Supporting Information

Engineering an Electrostatic Field Layer for High-Rate and Dendrite-Free Zn Metal Anode

Kaiping Zhu a,b, Can Guo e, Wenbin Gong f, Qinghua Xiao b, Yagang Yao a, Kenneth Davey c, Qinghong Wang b,*, Jianfeng Mao c,*, Pan Xue d,*, Zaiping Guo c,*

a College of Engineering and Applied Sciences, Nanjing University, Nanjing, Jiangsu 210093, China
b School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou, Jiangsu 221116, China
c School of Chemical Engineering, The University of Adelaide, Adelaide 5005, Australia.
d School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, China
e School of Chemistry, South China Normal University, Guangzhou, Guangdong 510006, China
f School of Physics and Energy, Xuzhou University of Technology, Xuzhou, Jiangsu 221018, China

[*] Email: wangqh@jsnu.edu.cn; panxue@yzu.edu.cn; jianfeng.mao@adelaide.edu.au, zaiping.guo@adelaide.edu.au
Materials Characterizations: XRD patterns for the samples were determined on a Rigaku D/max 2200 pc diffractometer equipped with Cu Kα radiation. The surface morphology and structure were characterized via a field-emission scanning electron microscope (Hitachi SU-8100) SEM system. TEM and HRTEM images were all determined via a JEM-2100F transmission electron microscope. AFM and KPFM images were obtained using an OmegaScope 1000 system from AIST-NT. XPS measurements were determined on a Thermo ESCALAB 250Xi spectrometer with monochromatic Al Kα radiation (hγ = 1486.6 eV). Zn dendrite growth was observed in situ via an optical microscope (Leica DM750 M) equipped with a digital camera.

Electrochemical Measurements: Electrochemical behavior(s) of the symmetric batteries were established using 2032-type coin-cells with bare ZnSO₄ or, Co(TAPC)/ZnSO₄ solution as electrolyte and Zn foils as working and counter, electrode. Full cells were assembled to assess the Co(TAPC)/ZnSO₄ electrolyte. The MnO₂ electrodes were fabricated via mixing MnO₂, super P, and polyvinyl difluoride at a mass ratio of 7:2:1 in NMP solvent. The loading of the active material was 1.3 to 1.5 mg cm⁻². Zn-foil was used as anodes. The cycling performance of the cells was determined by the LAND battery-testing system at selected current density. The cutoff potentials for charge and discharge were, respectively, 0.8 and 1.8 V (vs Zn²⁺/Zn). The CV with a voltage range of 0.8 to 1.8 V at a scan rate of 0.1 mV s⁻¹ was tested by CHI760E electrochemical workstation.

Molecular dynamics simulation: Simulations were performed in the NVT ensemble with target temperature 300 K using the LAMMPS package. A time step of 1 fs was set. Cut-off radius for the van der Waals and Coulomb interactions was set to 15 Å. The long-range electrostatic interactions were computed via particle–particle particle-mesh scheme. The Zn substrate was built with preset defects in the center of one square unit cell, marked in orange-color. The orthorhombic simulation cell was 10 × 10 × 30 nm³, and the periodic boundary condition was set in all three (3) directions. Four (4) Co(TAPC) layers with interlayer space of D = 3.5 Å were set to model the Co(TAPC) coating on Zn to investigate Zn²⁺ deposition mechanism(s). The optimized potentials for liquid simulation-all atom (OPLS-AA) was used in the simulation to determine interaction(s) between the ions and molecules (Zn²⁺ and SO₄²⁻).
The Zn substrates were described by the universal force field (UFF) and water molecules by the SPC/E model.

*The finite element method (FEM) Simulation of the Electric Field*: A simplified 3D electrodeposition model was established to compare proportional schematics of current density and electric field distribution. In the model the thickness of electrode was set to 30 µm and the length of the electrode was 30 µm. The height of Co(TAPC)/ZnSO₄ electrolyte and electrolyte was 3.25 µm. The protuberance of Zn surface was represented by seven (7) semicircles with a diameter of 1.5 µm and a height of 3.25 µm. The electrical conductivity for Co(TAPC)/ZnSO₄ electrolyte was set at 40 S m⁻¹. That for Zn metal was $1.67 \times 10^7$ S m⁻¹. The reported ionic conductivity of electrolyte is ca. 5 S m⁻¹. An overpotential of 500 mV was used as voltage excitation between electrode and electrolyte for simulation.

