

Supporting Information

Expediting ion migration and stabilizing interface deposition by pre-polarized ion channels for zinc- ion batteries

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I. Supporting Test

1.1. Experimental section

1.1.1. Preparation of MnO_2 material

To prepare the ϵ - MnO_2 , the $MnCO_3$ (purchased in Greagent) were calcined at 350°C for 10 hours with a heating rate of 5 °C min⁻¹.

1.1.2. Preparation of nanofiber BTO material

Polyvinylpyrrolidone (PVP) (2 g) was dissolved in a mixture of anhydrous ethanol (20 mL), ice acetic acid (16 mL), and deionized water (4 mL) with magnetic stirring. Then, the ethyl barium acetate (0.01 M) and butyl titanate (3.45 mL) were added to the above mixture and stirred for 4 hours. The precursor fibers were produced using electrospinning with a feed rate of 1.5 mL h⁻¹, a voltage of 15 kV, and a distance of 15 cm between the needle tip and the collector. The obtained precursor was calcined at 850 °C for 4 hours with a heating rate of 3 °C min⁻¹.

1.1.3. Fabrication of BTO coated separators

The calcined material was ground into powders and weighed to ensure that the loading of BTO on the separators was 1 mg cm⁻². Next, 10% PVDF (polyvinylidene fluoride) was added to the powder and the mixture was slurred in NMP (N-methyl-2-pyrrolidone). The resulting slurries was uniformly coated onto glass fiber and dried overnight.

1.1.4. Preparation of MnO_2 cathode

A certain amount of MnO_2 , PVDF (polyvinylidene difluoride), and Super P were mixed in a ratio of 7:2:1. The NMP solvent was added to the mixture, and uniformly

mixed in a mortar. The resulting slurries was coated onto a carbon cloth surface using the doctor–blade method and dried at 60°C in an oven for 12 hours.

1.1.5. Polarization of BTO modified separator

The assembled coin cell (CSR2032, without electrolyte) was placed in silicone oil preheated to 80°C and polarized using a voltage withstand tester (ENTAI ET2670A, China) at a voltage of 1.5 kV for a duration of 1 hour. Notably, high-resistance ceramics are connected in series to isolate and protect the device. After polarization, the cell was removed, wiped clean, and allowed to cool naturally to room temperature, then assemble the polarized BTO modified separator to a new cell.

1.1.6. Materials characterizations

The electrode was disassembled using a small hydraulic coin cell sealing machine (KeJing MSK–110, China). SEM images were obtained with a Gemini SEM 300, Zeiss. XRD data were recorded using an X-ray diffractometer (Bruker D8 Advance, Germany) with copper radiation and a maximum tube voltage of 60 kV. The piezoelectric testing data were obtained from a ferroelectric analyzer (aixACCT TF2000, Germany).

1.1.7. Electrochemical measurements

The CR2032 coin cell was assembled in the air. The electrolyte for the Zn||Zn symmetrical cell, Zn||Cu asymmetric cell, and Ti||Ti symmetrical cell was 2 m ZnSO₄ (Aladdin, China). The electrolyte for the Zn//MnO₂ cell was 2 m ZnSO₄ (Aladdin, China) and 0.2 m MnSO₄ (Aladdin, China). Cycle measurements and GITT measurements were performed using a battery testing instrument (LANHE CT3002A,

China), while cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), potentiostatic polarization (i-t), and Tafel measurement were performed using a potentiostatic/galvanostatic instrument (CorrTest CS2350M, China).

1.2. Calculation detail of the finite element

To simulate the concentration and potential distribution of different ion channels cells. Tertiary current distribution, Phase field, and Electrostatic modules of COMSOL Multiphysics 6.0 were used for finite element calculations. The stationary simulation of this process was conducted in an area filled with electrolyte.

The diffusion process followed Fick's law, and the relationship between the diffusion coefficient and the migration rate followed the Nernst–Einstein equation.

$$N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i$$

In the equation, N_i represents the ion flux, D_i is the diffusion coefficient of the electrolyte, and ∇c_i represents the concentration gradient, z_i represents the number of transferred electrons ($z_{Zn} = 2$), $u_{m,i}$ represents the electric migration rate coefficient, F represents the Faraday constant (96485 C mol^{-1}), and ϕ represents the potential of the electrolyte.

