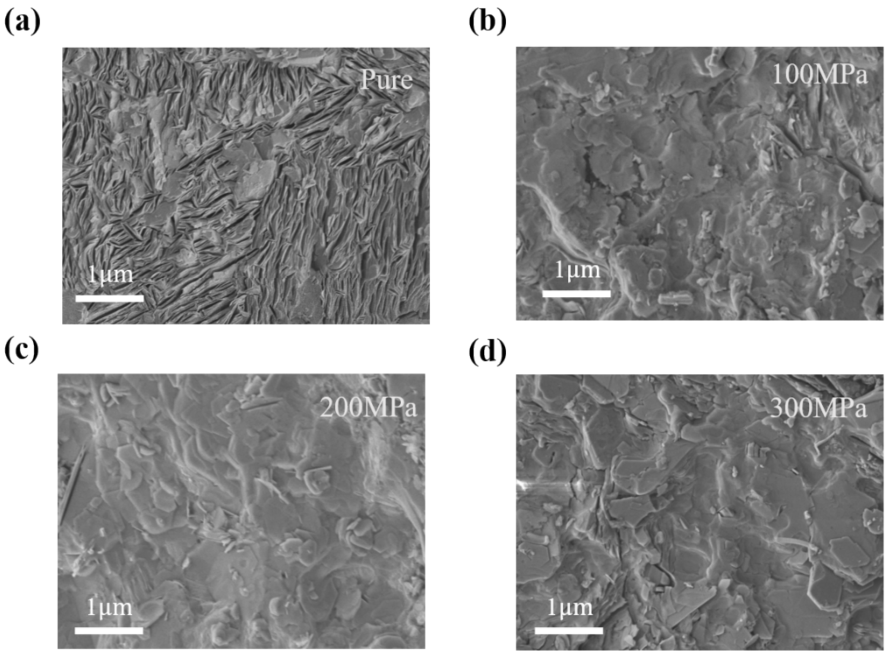


**Figure S13** Pure Zn, 100 MPa Zn, 200 MPa Zn and 300 MPa Zn surface dendrites SEM images of growth

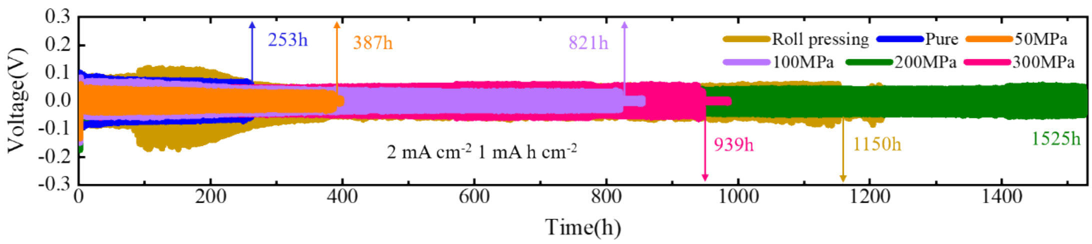

**Figure S14** Long cycle results of zinc foil treated with different pressures such as pure, 50 MPa, 100 MPa, 200 MPa, 300 MPa and ross pressing under the conditions of 2 mA cm$^{-2}$ and 1 mA h cm$^{-2}$

