

A Stable Fluoride-Based Interphase for Long Cycle Zn Metal Anode in Aqueous Zinc Ion Batteries

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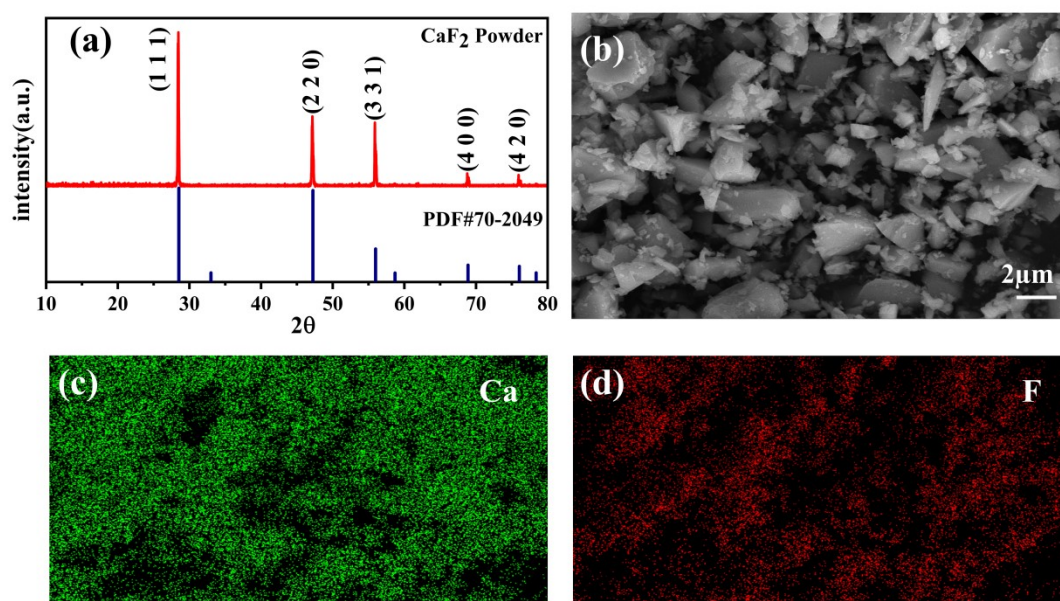


Figure S1. (a) XRD of the obtained CaF₂ powder materials. (b) The SEM image and corresponding (c) (d) elemental mapping of pure CaF₂ powder.

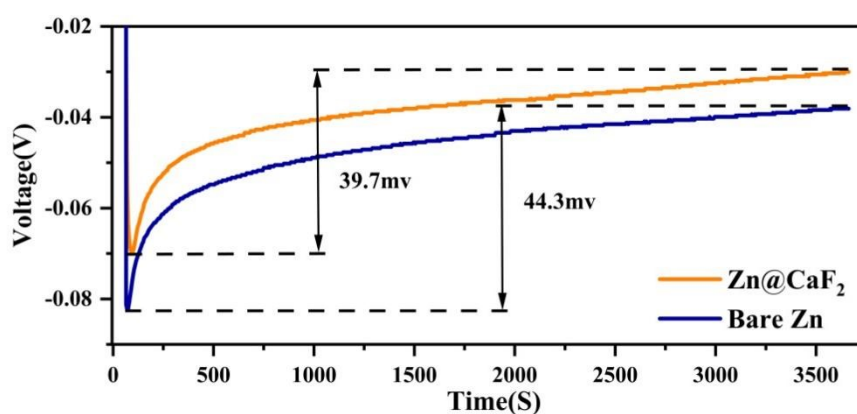


Figure S2. Nucleation overpotential results of the bare Zn and CaF₂@Zn symmetric cells at a current density of 1 mA cm⁻².

We also obtained the thicker (70um) and thinner (15um) CaF₂ coating layers. The cycling performance of symmetric cells is tested in Zn@CaF₂-70, Zn@CaF₂-35 and Zn@CaF₂-15 anode at a current density of 0.25mA cm⁻² with a capacity of 0.25mAh cm⁻². CaF₂ coating on the Zn surface can prolong the cycle-life of the cells, but the voltage hysteresis of symmetrical cells correspondingly raise with the thickness increasing. Furthermore, the excess of CaF₂ coating will hinder the diffusion of the ions, and raise the charge-transfer resistance accordingly [1]. However, the Zn@CaF₂-15 electrode is in the short circuit after a certain period of cycling (1600h) which may be that the thinner coating layer couldn't suppress the growth of dendrites. Furthermore, the continuous growth of dendrites caused the short circuit of the Zn@CaF₂-75 symmetric cell (1780h). Eventually, the battery was failure. Since the electrochemical performance under different thicknesses has not been explored, we select the coating with a moderate thickness of 35um for demonstrating its superiority in this work.

