Supplementary Information (SI) for ChemComm.
This journal is © The Royal Society of Chemistry 2026

Electronic Supplementary Information (ESI)

A COF-decorated nanocellulose separator affording modulated ion transport for advanced Zn metal battery

Chunhui Huang†, Meng Tian†, Ge Jin†, Yuhan Zou, Yuyuan Wang, Jiyun Hu*, Yang He, Ya-yun Li*, and Jingyu Sun*

†These authors contributed equally.

*Corresponding authors: sunjy86@suda.edu.cn; kittyli@szu.edu.cn; hujiyun@gbu.edu.cn

Experimental Section

Synthesis of TpPa-SO_3K in aqueous media

1,3,5-triformylphloroglucinol (Tp) was synthesized following the previous literature approach.2 84.7 mg DB-SO_3H (0.45 mmol), 25.0 mg KOH (0.45 mmol), 6.2 mL of water and 475 mg PTSA (2.5 mmol) were mixed and shaken in a vortex shaker for 2 min. Then, 63.0 mg of Tp (0.3 mmol) was added into the purple solution and shaken for another 20 min. The orange solution was transferred into an autoclave and heated at 120 °C for 24 h. Then, the product was washed using water (2 × 30 mL) and subsequently by acetone using Soxhlet extraction, then dried overnight under vacuum at 80 °C [1].

Synthesis of TpPa-SO_3K in non-aqueous media

TpPa-SO_3H was synthesized according to to a previously reported procedure. First, Tp (31.5 mg, 0.15 mmol) and p-aminobenzenesulfonic acid (24 mg, 0.225 mmol) were placed in a Pyrex tube. A mixture of 0.75 mL mesitylene, 0.75 mL dioxane, and 0.3 mL of 3M acetic acid was then added to the tube, followed by sonication to ensure even dispersion of the reactants. The tube was subsequently frozen in liquid nitrogen (77 K), evacuated, and allowed to thaw to room temperature; this process was repeated three times to remove any remaining air before sealing the tube with a flame. The reaction mixture was heated in a drying oven at 120 ℃ for 3 days. After heating, the solid product was extracted using a Soxhlet extractor with a mixed solvent of tetrahydrofuran and dichloromethane for 12 h. Finally, the extracted product was dried overnight under vacuum at 80 ℃, yielding a red powder (TpPa-SO_3H) [2]. In a 50 mL beaker, 2.8 g KOH was dissolved in 50 mL deionized water to prepare 1 M KOH solution. The as-synthesized COF powder was added to this solution and stirred at room temperature for 60 min. The resulting product was collected and thoroughly washed with excess tetrahydrofuran (THF), deionized water, and methanol, followed by vacuum drying to afford a dark-red powder.

Fabrication of COF-based separator

To prepare the COF-based separator, CNF suspension (1.25 g), COF powder (6.25 mg) and glycerol (1.3 μL) were added into a 25 mL glass beaker, followed by the addition of deionized water (10-15 mL). The mixture was homogenized using an ultrasonic cell disruptor for 10 min to obtain a uniform dispersion. The dispersion was then vacuum-filtered through an aqueous filtration membrane to form a free-standing film. The

filtration cake diameter was 42.7 mm, corresponding to the inner diameter of the cylindrical glass funnel. After filtration, the wet film together with the membrane was immersed in tert-butanol to detach the film from the membrane. The obtained film was subsequently soaked in an excess of tert-butanol for 24-36 h, during which the solvent was replaced every 8-12 h. The film was then rapidly transferred to a Petri dish to minimize tert-butanol evaporation, covered with plastic wrap with evenly distributed pinholes for ventilation, and frozen overnight in a freezer compartment. After the film was fully frozen, it was freeze-dried for ~6 h. The freeze dryer was pre-cooled and operated in advance, and the frozen film was transferred directly from the freezer to the freeze dryer to prevent thawing of tert-butanol.

Preparation of iodine cathodes

Iodine (300 mg), activated carbon (400 mg), CMC (100 mg), and Super P (75 mg) were mixed with 15 mL of deionized water to form a homogeneous slurry after stirring for 24 hours. Subsequently, the slurry was cast onto a Ti mesh (12 mm in diameter) and then dried at 60 °C for 1 h. The electrolyte used was a mixed solution of 1,3-dimethylimidazolium iodide and 2 M $ZnSO_4$.

Characterizations

The morphology of the as-prepared samples was observed by using Hitachi SU8010 scanning electron microscopy (SEM). XRD patterns were collected by Bruker D8 Advance Diffractometer to identify the crystal structures and the compositions of obtained samples.

