Supplementary Information (SI) for Green Chemistry.

Supporting Information

Molecular engineering of nitrile-based additives by oxygen incorporation for highly stable Zn anode

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Experimental Procedures

Materials

Zinc trifluoromethanesulfonate ($Zn(OTf)_2$, 99%) was purchased from Shang Fluoro Co. Ltd. Zn foil (200 μm, 99.9%), Cu foil (10μm, 99.99%), Ti foil (100μm, 99.9%), Super P, Polyvinylidene fluoride (PVDF), N-methyl-2-pyrrolidone (NMP), Glass fiber separator (GF/C) , Coin cell case (CR2025) and Carbon paper were purchased from Canrd Co. Ltd. The MnO_2 was purchased from Macklin. 2-Methoxyethanol, acrylonitrile (ACN, 99.9%), sodium hydroxide (NaOH) and 3-methoxypropionitrile (MON, 99%) were purchased from Adamas.

Synthesis of 3-(2-methoxyethoxy) propanenitrile (MEON)

Under ice-bath cooling, a mixture of 2-methoxyethanol (60 mL, 0.80 mol) and aqueous NaOH (1 mL, 0.02 mol) was combined in a 250 mL flask equipped with a reflux condenser. Acrylonitrile (52 mL, 0.80 mol) was then added dropwise over 2 h. The reaction mixture was stirred at room temperature for 24 h. Upon completion, neutralization was achieved by adding concentrated hydrochloric acid (to pH 7). The crude product was purified by vacuum distillation to afford 3-(2-methoxyethoxy) propanenitrile (MEON) as a colorless liquid in 70% isolated yield. The chemical structure was analyzed by NMR (Fig. S1): ^1H NMR (400 MHz, $CDCl_3$): 3.72 (t, 2H), 3.66 (m, 2H), 3.55 (m, 2H), 3.38 (s, 3H), 2.62 (t, 2H). bp. 125 °C/16 mmHg.

Preparation of electrolytes

The 1.0 M $Zn(OTf)_2$ electrolyte (BE) was prepared by dissolving 1.8 g $Zn(OTf)_2$ into 5 ml deionied water. The modified electrolytes were prepared by adding MEON to the BE electrolyte, where the volume ratio of MEON/MON/ACN ranged from 1, 5, to 10 (versus H_2O), the corresponding electrolytes were denoted as 1 vol% MEON, 5 vol% MEON/MON/CAN and 10 vol% MEON. The above electrolytes were stirred for 12 hours at 25 °C before using.

Electrochemical measurements and characterizations

The Zn foil was cut by rounded disks of 12 mm diameter, followed by washed with ethanol and dried at 60 °C under vacuum for 30 min. The cathode was fabricated by mixing the commercial MnO_2 powder, super P, and polyvinylidene fluoride (PVDF) with a weight ratio of 7:2:1 using N-methyl-2-pyrrolidone (NMP) as solvent. The mixture slurry was printed on hydrophilic carbon paper and then transferred to a vacuum oven drying under 60 °C for 12 h. Finally, cathodes were prepared by cutting to circular discs with a diameter of 1.2 cm and with the loading mass of cut disk within the scope of 1~2.0 mg. CR2025-type coin batteries with glass fiber (Whatman, GF/C) as separators with 120 μL electrolytes were assembled in an open-air environment and tested on a battery test system of Neware. For the Zn||Cu half-cell, the Cu disks (Φ=16 mm) were applied as a cathode. The Coulombic efficiencies (CE) of the Zn||Cu cells were measured at 2 mA cm^{-2} with cycling capacity of 0.5 mA h cm^{-2}. The linear sweep voltammetry (LSV), Cyclic voltammetry (CV) and Chronoamperometry (CA) were collected by Gamry interface 1000E. LSV was tested with a scan rate of 1 mV s^{-1}. Linear polarization curves tests were conducted on a CHI760E electrochemical workstation and performed in a three-electrode setup (Zn as the working electrode, counter electrode and Ag/AgCl as the reference electrode). Cyclic voltammetry (CV) tests were conducted on the voltage range of 0.9~1.9 V (vs. Zn/Zn^{2+}) for Zn||MnO_2 full cells in different electrolytes.After 50 cycles, the Zn||Zn symmetric cells were disassembled in an ambient atmosphere. The cycled Zn electrodes were carefully retrieved and thoroughly rinsed several times with deionized water to remove residual electrolyte. The electrodes were then dried under vacuum prior to further characterization. The surface morphology and structural evolution of the Zn anodes were subsequently investigated by scanning electron microscopy (SEM), while the surface chemical states were analyzed by X-ray photoelectron spectroscopy (XPS).