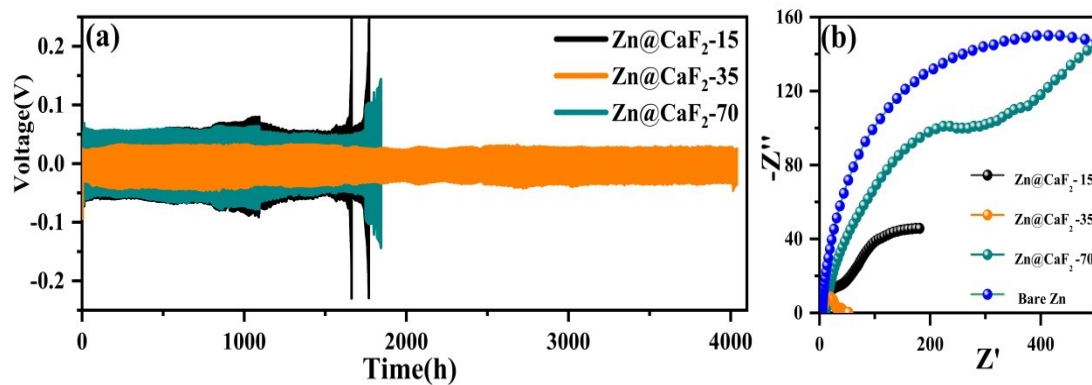


Figure S3. (a) Cycling performance of plating/stripping reversibility for the Zn@CaF₂ symmetric cells with different thicknesses at a current density of 0.25mA cm⁻² with a capacity of 0.25mAh cm⁻². (b) EIS spectra curves of Zn@CaF₂//Zn@CaF₂ symmetrical cells with different thicknesses.