The equilibrium potential on the electrode surface follows the Nernst equation.

$$E_{\text{eq}} = E_{\text{eq,ref}} - \frac{RT}{nF} \ln \Pi_i \left(\frac{a_i}{a_{i,\text{ref}}} \right)^{\nu_i}$$

The Butler–Volmer equation is used to describe the electrode reaction kinetics for all electrode reactions.

$$i_{loc,m} = i_{0,m} \left(\frac{c_{red}}{c_{ref}} \exp\left(\alpha_{a,m} \frac{F\eta_m}{RT}\right) - \frac{c_{ox}}{c_{ref}} \exp\left(\alpha_{c,m} \frac{F\eta_m}{RT}\right) \right)$$

In the equation, $i_{loc,m}$ represents the local current density at the electrode/electrolyte interface, i_0 represents the exchange current density ($i_0=1.0 \text{ A}\cdot\text{m}^{-2}$, $\alpha_{a,m}$ and $\alpha_{c,m}$ represent the anodic and cathodic charge transfer coefficients ($\alpha_{a,m}=1.5$, $\alpha_{c,m}=0.5$, and η_m represents the activation overpotential.

The charge of BTO nanoparticles on the separator surface follows Faraday's law.

$$E = -\nabla V$$

$$\rho = \nabla \cdot (\epsilon_0 E + P)$$

In the equation, ρ represents charge density, P represents polarization vector field, and ϵ_0 represents the permittivity of free space.

II. Supporting figures

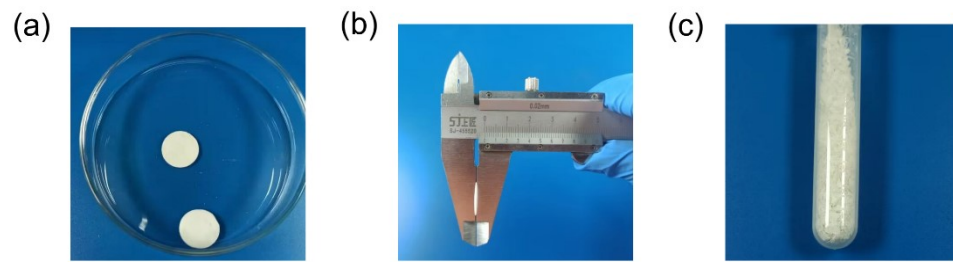


Figure S1. (a) The photographic image. (b) The thickness of BTO separators. (c) The BTO nanofibers.

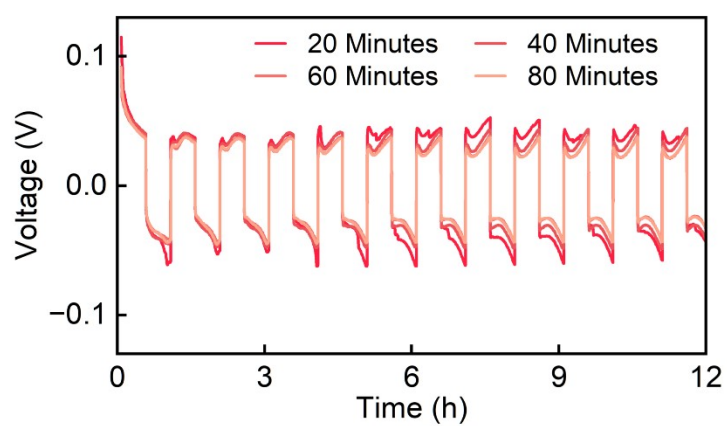


Figure S2. The relationship between polarization time and electrochemistry performance.

