Supplementary Information

Nitrogen doped carbon fibers coating embedded in the separator for stable zinc batteries

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1. Experimental Section

1.1. Material Synthesis

1.1.1 Synthesis of CDs and Carbon Fibers

The synthesis of CDs and carbon fibers was based on our previous reports.[1] NaOH (12 g) was gradually added into acetaldehyde solution (40 mL, 40% aqueous solution) under violent stirring, and the resulting mixture was continuously stirred for 2 hours. And then, the product was sonicated with diluted hydrochloric acid and water until flocculation occurred. Subsequently, the product underwent washing with deionized water until neutralization was achieved. The resulting CDs were then dried in a drying oven at 70 °C. For the synthesis of carbon fibers, a homogeneous mixture of carbon dots (0.4 g) and zinc chloride (2.4 g) was subjected to heating at 400 °C for 4 hours in an argon atmosphere, with a heating rate of 10 °C min^{-1}. The resulting calcined product (CF400) underwent washing with diluted hydrochloric acid and distilled water. The dried CF400 was then mixed with carbamide, followed by heating to 700 °C at a temperature rising rate of 3 °C min^{-1} under argon, and maintained for 2 hours. The washing and drying procedures for nitrogen-doped carbon fibers (NCF700) were identical to those for CF400. The synthesis of pure carbon fibers (CF700) followed the same process as NCF700, except for the absence of carbamide.

1.1.2 Preparation of modified separator

The coated separator was fabricated by blending carbon fibers (CF700 or NCF700) and carboxymethyl cellulose (CMC) at a mass ratio of 8:2 in an appropriate quantity of deionized (DI) solvent. Following magnetic stirring for 12 hours at room temperature, the resulting homogeneous slurry was applied onto a glass fiber separator using the doctor blading technique. Subsequently, the coated separator was subjected to vacuum drying at 60 °C for 12 hours to eliminate excess water solvent, yielding the products termed CF700@GF or NCF700@GF. After obtaining the dried composite separator, it is cut into circular pieces of uniform diameter. Subsequently, these separator pieces, laden with identical loads of carbon fiber, are assembled together in a coated juxtaposition manner to form the composite separator. This resultant structure is designated as GF@CF700@GF and GF@NCF700@GF. Two pieces of separator with the same size were assembled with their coated sides facing

the electrode and designated as GF@GF@NCF700. The blank control group employs two uncoated separator pieces for identical assembly procedures, designated as GF@GF. In all electrochemical tests conducted in this paper, bilayer assembled separators were utilized.

1.1.3 Preparation of Mg-Doped $NH_4V_4O_{10}$ (MNVO) cathode materials

The MNVO was synthesized using a modified hydrothermal method as described in previous literature.[2] $NH_4V_4O_{10}$ was synthesized through a single-step hydrothermal method, wherein 0.64 g NH_4VO_3 was dissolved in 80 ml of deionized (DI) water at 60 °C with stirring. Subsequently, 1.16 g $H_2C_2O_4 \cdot 2H_2O$ was added to the solution until it attained a dark green color. Upon complete dissolution, magnesium oxalate was introduced into the dark green solution at a predetermined ratio (Mg:V = 1:16). The resulting mixture was transferred to a 100 ml Teflon-lined autoclave and maintained at 180 °C for 3 hours. The resulting dark green powder was obtained by successive rinsing with distilled water/alcohol and subsequent vacuum drying at 60 °C for 24 hours. The MNVO cathodes were prepared by blending 60 wt% of active materials, 20 wt% of polyvinylidene fluoride (PVDF) binder, and 20 wt% of conductive carbon (Super P) in N-methyl pyrrolidinone (NMP). These slurries were then coated onto stainless-steel mesh substrates containing the active materials. Finally, the prepared electrodes were obtained for further use after vacuum drying at 100 °C for 10 hours.

2. Materials Characterizations

X-ray diffraction (XRD) data were acquired using a Rigaku Ultima IV X-ray diffractometer operating at a scan rate of $10°min^{-1}$. High-resolution transmission electron microscopy (HRTEM), elemental mapping, and selected-area electron diffraction (SAED) patterns were obtained using a JEOL JEM 2100F transmission electron microscope (TEM). The scanning electron microscope (SEM) images of the separators and carbon fibers were captured using a JEOL JSM-7610F Plus and a TESCAN MIRA4. Optical images of the electrodes were acquired using a Digital Microscope KH-7700. Contact angle measurements between the GF@GF/GF@NCF700@GF and the 2 M $ZnSO_4$ electrolyte were performed using a Contact Angle Goniometer (SDC-100 China, Dongguan). Electron probe microanalysis (EPMA) was conducted using a JXA152 8530F-PLUS instrument.

