# Supporting information

**Insight into Aqueous Electrolyte Additives: Unraveling Functional Principles, Electrochemical Performance, and Beyond**

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Table S1. The pH buffer electrolyte additive and equation.

| Cathode | Electrolyte | Additive | Potential | Equation | Ref |
|---|---|---|---|---|---|
| $NH_4V_4O_{10}$ | $ZnSO_4$ | Taurine | 0.2~1.6 | $N_2H-(CH_2)_2 \leftrightarrow H_2N-(CH_2)_2-SO_3H$<br>$H_2N-(CH_2)_2-SO_3H \leftrightarrow H_3N^+-(CH_2)_2-SO_3H$ | 1 |
| $NH_4V_4O_{10}$ | $ZnSO_4$ | $(NH_4)_2S_2O_8$ | 0.2~1.6 | $S_2O_8^{2-}+H_2O \leftrightarrow 2HSO_4^{2-}+H_2O_2$<br>$S_2O_8^{2-}+H^+ \leftrightarrow HS_2O_8^-$<br>$NH_4^++OH^- \leftrightarrow NH_3 \cdot H_2O$ | 2 |
| $MnO_2$ | $ZnSO_4$ | $NH_4H_2PO_4$ | 0.8~1.8 | $H_2PO_4^-+OH^- \leftrightarrow HPO_4^{2-}+H_2O$<br>$H_2PO_4^-+H^+ \leftrightarrow H_3PO_4$<br>$NH_4^++OH^- \leftrightarrow NH_3 \cdot H_2O$ | 3 |
| Od-NVO | $ZnSO_4$ | $NH_4OAc$ | 0.3~1.8 | $CH_3COO^-+H^+ \leftrightarrow CH_3COOH$<br>$CH_3COOH+OH^- \leftrightarrow CH_3COO^-+H_2O$ | 4 |
| $MnO_2$ | $ZnSO_4$ | $CH_3COONH_4$ | 0.8~1.8 | $CH_3COO^-+H^+ \leftrightarrow CH_3COOH$<br>$CH_3COOH+OH^- \leftrightarrow CH_3COO^-+H_2O$ | 5 |

Table S2. Mechanism of desolvation sheaths electrolyte additives.

| Cathode | Electrolyte | Additive | Potential | Mechanism | Ref |
|---|---|---|---|---|---|
| $Na_{0.92}V_2O_5 \cdot nH_2O$ | $Zn(CF_3SO_3)_2$ | Fibroin (FI) | 0.4~1.5 | Interaction of FI electron groups with $H_2O$ regulates the $Zn^{2+}$ | 6 |

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|---|---|---|---|---|---|
| | | | | coordination | |
| $H_{11}Al_2V_6O_{23.2}$ | $Zn(CF_3SO_3)_2$ | [BMIM]OTF | 0.4~1.4 | Additives preferentially adsorb at the electrodes, regulating $Zn^{2+}$ solvation sheaths | 7 |
| $VS_2$ | $ZnSO_4$ | NMP | 0.4~1.0 | Polar additives contribute to structural remodeling of $Zn^{2+}$ solvation sheaths | 8 |
| $MnO_2$ | $ZnSO_4$ | TG | 0.8~1.8 | TG is involved in $Zn^{2+}$ solvation sheaths reorganization | 9 |
| $MnO_2$ | $ZnSO_4$ | CTAB | 0.8~1.8 | CTAB alters the solvated structure of $Zn^{2+}$ and increased interfacial stability | 10 |
| $NH_4V_4O_{10}$ | $Zn(CF_3SO_3)_2$ | TMU | 0.2~1.6 | Remodeling of $Zn^{2+}$ solvation structure through group formation interactions with $Zn^{2+}$ and $H_2O$ | 11 |

Table S3. Electrolyte additives for SEI formation.

| Cathode | Electrolyte | Additive | Potential | Mechanism | Ref |
|---|---|---|---|---|---|
| $V_2O_5$ | $ZnSO_4$ | [EMIM]OTF | 0.2~1.6 | $OTF^-$ ions constitute the SEI, mitigating side reactions and zinc dendrite formation | 12 |
| $MnO_2$ | $ZnSO_4$ | DPA | 0.8~1.8 | DPA preferentially adsorbs at the zinc anode and forms SEI, and $Zn^{2+}$ is uniformly deposited | 13 |
| Mn-doped $V_6O_{13}$ | $ZnSO_4$ | Succinonitrile | 0.2~1.6 | SN has a higher affinity for SEI and forms dense SEI on the zinc anode surface | 14 |
| $V_2O_5$ | $ZnSO_4$ | TMB | 0.2~1.6 | The TMB forms a $ZnF_2$ SEI layer that isolates the zinc anode from the $H_2O$ in the electrolyte | 15 |