Electrochemical measurements

Electrochemical measurements were conducted using symmetric, asymmetric, and full cells assembled in 2032-type coin configurations. For all cell configurations except the full cells, 2 M $ZnSO_4$ was employed as the electrolyte. Symmetric cells were fabricated using GF or ACOF@CNF separators for galvanostatic charge/discharge (GCD) cycling tests. Additionally, these cells were used to record i-t curves, chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) (0.01 Hz to 100 kHz), and Tafel measurements. Asymmetric cells were constructed using Cu as the working electrode and bare Zn as the counter electrode, with ACOF@CNF, CNF, or GF serving as the separator. These cells were used to collect Coulombic efficiency (CE) measurements for nucleation studies. Full cells with different areal loadings were assembled using bare Zn as the anode, I_2@AC as the cathode, and GF or ACOF@CNF as the separator. All electrochemical measurements were performed on a Neware battery testing system.

The ionic conductivity was tested by inserting different separators between two stainless steels. The ion conductivity was calculated by the equation:

$$\sigma = \frac{L}{R_b * A}$$

where σ is the Zn^{2+} conductivity, L is the thickness of the separator, R_b is the bulk resistance, and A is the area of the working electrode.

The Zn^{2+} transference numbers were assessed through EIS and CA on Zn symmetrical cell, and were calculated by the following equation:

$$t_{Zn^{2+}} = \frac{I_s}{I_0} * \frac{V - I_0 R_0}{V - I_s R_s}$$

where V is applied polarization voltage (2 mV), I_0 and I_s are the initial and steady-state current values during polarization, and R_0 and R_s are the resistance values before and after polarization at constant potential, respectively.

Theoretical calculations

First-principles calculations were implemented using the Vienna Ab initio Simulation Package (VASP) [3] with the Perdew-Burke-Ernzerhof functional [4] with the generalized gradient approximation (GGA). All slab systems were built with a large vacuum thickness of 20-Å. According to the size of crystal, the Gamma K-points were set as 1 × 1 × 1 and 4 × 4 × 1 for COF and Zn systems, respectively. The plane-wave of cutoff energy was set as 500 eV, and the energy threshold was 10^{-5} eV. The spin-orbit coupling was considered for the transition metal of Zn. The adsorption energy was computed based on the free energy difference between the reactant and product.

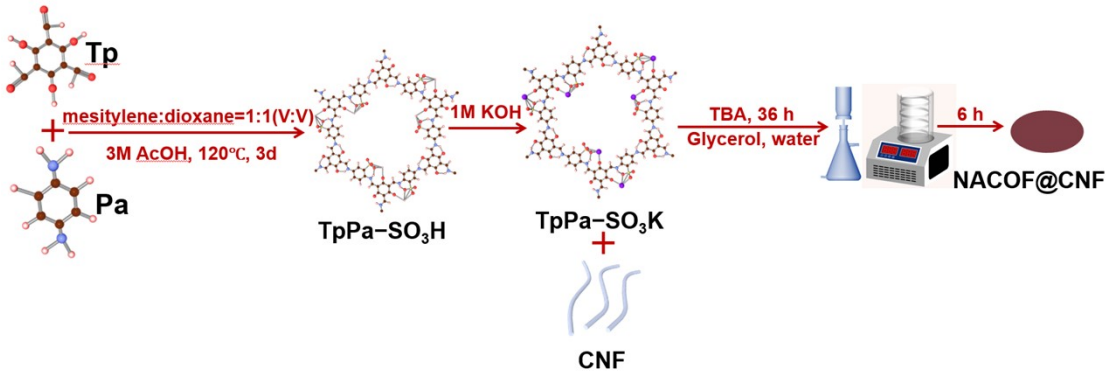

Fig. S1 Synthetic route of NACOF@CNF.

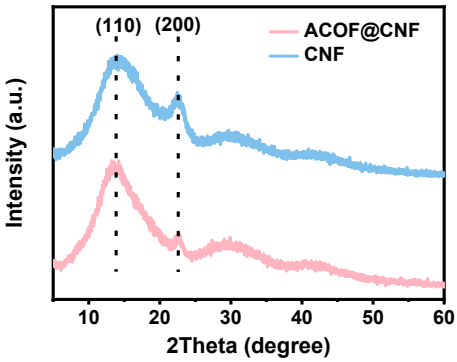

Fig. S2 XRD patterns of AOF@CNF and CNF film.

