Supporting Information

Biomimetic Fluoride-Coated Zinc Anodes: Pediatric Dentistry Inspires Stable Zinc Batteries

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Experimental Section

Materials

Zinc trifluoromethanesulfonate ($Zn(OTf)_2$, 98%, Aladdin), Tooth dressing agent (Cofoe), Vanadium pentoxide(V_2O_5, 99.5%, Macklin) and Zinc Foil (99.9%, Sigma-Aldrich) were used directly without other treatment. All reagents are directly applicable unless otherwise stated.

Preparation of electrolytes

$Zn(OTF)_2$ aqueous solution with 3 M concentrations was obtained by dissolving $Zn(OTf)_2$ in deionized water.

Modification of electrode active material (V_2O_5)

V_2O_5 was ball-milling before use. Typically, 2.0 g of V_2O_5 was first added to a ball mill tank, then stirred vigorously at room temperature for 48 h.

Characterization

XPS spectra were performed on an ESCALAB 250Xi spectrometer (Thermo Fisher). SEM images were performed using a Field Emission Scanning Electron Microscope (FESEM, Hitachi SU8010).

Preparation of Cathodes

The cathode material of V_2O_5 was mixed with super P and polyvinylidene difluoride (PVDF) with a weight ratio of 7:2:1 by using N-methyl-2-pyrrolidone (NMP) as solvent. The slurry was then cast onto a Ti foil (thickness: 10 μm) by the casting method and then dried under a vacuum at 100 °C overnight.

Preparation of modified Zn anode

The modified Zn anode was prepared by directly spraying a fluoride-containing agent rich in monofluorophosphate onto the zinc foil surface at room temperature. Further use a scraper to scrape evenly, control the uniform thickness, and let it stand for 20 minutes. The fluoride-containing agent was used without other treatment.

Electrochemical measurements

The basic electrochemical properties of electrolytes were measured by Zennium Electrochemical workstation (ZahnerEnnium). [1] Electrochemical impedance spectroscopy (EIS) tests were carried out in DH7000D electrochemical workstation (Jiangsu Donghua Analytical Instrument Co., Ltd.). All types of cells are tested by Neware battery test system.

Theoretical method

Molecular dynamics simulations

Classical molecular dynamics (MD) simulations were performed by Gromacs2016.3 simulation package[2] with the SPC/E water model. All the partials used in the molecular simulation system are described by AMBER03 force field[3]. And the vdW interactions and short range repulsions between *i* and *j* atoms were modeled by Lennard-Jones (LJ) interactions with a cutoff of 10 Å, and evaluated by the Lorentz-Berthelot rules, $\varepsilon_{ij} = (\varepsilon_{ii}\,\varepsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, where ε_{ij} is the effective well depth and σ_{ij} is the minimum position. The electrostatic interactions were evaluated by the particle-mesh Ewald method[4] with a real-space cutoff of 10 Å, and the periodic boundary conditions applied in all directions. Each system was firstly energy minimized, thermalized at $T = 298\ K$. And then 1 ns equilibrium simulation were carried out in a NVT and NPT ensemble, respectively, to reach equilibrium. Lastly, 20 ns simulations were done in NPT ensemble with a time step of 1.0 fs. The temperature and pressure were controlled by a Nose-Hoover and Parrinello-Rahman methods with a relaxation time of 0.1 ps at 298 K, respectively. The simulation results were visualized using Visual Molecular Dynamics (VMD)[5].

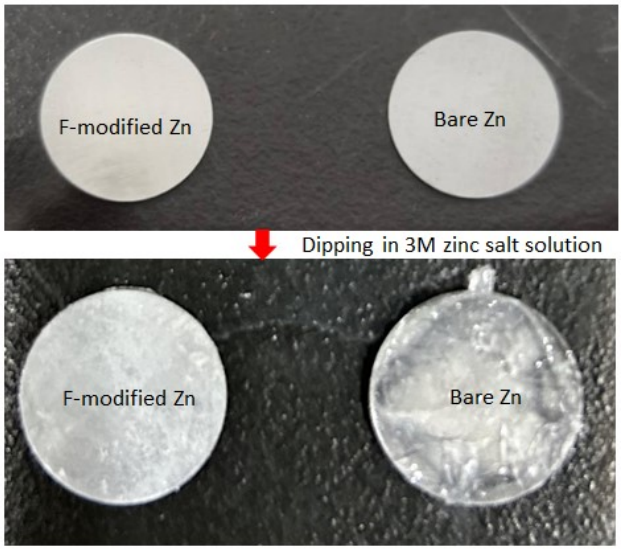

Figure S1. Comparison of the surface morphology of F-modified Zn and bare Zn before and after soaked in electrolyte for 20 h

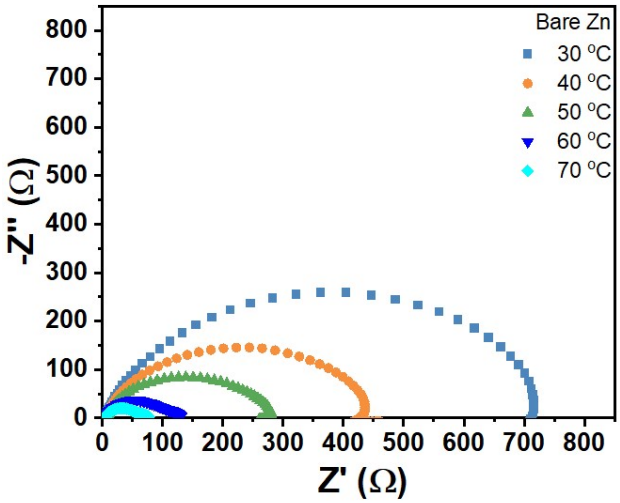

Figure S2. EIS based on bare symmetrical zinc battery at various temperature

Table S1. Performance comparison of cell based on F-modified Zn with other works

Samples	Averange Coulombic Efficiency of Zn/Cu	Cycle performance of AZIBs	Ref.
Gum additive	180 cycles, 99.6%	600 cycles at 2 A g^{-1}, average capacity ~200 mAh g^{-1}	Energy Environ. Sci. 2025,18, 1398-1407
β-cyclodextrin additive	20 cycles, 98.7%	600 cycles at 5 A g^{-1}, average capacity ~140 mAh g^{-1}	Nat. Commun. 2024, 15, 6471
Polyhydroxy sodium salt additive	250 cycles, 99.14%	500 cycles at 1 A g^{-1}, average capacity ~200 mAh g^{-1}	Small 2025, 21, 2501324
Multiple zincophilic polymer electrolyte	380 cycles, 98.4%	500 cycles at 0.5 A g^{-1}, average capacity ~350 mAh g^{-1}	Chem. Eng. J. 2024, 496, 153815
F-modified Zn	~350 cycles, 99.7%	500 cycles at 1 A g^{-1}, average capacity 300 mAh g^{-1}	**This work**

References

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