Morphologies of the Zn anode was observed using a field emission scanning electron microscope (SEM, TESCAN MAIA3) at 20 kV. Nuclear magnetic resonance spectra (NMR) was performed to characterize the electrolytes by Bruker Ascend 400. Raman spectra of the electrolytes were obtained using a Renishaw Invia confocal Raman microscope (532 nm laser excitation). Surface and depth chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher KAlpha system (Ar^+ sputtering, 2×10^{-6} Pa vacuum).

Theoretical calculations

The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy were calculated by using the Gaussian 16 package. The B3LYP-D3 (BJ) combined with 6-31g (d, p) basis set was used in the optimization and single-point calculations.[1, 2] The universal solvent model based on density (SMD) model was used to simulate the solvent phase.

The binding energy, E_b, was evaluated using the following equation:

$E_b = E_{H2O+H2O/MEON} – E_{H2O} – E_{MEON}$

where $E_{H2O+H2O}$ and $E_{MEON+H2O}$ represent the total energy of H_2O-H_2O and MEON-H_2O. E_{H2O} and E_{MEON} are the total energies of H_2O and MEON.

The effect of MEON on solvation structure was simulated by molecular dynamics (MD) simulation by using GROMACS 2023 software[3]. The atomistic simulation studies OPLSS-AA force field was used to parametrize all atoms. The simulation cell contained 60 $Zn(OTf)_2$, 2820 H_2O, 20 MEON molecules were randomly inserted into a cube box with a side length of 6.5 nm. The simulation cell was initialized with a cubic box containing all the molecules and ions via Packmol. The steepest descent method was applied for the energy minimization of the system. Then, 10 cycles of quench-annealing dynamics between 298K and 698K were conducted to eliminate the persistence of metastable states. After that, 50 ns MD simulation in the isothermal-isobaric ensemble was conducted at a temperate of 298 K and pressure of 1 bar, and the last 20 ns MD trajectory was used for analysis. During simulations, the temperature was controlled by the Nosé-Hoover thermostat algorithm with a coupling constant of 0.2 ps, and the pressure was controlled by the Parrinello-Rahman algorithm. The LINCS algorithm was employed for bond constraints. The long-range electrostatic interactions were treated with the Particle Mesh Ewald (PME) method. The non-bonded potential truncation was performed with the cut-off radius of 1.0 Å for the Lennard-Jones potential. Periodic boundary conditions were used in all three directions. The time step was set as 1 fs. The visualization and analysis of simulation results were performed using VMD and internal codes.

The adsorption energy (Eads) calculations were carried out using the Vienna Ab initio Simulation Package (VASP) with the project-augmented wave (PAW) method [4]. The Zn (002) slab was modeled by a four-layer 6×6 surface supercell (144 Zn atoms), and a 20 Å vacuum layer was constructed along the z-direction. The Perdew−Burke−Ernzerhof (PBE) of the generalized gradient approximation (GGA) method was used as the exchange-correlation functional and the DFT-D3(Grimme) was employed for the van der Waals interactions. The plane-wave cutoff energy was set to 500 eV. The convergence for the total energy was 10−5 eV, and the force on each atom was less than 0.03 eV $Å^{-1}$. Γ-only k-meshes were used and only the top two layers of the Zn-slab were allowed for the geometry relaxation calculations. The Eads were defined as follows:

$$Eads = E_{Zn002+molecule} - E_{Zn002} - E_{molecule}$$

where $E_{Zn002+molecule}$ is the total energy of Zn (002)-slab with the adsorbed molecule, E_{Zn002} is the energy of a free Zn (002)-slab, and $E_{molecule}$ is the energy of H_2O or MEON.