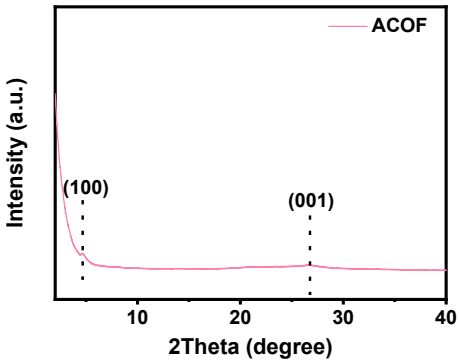

Fig. S3 XRD pattern of ACOF.

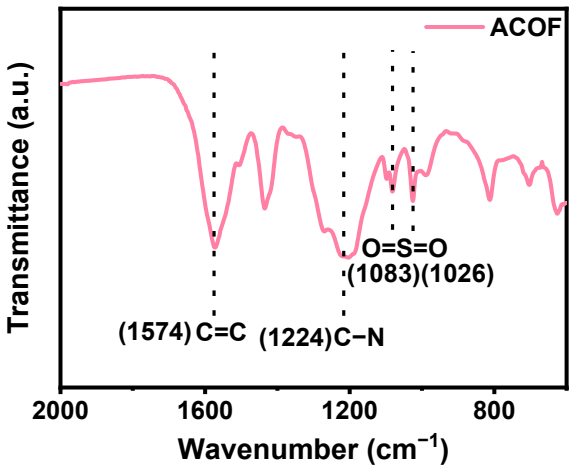

Fig. S4 FT-IR spectrum for ACOF.

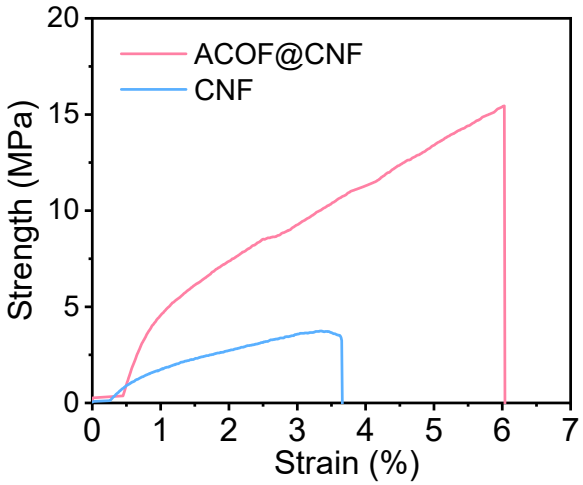

Fig. S5 Stress-strain curves of ACOF@CNF and CNF separator.

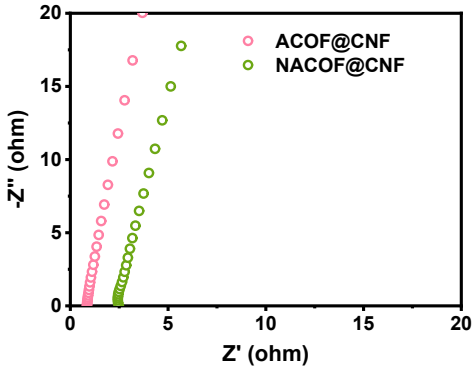

Fig. S6 EIS profiles of symmetric cells with ACOF@CNF and NACOF@CNF.

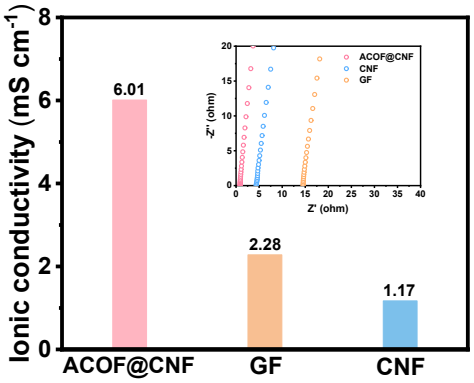

Fig. S7 Ionic conductivity of ACOF@CNF, GF, and CNF separators.

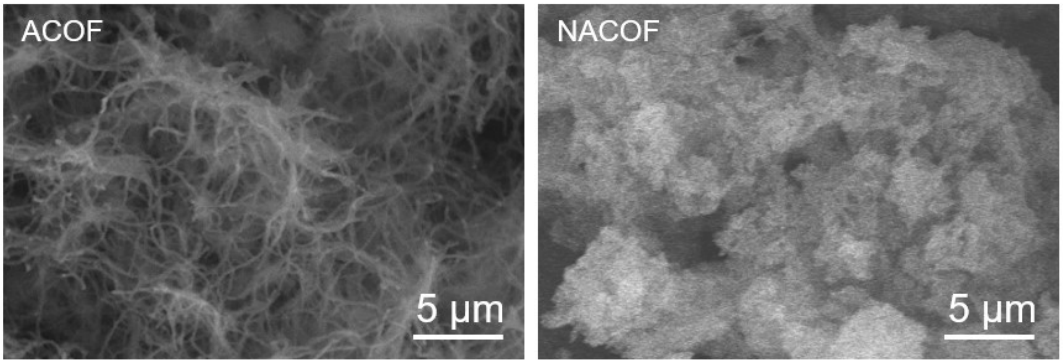

Fig. S8 SEM images of the ACOF and NACOF.