*Density functional theory simulation*: The density functional theory (DFT) computation was used to determine the binding energy of H₂O and Co(TAPC) molecules on Zn substrate, together with that for Zn atoms on Co(TAPC) and Zn substrate. Binding energy was computed using the Vienna *ab initio* simulation package (VASP). Generalized gradient approximation with the Perdew–Burke–Ernzerh functional was adopted for the total energy computations. The projector-augmented wave (PAW) was used to treat electrons. The energy cut-off was set to 550 eV. The geometry convergence tolerance was set to $1 \times 10^{-6}$ eV for energy and $2.0 \times 10^{-2}$ eV Å⁻¹ for maximum force. The vacuum region between slabs was 15 Å in all simulations. The Brillouin zones of all models were sampled by Gamma grids, and k-meshes were generated using the VASPKIT toolkit with kmesh-resolved value of 0.04 2π/Å. Common facets of Zn(001) were determined in this simulation. The Zn substrate was set as 9 × 9 × 1 super cell with top three-layer atoms releasable. The binding energy ($E_b$) was computed from:

$$E_b = E_{total} - E_{sub} - E_{mol/Zn}$$  \hspace{1cm} (S1)

where $E_{total}$, $E_{sub}$ and $E_{Zn}$ represent total energy of the substrate bounded with the H₂O, Co(TAPC) molecules or Zn atom, energy of the Zn or Co(TAPC) substrate, and energy of H₂O, Co(TAPC) molecules or Zn atom, respectively.
Preparation of Co(TAPC) EFL: Firstly, An appropriate amount of Co(TAPC) was dissolved in 1 M L⁻¹ ZnSO₄ electrolyte to obtain a Co(TAPC)/ZnSO₄ electrolyte with a Co(TAPC) concentration of 15 mM. The protective layer on the surface of Zn electrode was then self-constructed by the interaction force between Co(TAPC) and Zn substrate in the above electrolyte.
**Fig. S1** Raman spectra for ZnSO$_4$ electrolyte containing differing concentration of Co(TAPC).

**Fig. S2** FTIR spectrum for ZnSO$_4$ electrolyte containing differing concentration of Co(TAPC) and pure Co(TAPC).
Fig. S3 Solution samples for ZnSO$_4$ electrolyte containing differing concentration of Co(TAPC).

Fig. S4 Optimized configuration for one H$_2$O absorbed on Zn surface.
**Fig. S5** LSV curves for Zn foils in different electrolyte.

**Fig. S6** (a-c) SEM images and d) Element mapping analysis, for Zn anode following infiltration in bare ZnSO₄ electrolyte.
Fig. S7 (a-c) SEM images and d) Element mapping analysis, for Zn anode following infiltration in Co(TAPC)/ZnSO₄ electrolyte.

Fig. S8 High-resolution O 1s XPS spectra for Zn anode following infiltration in Co(TAPC)/ZnSO₄ electrolyte.
**Fig. S9** High-resolution O 1s XPS spectra for Zn anode following infiltration in bare ZnSO$_4$ electrolyte.

**Fig. S10** (a, b) Nyquist plots for Zn foils in different electrolytes at different temperature. (c) Corresponding Arrhenius curves and comparison of activation energies of Zn foils in different electrolytes.

**Fig. S11** Optimized configuration of one Zn absorbed on Co(TAPC).
**Fig. S12** Optimized configuration of one Zn absorbed on Zn surface.

**Fig. S13** Binding energy of a Zn on Zn (001) and Co(TAPC) surface.
**Fig. S14** 3D model of current density distribution for Zn anode in a) Co(TAPC)/ZnSO$_4$ and b) bare ZnSO$_4$ electrolytes.

**Fig. S15** 3D model of relative intensity distribution of localized electric field for Zn anode in a) Co(TAPC)/ZnSO$_4$ and b) bare ZnSO$_4$ electrolytes, during Zn nucleation.

**Fig. S16** AFM and KPFM images of Zn anode surfaces in differing electrolytes following 100th cycles at 50 mA cm$^{-2}$, 1 mAh cm$^{-2}$. 
Fig. S17 Detailed voltage profile with cycle time for symmetrical cells using Co(TAPC)/ZnSO$_4$ electrolyte with current density 20 mA cm$^{-2}$.

Fig. S18 Detailed voltage profile with cycle time for symmetrical cells using bare Co(TAPC)/ZnSO$_4$ electrolyte under current density 50 mA cm$^{-2}$. 
Fig. S19  Cycling performance for symmetrical cells using Co(TAPC)/ZnSO₄ electrolyte under current density 1 mA cm⁻² with fixed capacity of 1 mAh cm⁻².