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| $MnO_2$ | Zn $(CF_3SO_3)_2$ | Zn $(NO_3)_2$ | 0.8~1.8 | Formation of inorganic $ZnF_2$-$Zn_5(CO_3)_2(OH)_6$-organic bilayer SEI on the surface of the zinc anode | 16 |
| $NH_4V_4O_{10}$ | $ZnSO_4$ | L-glutamine | 0.2~1.6 | ZnS and Gln formed a composite SEI, which inhibited the side reaction | 17 |

Table S4. Mechanism of electrostatic shielding electrolyte additives.

| Cathode | Electrolyte | Additive | Potential | Mechanism | Ref |
|---|---|---|---|---|---|
| $VO_2$ | $ZnSO_4$ | $Rb_2SO_4$ | 0.2~1.6 | $Rb^+$ is preferentially adsorbed on the Zn surface, which produces a strong shielding effect | 18 |
| α-$MnO_2$ | $ZnSO_4$ | $TBA_2SO_4$ | 0.8~1.8 | $TBA^+$ electrostatically adsorbed on the surface of the zinc anode, shielding the electrolyte from hydrated Zn ions | 19 |
| $NH_4V_4O_{10}$ | $ZnSO_4$ | MBA | 0.2~1.6 | MBA regulates the molecular distribution on the surface of the zinc anode and prevents the decomposition of activated water | 20 |
| $NH_4V_4O_{10}$ | $ZnSO_4$ | B2AA | 0.2~1.6 | B2AA is preferentially adsorbed at the zinc anode interface, repelling reactive $H_2O$, and inhibiting the | 21 |
| $V_2O_5$ | $ZnSO_4$ | SA | 0.2~1.6 | Regulation of electric field distribution in the vicinity of zinc electrodes promotes uniform $Zn^{2+}$ deposition and transport kinetics | 22 |

Table S5. The classification of electrolyte additives working on the cathode.

| Cathode | Electrolyte | Additive | Effect | Performance | Ref |
|---|---|---|---|---|---|
| $ZnMn_2O_4$（ZMO） | $ZnSO_4$ | $MnSO_4$ | Electrochemical equilibrium between $Mn^{2+}$ and $Zn^{2+}$ promotes performance | 79 % (2 A $g^{-1}$ 1000 cycles) | [23] |
| $NaV_3O_8$ | $ZnSO_4$ | $Na_2SO_4$ | $Na^+$ possesses a lower reduction potential than $Zn^{2+}$ restricts the growth of Zn dendrites | 90 % 221 mAh $g^{-1}$ (1 A $g^{-1}$ 100 cycles) | [23] |
| $MnO_2$ | $ZnSO_4$ | $H_2SO_4$+$MnSO_4$ | Addition of $H_2SO_4$ to the electrolyte to lower the pH and inhibit gas evolution | —— | [24] |
| MgVO | $ZnSO_4$ | $MgSO_4$ | $Mg^{2+}$ inhibits the continuous dissolution of active substances | 90.3 % (1 A $g^{-1}$ 200 cycles) | [11] |
| $VOPO_4·H_2O$ | $ZnCl_2$ | $H_3PO_4$ | Dissolution of VOP is inhibited by the combination of $PO_4^{3-}$ groups and zinc concentration | 170 mAh $g^{-1}$ (0.1 A $g^{-1}$ 500 cycles) | [25] |
| $K_{0.51}V_2O_5$ | Zn $(CF_3SO_3)_2$ $KCF_3SO_3$ | Al $(CF_3SO_3)_3$ | Co-embedding of Al and Zn to enhance crystal structure and inhibit dendrite growth | 91% 205 mAh $g^{-1}$ (0.1 A $g^{-1}$ 360 cycles) | [26] |

Table S6. The classification of multifunctional electrolyte additive mechanism.