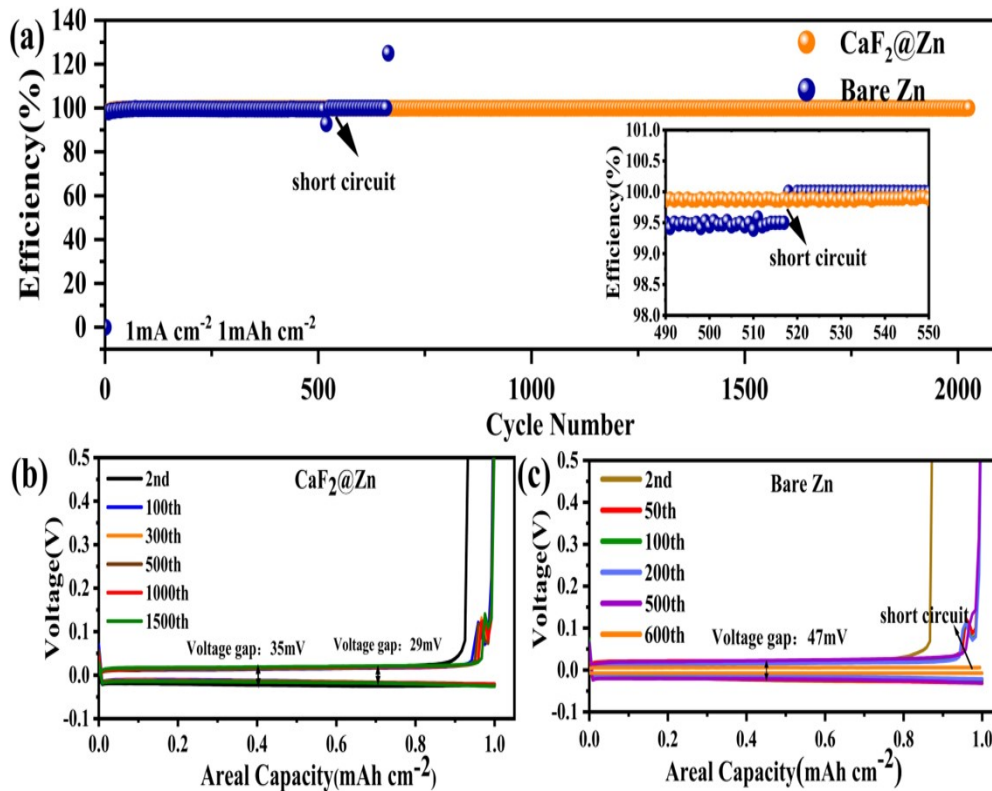


Figure S4. (a) Coulombic efficiencies of Zn plating/stripping in Zn//Cu and Zn@CaF₂//Cu asymmetric cell at 1 mA cm⁻² with a capacity of 1mAh cm⁻². (b) Voltage profiles of Zn@CaF₂//Cu asymmetric cell at the 2nd, 100th, 300th, 500th, 1000th, and 1500th cycles. (c) Voltage profiles of Zn//Cu asymmetric cell at the 2nd, 50th, 100th, 200th, 500th, and 1000th cycles.