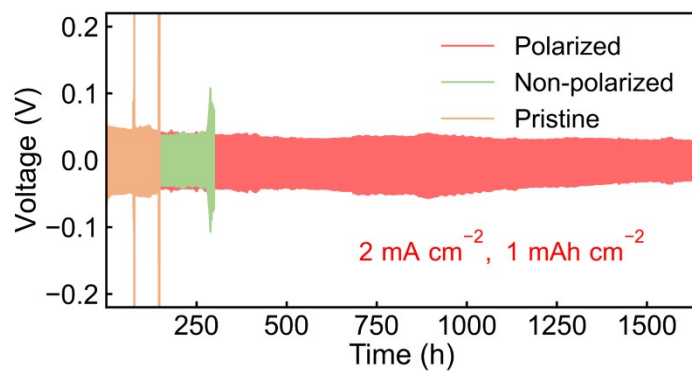


Figure S3. Voltage profiles of the Zn||Zn symmetric cells employing pristine ion channels, non-polarized ion channels and pre-polarized ion channels at 2 mA cm^{-2} with 1 mAh cm^{-2} .

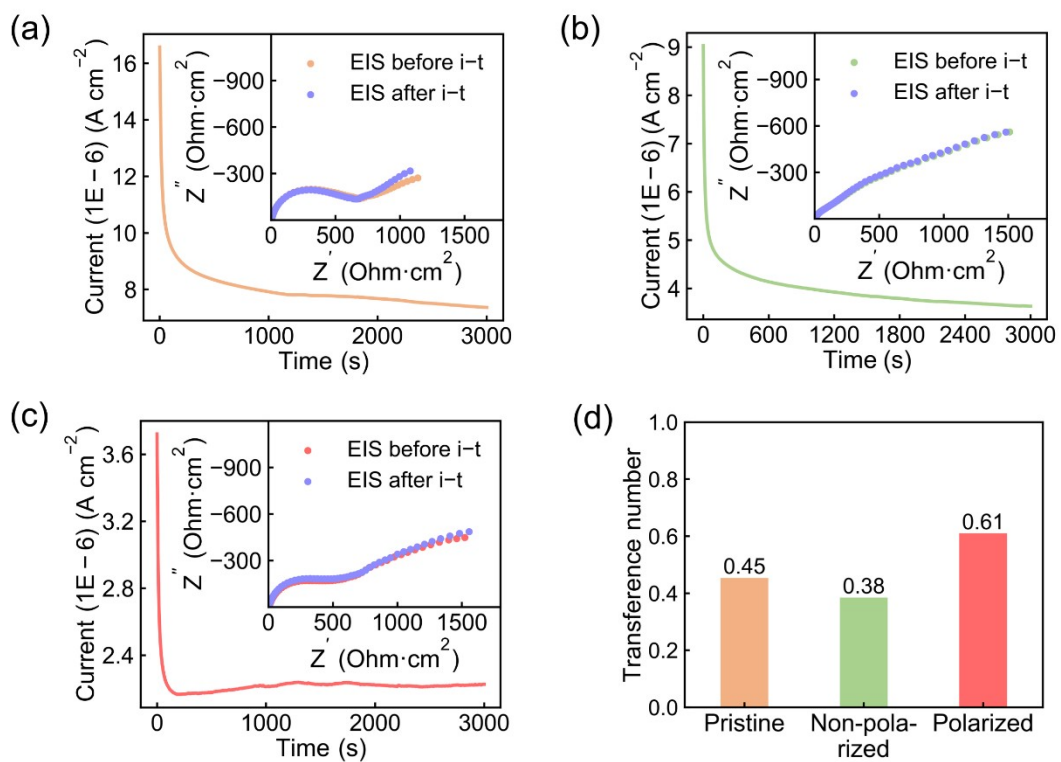


Figure S4. The transference number of Zn||Zn symmetrical cell with pristine ion channels, non-polarized ion channels and pre-polarized ion channels, respectively.

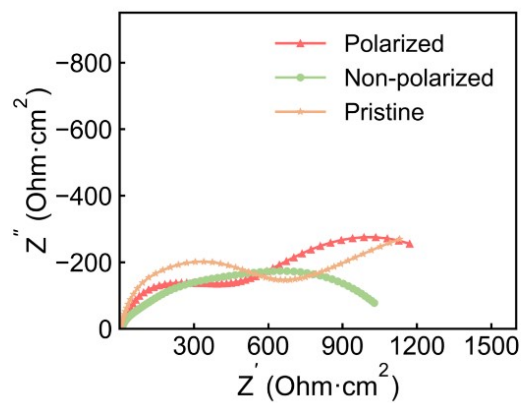


Figure S5. Nyquist plots of the Zn||Zn symmetric cells with pristine ion channels, non-polarized ion channels and pre-polarized ion channels.