| Cathode | Electrolyte | Additive | Potential | Mechanism | Ref |
|---|---|---|---|---|---|
| PANI | $ZnSO_4$ | 1-phenylethyl amine hydrochloride (PEA) | 0.8~1.4 | PEA modulates $Zn^{2+}$ solvation sheaths and generates a protective layer at the anode | [27] |
| $V_2O_5$ | Zn $(CF_3SO_3)_2$ | Dextran | 0.2~1.6 | The zinc surface forms a protective layer, and it promotes the gradual detachment of Zn $(H_2O)_6^{2+}$, preferentially adsorbed on the Zn (0002) plane | [28] |
| $V_2O_3$/C | Zn $(CF_3SO_3)_2$ | PEG 400 | 0.2~1.6 | PEG 400 modulates the structure of $Zn^{2+}$ solvation sheaths to achieve smaller lattice expansion of $V_2O_3$ and inhibit side reactions | [29] |
| Al-V-O | Zn $(CF_3SO_3)_2$ | Acetonitrile (AN) | 0.4~1.6 | AN interaction with $Zn^{2+}$ attenuates the $H_2O$ activity and | [30] |

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| | | | | molecules are adsorbed on the anode surface to form a protective layer | |
| $V_2O_5$ | $ZnSO_4$ | Diethylenetriamine (DETA) | 0.2~1.6 | Reshaping the structure of solvation sheaths in the electrolyte inhibits the solvation of active substances and induces crystal transitions at the cathode | 31 |
| $MnO_2$ | $ZnSO_4$ | Nitrogen-doped and sulfonated carbon dots (NSCDs) | 0.8~1.8 | The abundance of polar groups in CDs reduces the amount of reactive $H_2O$, and part of the negatively charged NSCDs adsorbs on the surface of the Zn anode to inhibit corrosion | 32 |

Table S7. Electrolyte additives optimize the performance mechanism of AZIBs at extreme temperatures

| Cathode | Electrolyte | Additive | Temperature | Mechanism | Ref |
|---|---|---|---|---|---|
| PANI | $ZnCl_2$ | α-D-glucose (αDG) | -25 °C | The αDG hydroxyl-rich structure breaks hydrogen bonds to obtain a low freezing point of -55.3 °C | 33 |
| $MnO_2$ | $ZnSO_4$ | N, N-dimethyl acetamide (DMA) | -18°C | DMA solvent additives with high donor number tend to limit free water distribution, rebuild the ligand $H_2O$ network in the environment and lower the freezing point | 34 |
| $MnO_2$ | $ZnSO_4$ | Ethylene glycol | -25 °C | Hydroxyl groups on EG improve the antifreeze ability of aqueous electrolytes and improve the conductivity of electrolytes at low temperatures | 35 |
| $MnO_2$ | $ZnSO_4$ | Dimethyl sulfoxide (DMSO) | -20 °C | Stable reconstituted hydrogen bonding between DMSO and $H_2O$ lowers the freezing point of the electrolyte, thereby increasing the ionic conductivity of the aqueous cell at sub-zero temperatures | 36 |
| Pyrene-4,5,9,10-tetraone | Zn $(ClO_4)_2$ | Mg $(ClO_4)_2$ | -70 °C | Disruption of hydrogen bonding networks of water molecules by the synergistic action of cations | 11 |

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|---|---|---|---|---|
| (PTO) | | | and anions | |

Table S8. Practical application of advanced characterization techniques to AZIBs electrolyte additives.

| Electrolyte | Additive | Characterization technique | Characterization purpuse | Ref |
|---|---|---|---|---|
| $ZnSO_4$ | Tripropylene glycol (TG) | *In-situ FTIR* | Reversible displacement of O-H stretching vibrations at 3200 $cm^{-1}$ for de-solvation sheaths | 9 |
| $ZnSO_4$ | Cetyltrimethyl ammonium bromide (CTAB) | *In-situ FTIR* | The stretching intensity of O-H located at 3200-3600 $cm^{-1}$ is weakened and the surface zinc deposition process de-solvation sheaths are achieved | 10 |
| $ZnSO_4$ | Sorbitol | *Operando* Raman | Zn-$OH_2$ vibrations could be observed in the 300-500 $cm^{-1}$ region to detect zinc deposition | 37 |
| $ZnSO_4$ | Sucrose | FT-EXAFS | The spectrum further surfaces an increase in Zn-O bond lengths, expanding the $Zn^{2+}$ solvation shells | 38 |
| $ZnSO_4$ | Tetradecafluorononane-1,9-diol (TDFND) | CLSM | CLSM scanning of the surface roughness of the anode after cycling demonstrated the uniform deposition of zinc with the addition of additives | 39 |

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