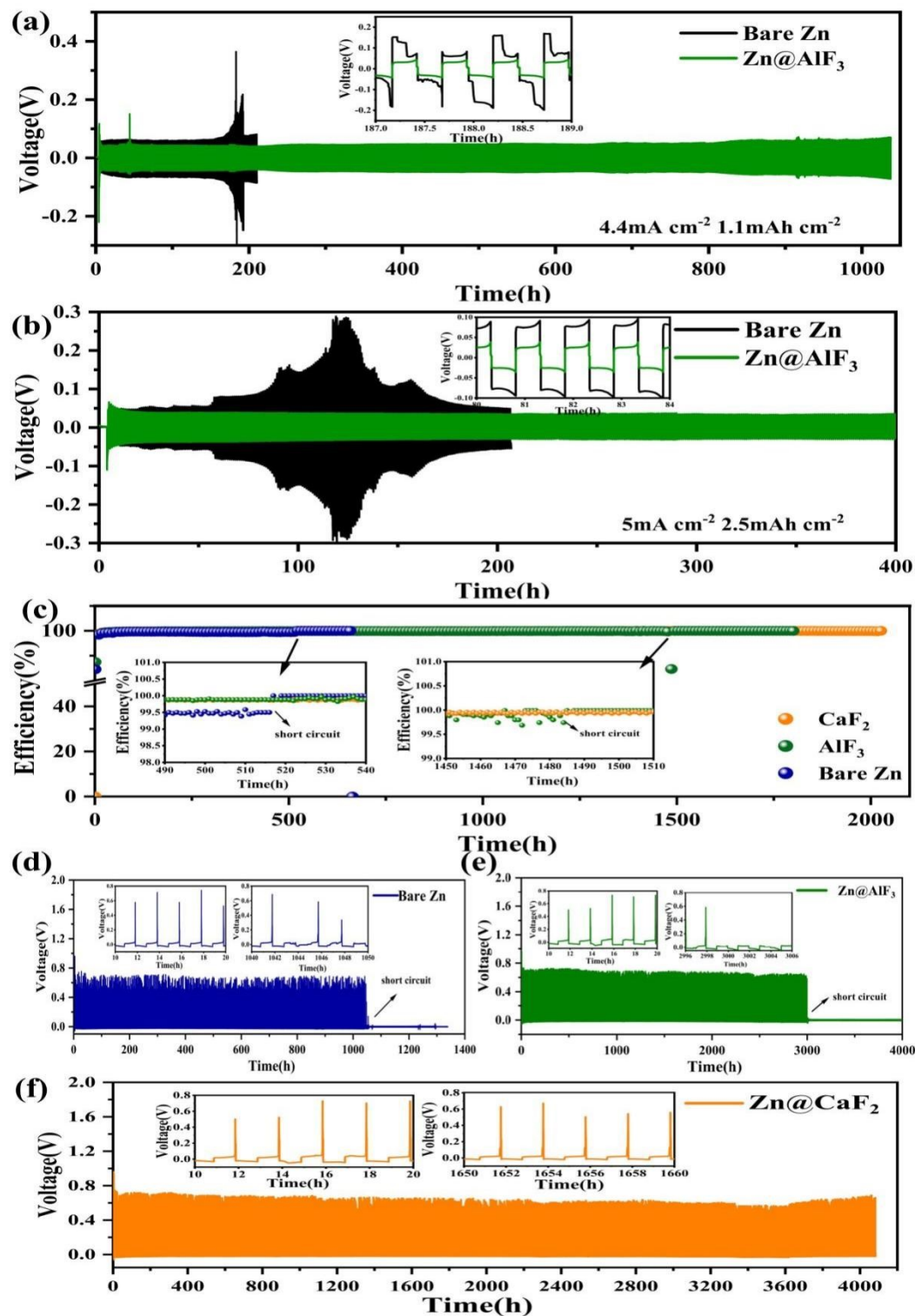


Figure S5. Cycling performance of plating/stripping reversibility of the bare Zn, the CaF₂@Zn and the AlF₃@Zn symmetric cells, (a) at 4.4 mA cm⁻² with a capacity of 1.1 mAh cm⁻², (b) at 5 mA cm⁻² with a capacity of 2.5 mAh cm⁻², (c) Coulombic efficiencies of Zn plating/stripping in Zn//Cu, Zn@CaF₂//Cu, Zn@AlF₃//Cu asymmetric cell at 1 mA cm⁻² with a capacity of 1 mAh cm⁻², (e) (f) the corresponding time-voltage diagram.

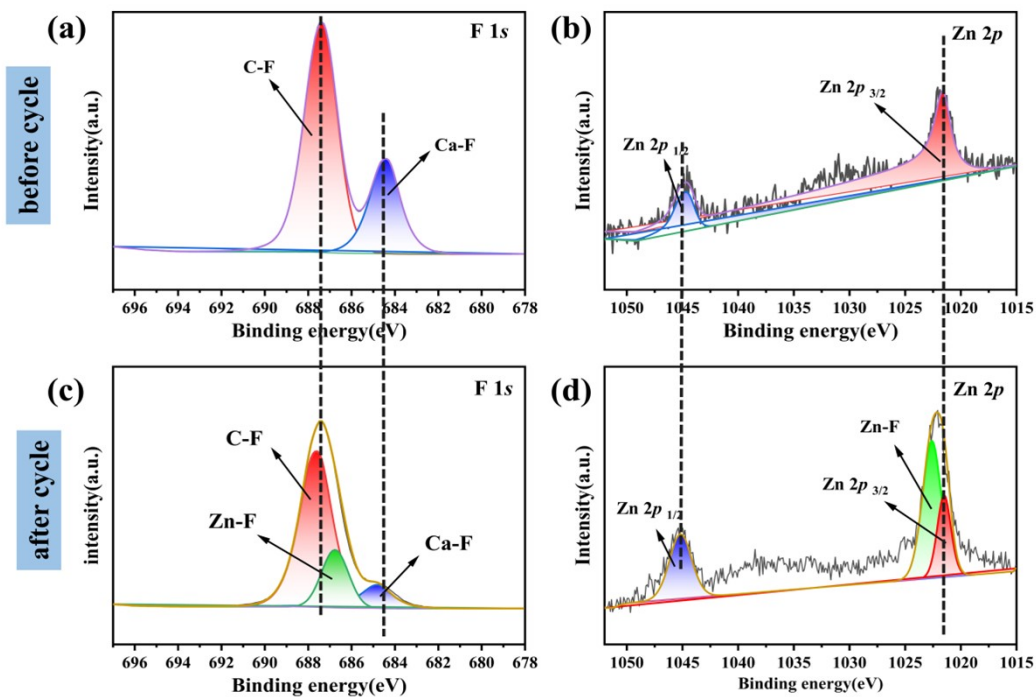


Figure S6. XPS results of the F 1s and Zn 2p at the Zn@CaF₂ interface (a) (b) before cycle and (c) (d) after cycle.