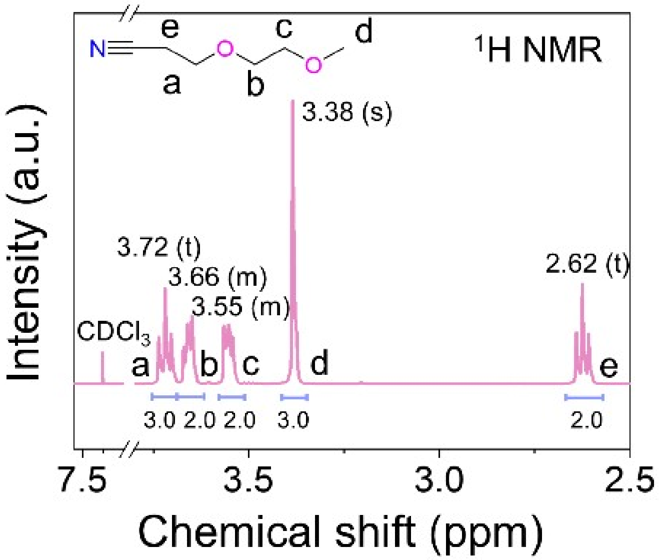

Fig. S1 ^{1}H-NMR spectra of MEON compound.

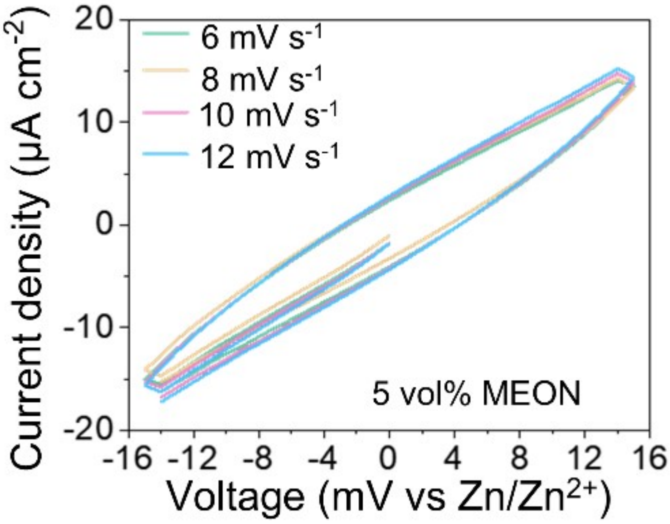

Fig. S2 CV curves for Zn||Zn cells with the voltage range of -15 mV to 15 mV under various scanning rates in the electrolyte with 5 vol% MEON.

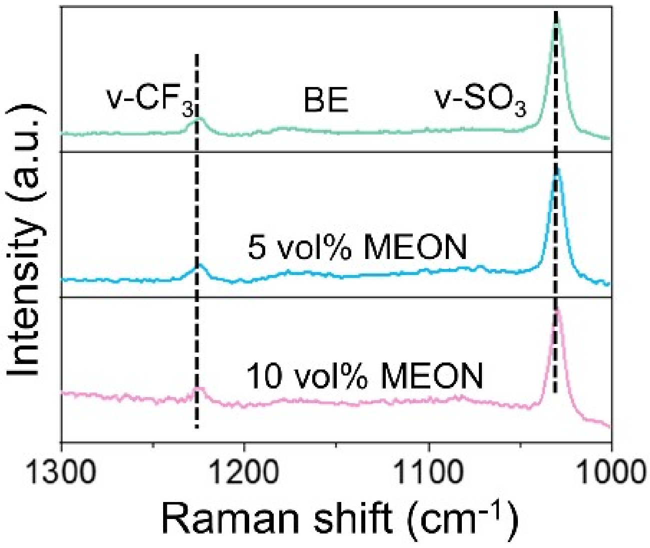

Fig. S3 Raman spectra of the electrolytes with different concentration of MEON.