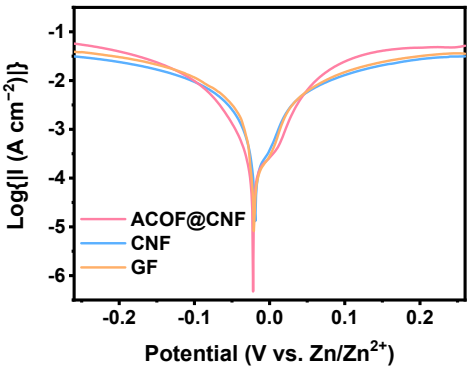

Fig. S9 Linear polarization curves of ACOF@CNF, CNF and GF cells.

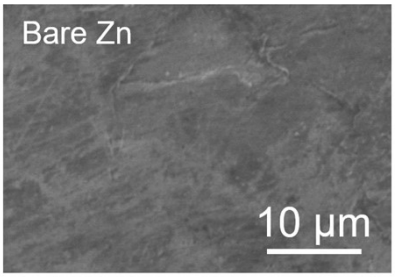

Fig. S10 SEM image of the bare Zn.

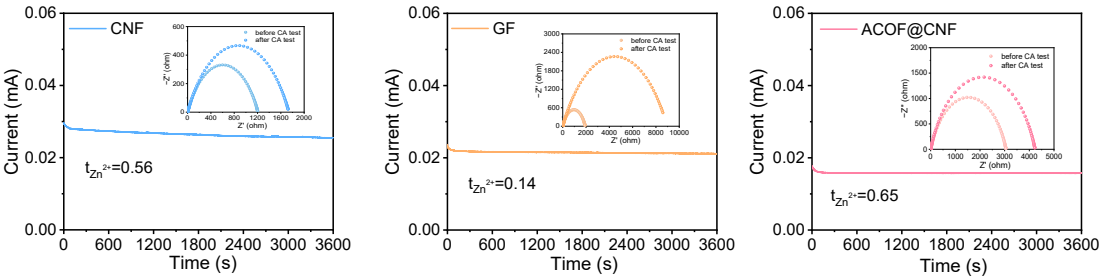

Fig. S11 Calculated Zn^{2+} transference numbers for different separators.

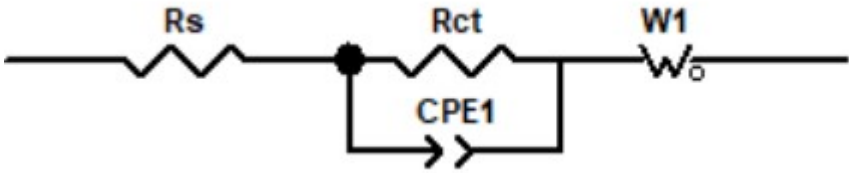

Fig. S12 Equivalent electrical circuit of the EIS spectrum.

Table S1 Comparison of ionic conductivity for separator engineering in aqueous Zn batteries.

System No.	Ionic conductivity (mS cm^{-1})	Ref.
1	1.99	*Adv. Energy. Mater.* 2021, 11, 2101299
2	3.83	*Adv. Mater.* 2023, 35, 2304667
3	4.50	*Adv. Funct. Mater.* 2025, e17715
4	2.87	*Adv. Funct. Mater.* 2025, e19947
5	5.10	*Angew. Chem. Int. Ed.* 2025, 64, e202423 118
6	4.47	*Adv. Funct. Mater.* 2023, 33, 2304280
7	2.64	*Adv. Funct. Mater.* 2024, 34, 2407262
8	6.01	**this work**

Supporting References

[1] C. Li, J. Yang, P. Pachfule, S. Li, M.-Y. Ye, J. Schmidt and A. Thomas, *Nat. Commun.*, 2020, 11, 4712.

[2] J. Xu, Y. Yang, Q. Dai, Z. Zheng, Y. Cao, Y. Cheng, B. Peng, L. Ma and Y. Wang, *Angew. Chem. Int. Ed.*, DOI:10.1002/anie.202423118.

[3] G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, 59, 1758-1775.

[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, 77, 3865-3868.