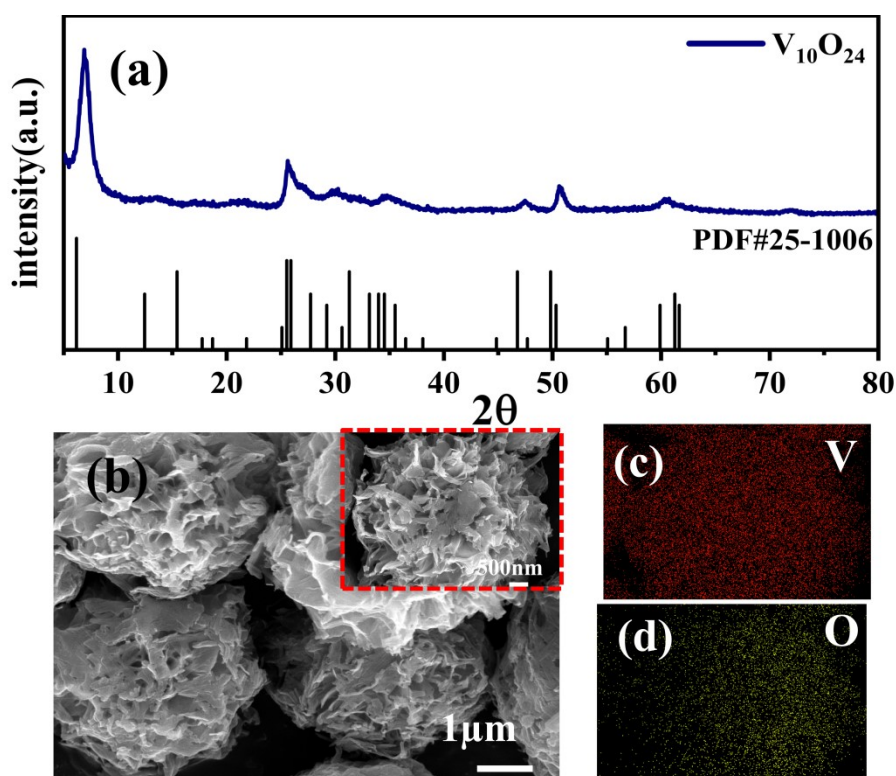


Figure S7. (a) XRD of the obtained V₁₀O₂₄ cathode materials. (b) The SEM image and corresponding elemental mapping of V₁₀O₂₄ cathode materials.

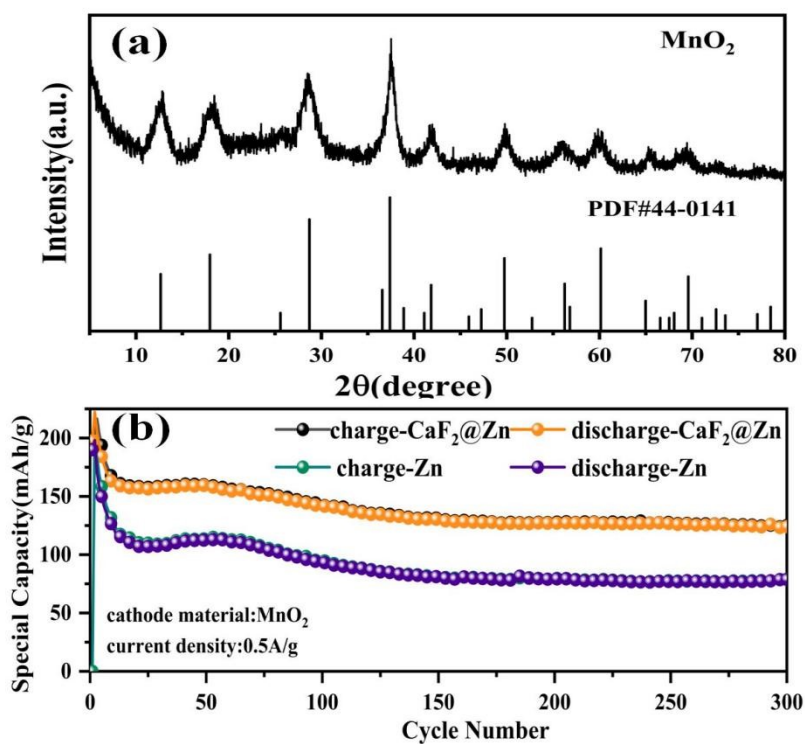


Figure S8. a) XRD patterns of MnO_2 . b) The cycle performance of the $\text{Zn}@CaF_2//\text{MnO}_2$ battery and the $\text{Zn}//\text{MnO}_2$ battery at a current density of 0.5A/g .

- [1] X.-P. Li, H. Yang, Z.-F. Tian, J.-L. Liu, X.-M. Ren, Investigation of the structure and ionic conductivity of intercalated kaolinites with potassium acetate in hydrous and anhydrous phases. Dalton Trans. 2015, 44 (10), 4665-4670.