Fig. S20  Cycling performance for symmetrical cells using ZnSO₄ electrolyte containing differing concentration of Co(TAPC) under current density 50 mA cm⁻² with fixed capacity of 1 mAh cm⁻².
Fig. S21 Digital image of contact angle for ZnSO₄ electrolyte containing differing concentrations of Co(TAPC).

Fig. S22 SEM images of Zn anode using (a-c) bare ZnSO₄ and (d-f) Co(TAPC)/ZnSO₄ electrolytes, following 100 cycles at 50 mA cm⁻² with capacity 1 mAh cm⁻².
**Fig. S23** Element mapping analysis for Zn anode following 100 cycles at 50 mA cm$^{-2}$ with capacity 1 mAh cm$^{-2}$ in Co(TAPC)/ZnSO$_4$ electrolyte.

**Fig. S24** XRD pattern of Zn anode using bare ZnSO$_4$ and Co(TAPC)/ZnSO$_4$ electrolytes, following 100 cycles at 50 mA cm$^{-2}$ with capacity 1 mAh cm$^{-2}$.
**Fig. S25** Rate performance for Zn symmetric cell using Co(TAPC)/ZnSO$_4$ and bare ZnSO$_4$, electrolyte.

**Fig. S26** Cycling performance for symmetrical cells using Co(TAPC)/ZnSO$_4$ electrolyte under current density 10 mA cm$^{-2}$ with fixed capacity of 5 mAh cm$^{-2}$. 
Fig. S27 (a) Comparison of 5th cycle CV curves for Zn||MnO$_2$ batteries in different electrolyte. (b) Galvanostatic charge-discharge profiles for Zn||MnO$_2$ batteries in different electrolyte with current density 200 mA g$^{-1}$. Cycling performance for Zn||MnO$_2$ batteries in different electrolyte with the current density of: (c) 200 and (d) 1000, mA g$^{-1}$.

Fig. S28 Rate performance for Zn||MnO$_2$ batteries in different electrolyte with different current densities.
Table S1. Comparison of electrochemical performance of symmetric batteries with selected reported values involving electrolyte additives.

<table>
<thead>
<tr>
<th>Electrolyte component</th>
<th>Maximum plating/stripping capacity</th>
<th>Cycle life (cycles)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>1 M ZnSO₄ +5% 4-dioxane</td>
<td>2.5 mAh cm⁻²</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>2 M ZnSO₄ +0.05 M NH₄OAc</td>
<td>1 mAh cm⁻²</td>
<td>1000</td>
<td>2</td>
</tr>
<tr>
<td>1 M ZnSO₄ +0.1 M TSC</td>
<td>1.25 mAh cm⁻²</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>3 M Zn(CF₃SO₃) +20 mM Zn(NO₃)₂</td>
<td>0.5 mAh cm⁻²</td>
<td>1200</td>
<td>4</td>
</tr>
<tr>
<td>3 M ZnSO₄ in H₂O/68 vol% EG</td>
<td>0.5 mAh cm⁻²</td>
<td>2268</td>
<td>5</td>
</tr>
<tr>
<td>1 M ZnSO₄ +10 mM glucose</td>
<td>5 mAh cm⁻²</td>
<td>2000</td>
<td>6</td>
</tr>
<tr>
<td>2 M ZnSO₄ +0.08 M ZnF₂</td>
<td>1 mAh cm⁻²</td>
<td>600</td>
<td>7</td>
</tr>
<tr>
<td>1 M ZnSO₄ +4 M EMImCl</td>
<td>1 mAh cm⁻²</td>
<td>500</td>
<td>8</td>
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<tr>
<td>1 M ZnSO₄ +75 mM Na₄EDTA</td>
<td>2 mAh cm⁻²</td>
<td>2000</td>
<td>9</td>
</tr>
<tr>
<td>2 M ZnSO₄ +5 mM vanilli</td>
<td>1 mAh cm⁻²</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>2 M ZnSO₄ +0.1 M MgSO₄</td>
<td>0.25 mAh cm⁻²</td>
<td>600</td>
<td>11</td>
</tr>
<tr>
<td>1 M ZnSO₄ +15 mM Co(TAPC)</td>
<td>5 mAh cm⁻²</td>
<td>8000</td>
<td>This work</td>
</tr>
</tbody>
</table>

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References


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