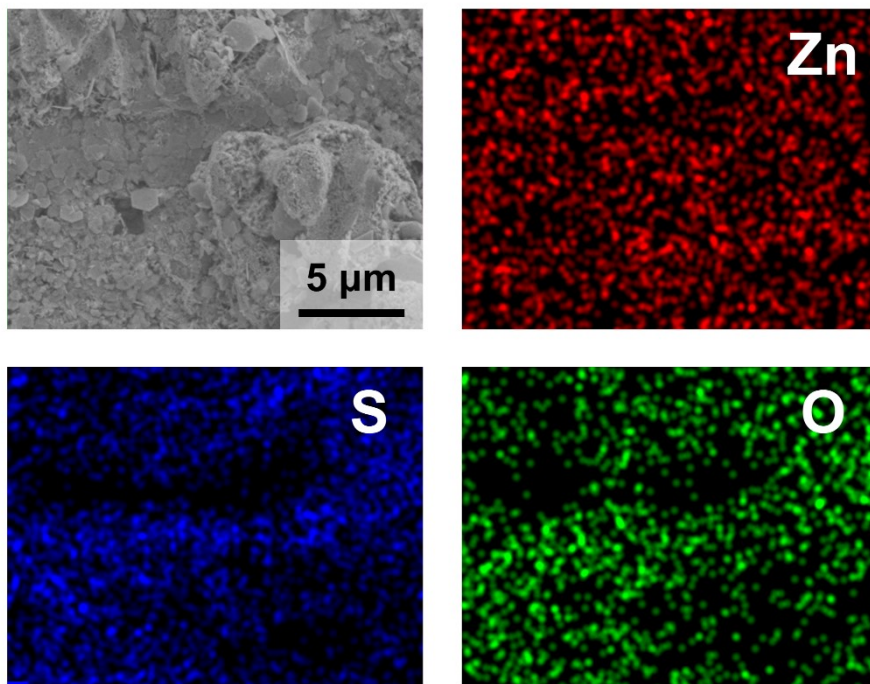


Figure S6. Element mapping of zinc anode employing pristine ion channel.

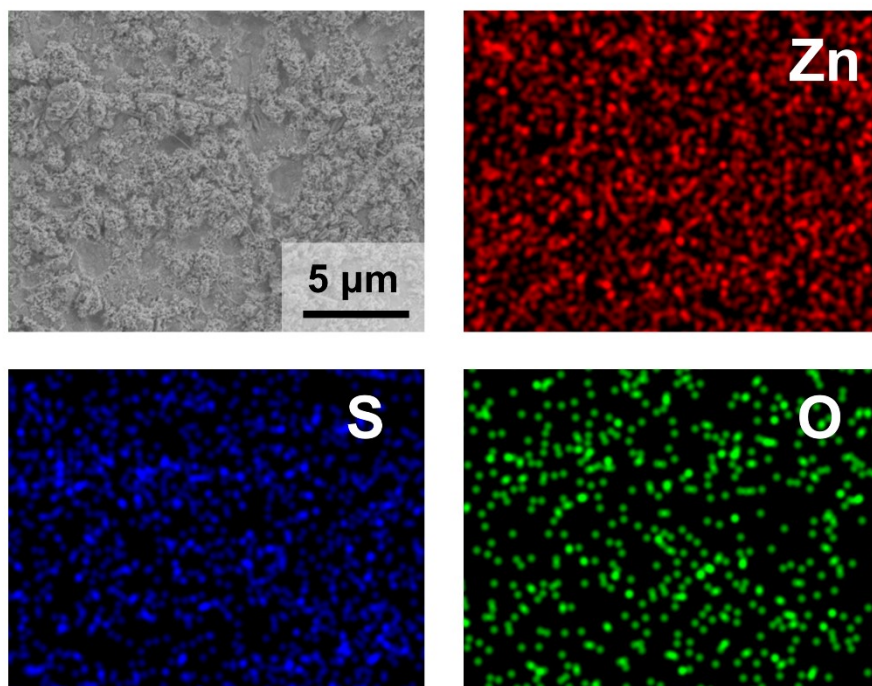


Figure S7. Element mapping of zinc anode employing non-polarized ion channel.