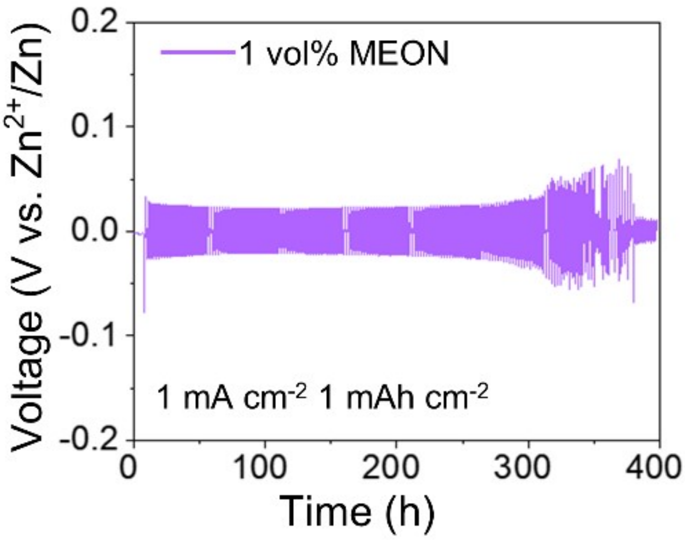

Fig. S4 Long-term cycling performance of Zn||Zn cell with 1vol% MEON at 1 mA cm^{-2} and 1 mAh cm^{-2}.

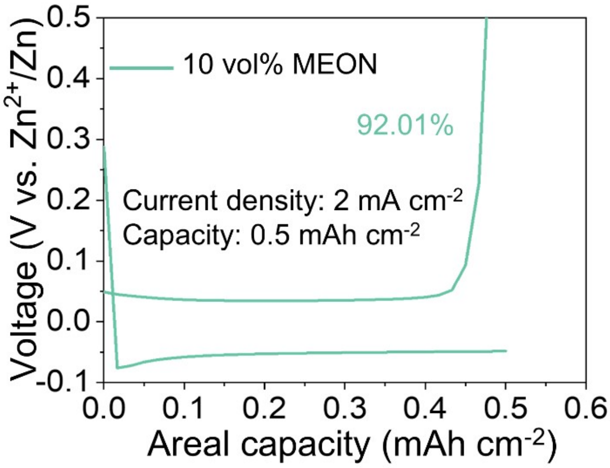

Fig. S5 Initial cycle voltage capacity curves of Zn||Cu cells using 10 vol% MEON electrolyte.

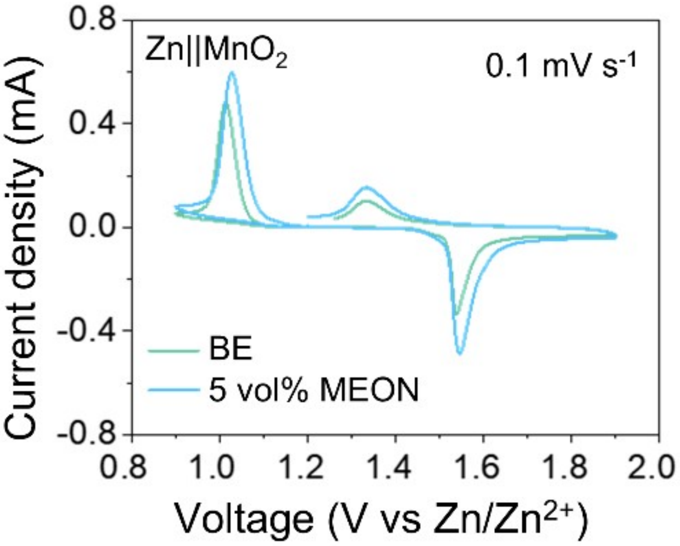

Fig. S6 CV of the Zn||MnO_2 cells with BE and 5 vol% MEON electrolytes at a scan rate of 0.1 mV s^{-1}.

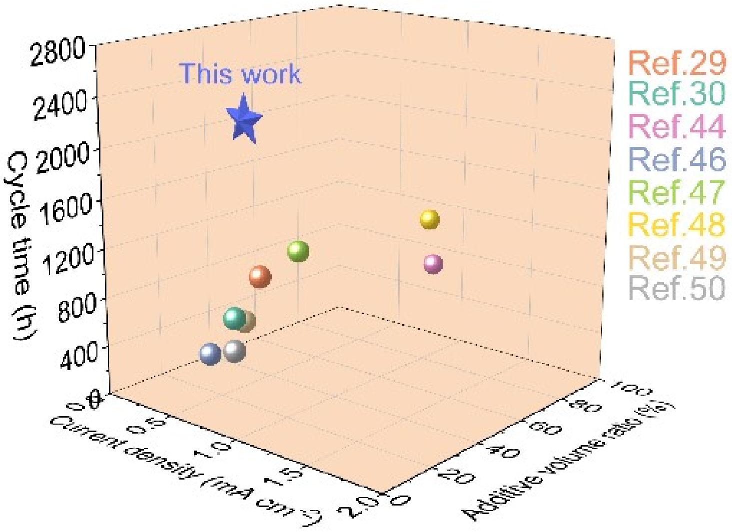

Fig. S7 Comparative analysis of the 5 vol% MEON additives with previous studies of DME, HTCN, ACN, and SN for AIZBs.