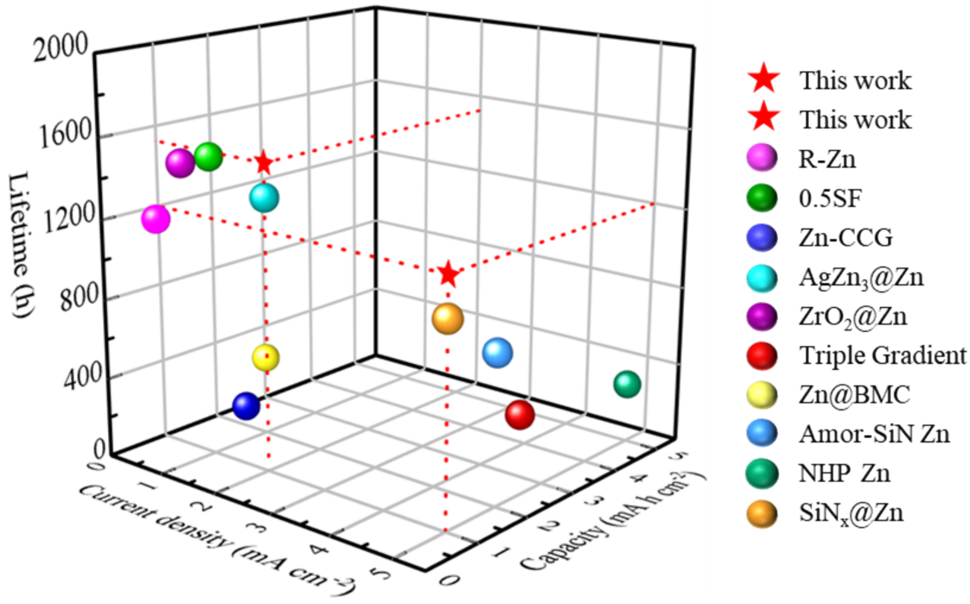


**Figure S15** Comparison of the performance of this work with other recently reported zinc symmetric batteries

## Tables

**Table S1** Overpotential and exchange current density evaluation of 200 MPa Zn and pure Zn symmetric cells at different current densities.

| Current density $\boldsymbol{i}$ (mA cm$^{-2}$) | Overpotential $\boldsymbol{\eta}$ (mV) | |
|---|---|---|
| | 200 MPa Zn symmetrical cell | Pure Zn symmetrical cell |
| 2 | 26.0 | 30.5 |
| 4 | 46.0 | 49.0 |
| 6 | 53.0 | 63.1 |
| 8 | 55.6 | 71.9 |
| 10 | 64.0 | 83.1 |

| | | |
|---|---|---|
| Linear fit | $\eta_1$=4.28 $i$+23.24 | $\eta_2$=6.41 $i$+21.09 |

These data can be obtained directly from the symmetric cell data, and the exchange current density can be calculated using the equation:

$$i = i_0 \frac{zF}{RT}(E - E_{eq})$$

Where $\boldsymbol{i_0}$ is the exchange current density; $\boldsymbol{i}$ is the current density; $E - E_{eq}$ is the total overpotential, which is denoted by $\boldsymbol{\eta}$ in the article; $\boldsymbol{R}$ is the gas constant; $\boldsymbol{T}$ is the thermodynamic temperature; $\boldsymbol{F}$ is the Faraday constant; $\boldsymbol{z}$ is the number of electrons involved in the electrode reaction.

in the equation:

z=2，R=8.314 J/(mol K)，F=96485 J/(V mol)

T=25℃=273.15+25=298.15K

$$k = \eta/i, \eta = E - E_{eq}$$

$$i_0 = \frac{RT}{zF(E - E_{eq})} i = \frac{1}{k}\frac{RT}{zF} = \frac{1}{4.28}\frac{8.314 * 298.15}{2 * 96485} = 3.0013 \text{ mA cm}^{-2}$$

$$i_0 = \frac{RT}{zF(E - E_{eq})} i = \frac{1}{k}\frac{RT}{zF} = \frac{1}{6.41}\frac{8.314 * 298.15}{2 * 96485} = 2.004 \text{ mA cm}^{-2}$$

After calculation, the exchange current density of the 200 MPa zinc-ion battery is 2.004 mA $cm^{-2}$, which is lower than that of pure Zn (3.0013 mA $cm^{-2}$). It shows that 200 MPa Zn has small overpotential and good zinc ion deposition kinetics.

**Table S2** Performance comparison of Zn symmetric cell of this work and other reported works

| Electrode | Current density (mA $cm^{-2}$) | Capacity (mA h $cm^{-2}$) | Life(h) | Reference |
|---|---|---|---|---|
| **200MPa Zn** | **2** | **1** | **1525** | **This work** |
| **200MPa Zn** | **5** | **1** | **1200** | **This work** |
| R-Zn | 0.5 | 0.5 | 1200 | [1] |
| Zn-CCG | 1.3 | 1.3 | 239 | [6] |
| 0.5SF | 1 | 1 | 1500 | [14] |

| | | | | |
|---|---|---|---|---|
| $AgZn_3$@Zn | 2 | 1 | 1360 | [20] |
| $ZrO_2$@Zn | 1 | 0.5 | 1500 | [24] |
| Triple Gradient | 5 | 2.5 | 400 | [31] |
| Zn@BMC | 1 | 2 | 400 | [33] |
| Amor-SiN Zn | 5 | 2 | 750 | [35] |
| NHP Zn | 5 | 5 | 300 | [43] |
| $SiN_x$@Zn | 5 | 1 | 1000 | [44] |