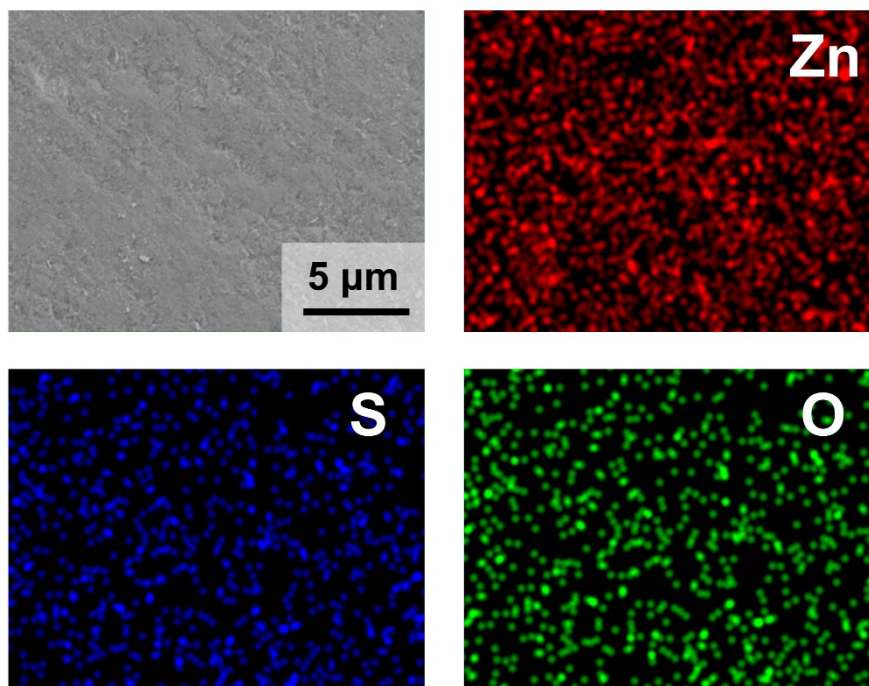


Figure S8. Element mapping of zinc anode employing pre-polarized ion channel.