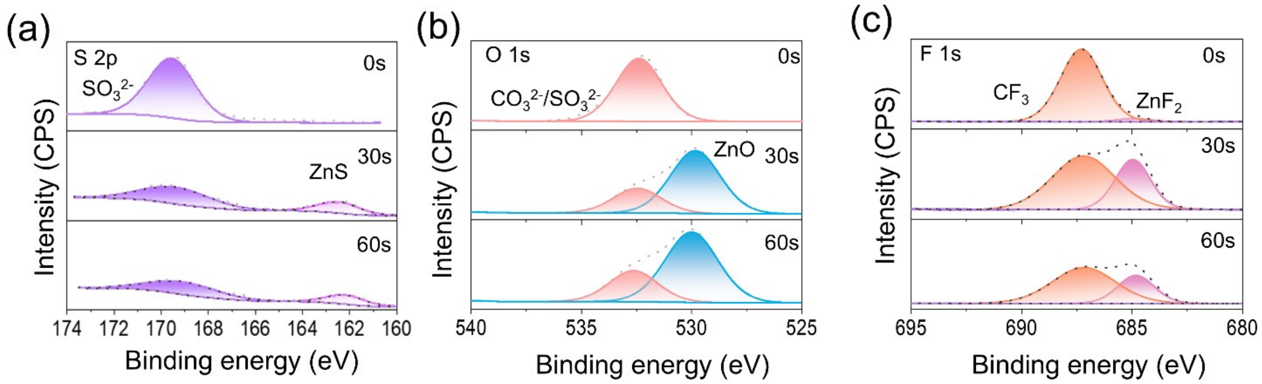

Fig. S8 Elemental S (a), O (b), and F (c) XPS pattern of Ar^+ sputtered Zn anode after 50 cycles in BE electrolyte at 1mA cm^{-2} and 1 mAh cm^{-2}.

Table S1 Comparative summary of ACN, MON and MEON

Solvent	Boiling point	Water solubility	Flash point
ACN	80 ^{o}C	good	2 ^{o}C
MON	165 ^{o}C	good	63 ^{o}C
MEON	225 ^{o}C	good	94 ^{o}C

Table S2 Comparative the performance of AIZBs using different additives.

Electrolyte	Volume ratio of additive	Current density	Cycle time	Reference
1M $Zn(OTf)_2$ / H_2O + 10 vol% ACN	10 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	1200 h	[29]
1M $Zn(OTf)_2$ / H_2O + 85 vol% ACN	85 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	800 h	[44]
1M $Zn(OTf)_2$ / H_2O + 25 vol% ACN	25 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	1300 h	[47]
1M $Zn(OTf)_2$ / H_2O +CAN (0.625:1, by mol)	83 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	1200 h	[48]
2M $ZnSO_4$ / H_2O + 1 vol% DME	1 vol%	0.8 mA cm^{-2} 0.8 mAh cm^{-2}	600 h	[46]
3M $Zn(OTf)_2$ / H_2O + 4 vol% SN	4 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	900 h	[49]
2M $ZnSO_4$ / H_2O + 0.05 vol% SN	0.05 vol%	1.0 mA cm^{-2} 2.0 mAh cm^{-2}	700 h	[50]
2M $Zn(OTf)_2$ / H_2O + 0.3 vol% HTCN	0.3 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2}	950 h	[30]
1M $Zn(OTf)_2$ / H_2O + 5 vol% MEON	5 vol%	1.0 mA cm^{-2} 1.0 mAh cm^{-2} 5.0 mA cm^{-2} 5.0 mAh cm^{-2}	2400 h 400h	This work

References

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2. W. Humphrey, A. Dalke and K. Schulten, *Journal of Molecular Graphics*, 1996, **14**, 33-38.
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