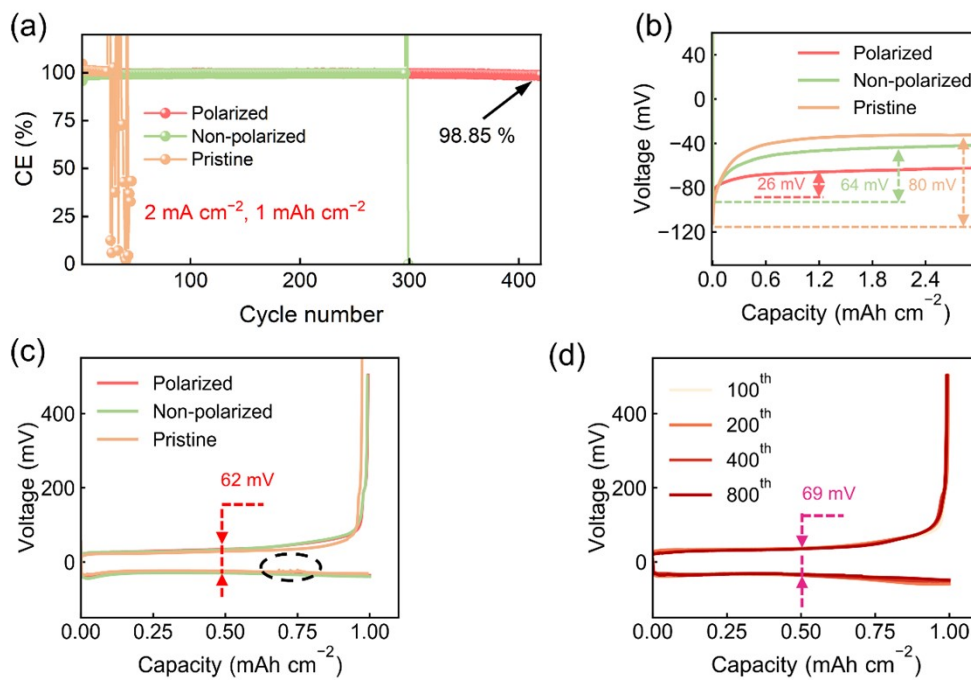


Figure S9. (a) The CE of Zn plating/stripping process in Zn||Cu asymmetric cells at the current density of 2 mA cm^{-2} . (b) The nucleation overpotential of Zn||Cu with pristine ion channels, non-polarized ion channels and pre-polarized ion channels. (c) The corresponding charge–discharge curves of Zn||Cu asymmetric cells in 30th cycle. (d) The charge–discharge curves of Zn||Cu asymmetric cells assembled with pre-polarized ion channels in different cycles.

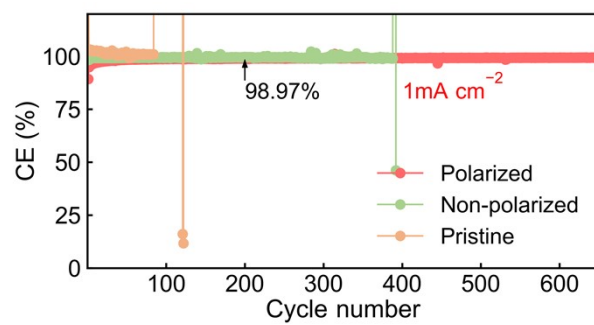


Figure S10. CE profiles of the Zn||Cu asymmetric cells with pristine ion channels, non-polarized ion channels and pre-polarized ion channels at 1 mA cm^{-2} with 0.5 mAh cm^{-2} .

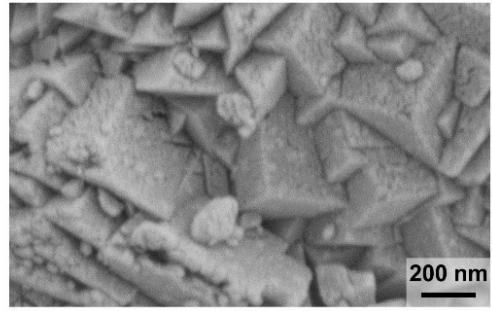
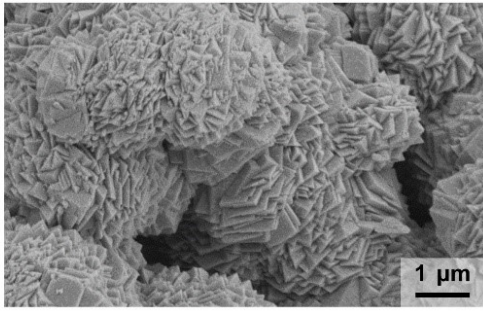


Figure S11. Morphology images of MnO₂.

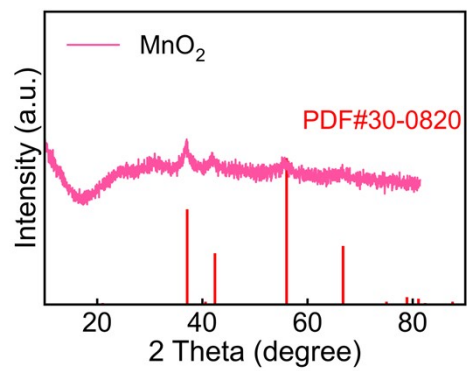


Figure S12. The XRD pattern of MnO₂.

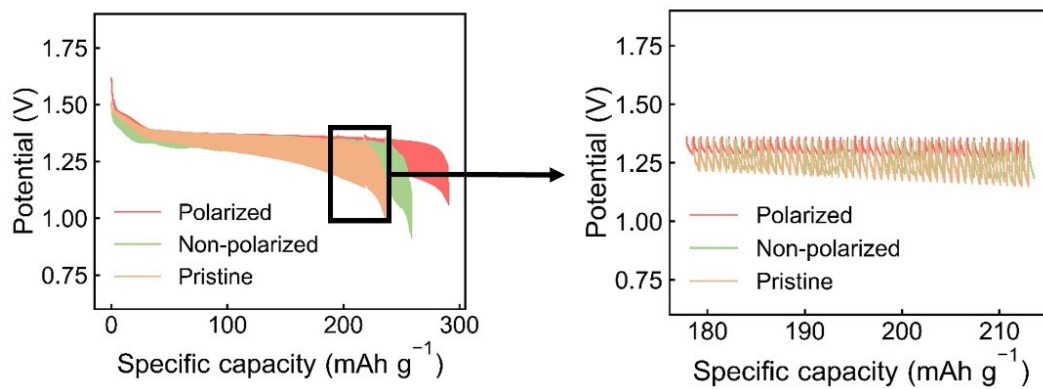


Figure S13. The discharge GITT profiles for initial cycle of Zn//MnO₂ cells with pristine ion channels, non-polarized ion channels and pre-polarized ion channels. And the cells were discharged at 0.05 A g⁻¹ for 1 min, and took a rest for 30 min.

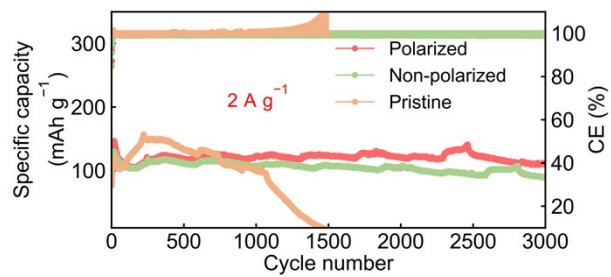


Figure S14. The cycling performance of Zn//MnO₂ cells with different ion channels at 2 A g⁻¹.

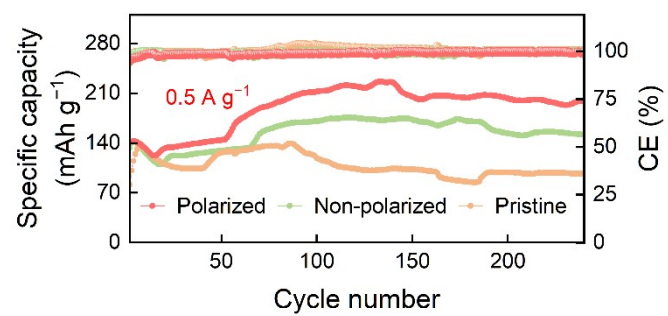


Figure S15. The cycling performance of Zn//MnO₂ cells with different ion channels at 0.5 A g⁻¹.

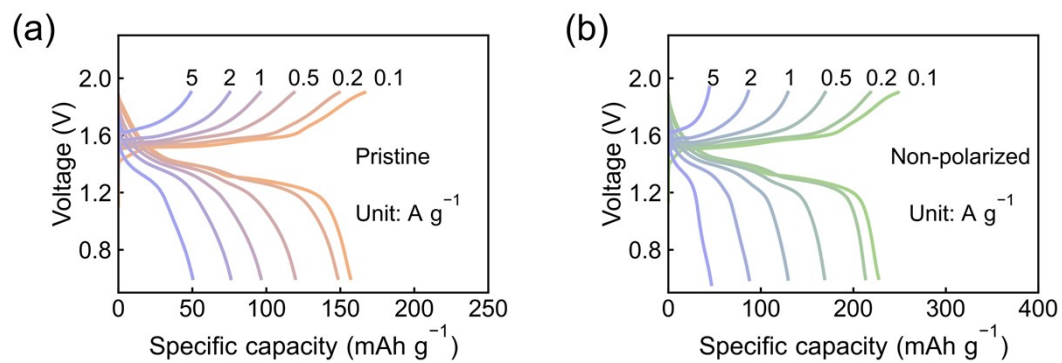


Figure S16. The GCD of Zn//MnO₂ cells with pristine ion channels, non-polarized ion channels and pre-polarized ion channels.