3. Electrochemical measurements

All experiments were conducted using CR2016 coin cells, employing GF@ GF/GF@CF700@GF/GF@NCF700@GF separators and a 2 M $ZnSO_4$ electrolyte. Electrodes were shaped into circular disks with a diameter of 12 mm. Symmetric cells were constructed using two identical disks, resulting in both the anode and cathode being identical. Half cells were assembled using two different disks, with the anode being a bare Zn anode and the cathode a bare Cu electrode. Assembly of Zn||GF@GF/GF@NCF700@GF||MNVO full cells followed a similar procedure to Zn||GF@GF/GF@NCF700@GF||Zn symmetric cells, except one Zn electrode was replaced with an MNVO cathode.

Electrochemical characterization, including electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), Tafel curves, and Chronoamperometry (CA), was performed using a CHI660E electrochemical workstation. CV analysis of half cells was conducted at a scan rate of 1 mV s^{-1}, while CV analysis of full cells was conducted at a scan rate of 0.2 mV s^{-1}. Contact angle (CA) measurements were conducted in Zn||GF@GF/GF@NCF700@GF||Zn symmetric cells at an overpotential of -150 mV. The electrochemical performance of Zn||GF@GF||MNVO and Zn||GF@NCF700@GF||MNVO full cells was assessed using a Neware BTS4000 test system within a voltage window of 0.2 to 1.5 V.

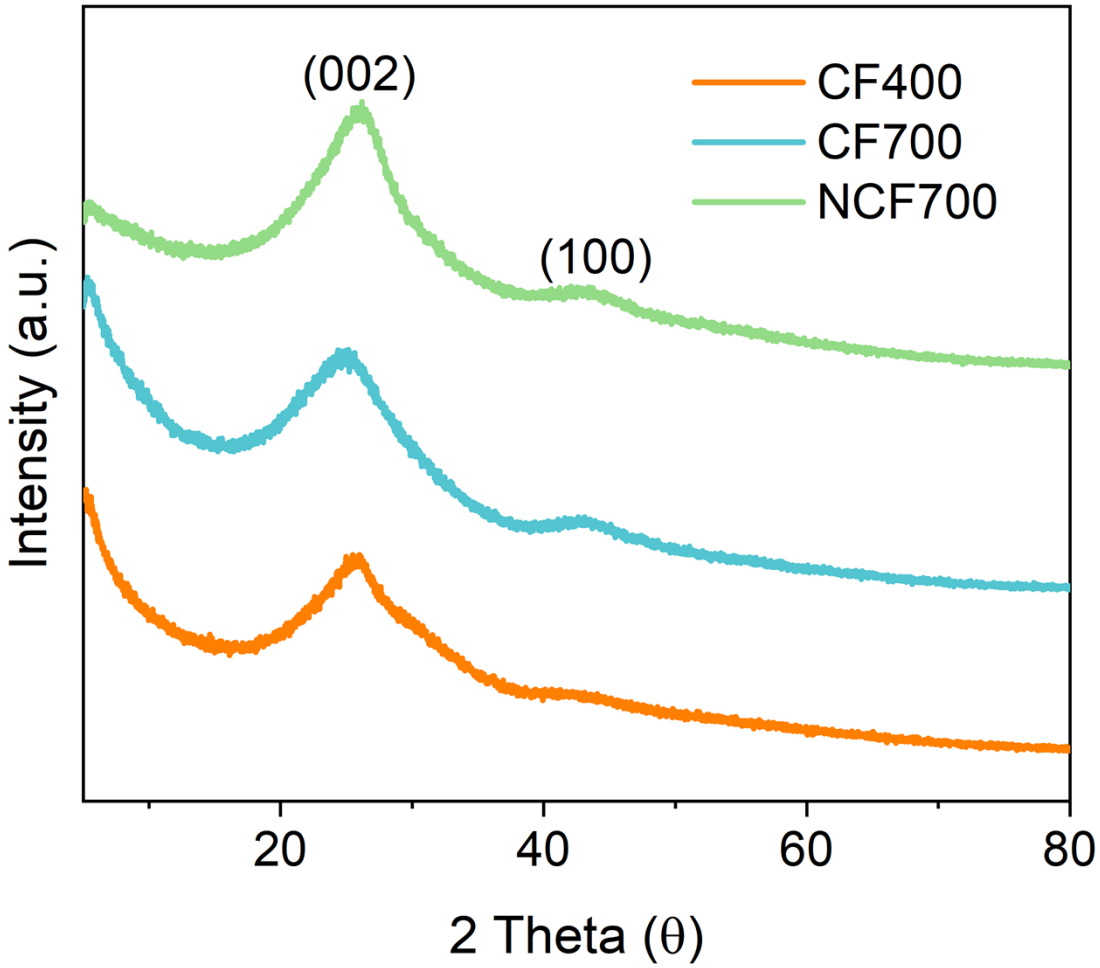


Fig. S1 XRD patterns of CF400, CF700 and NCF700.

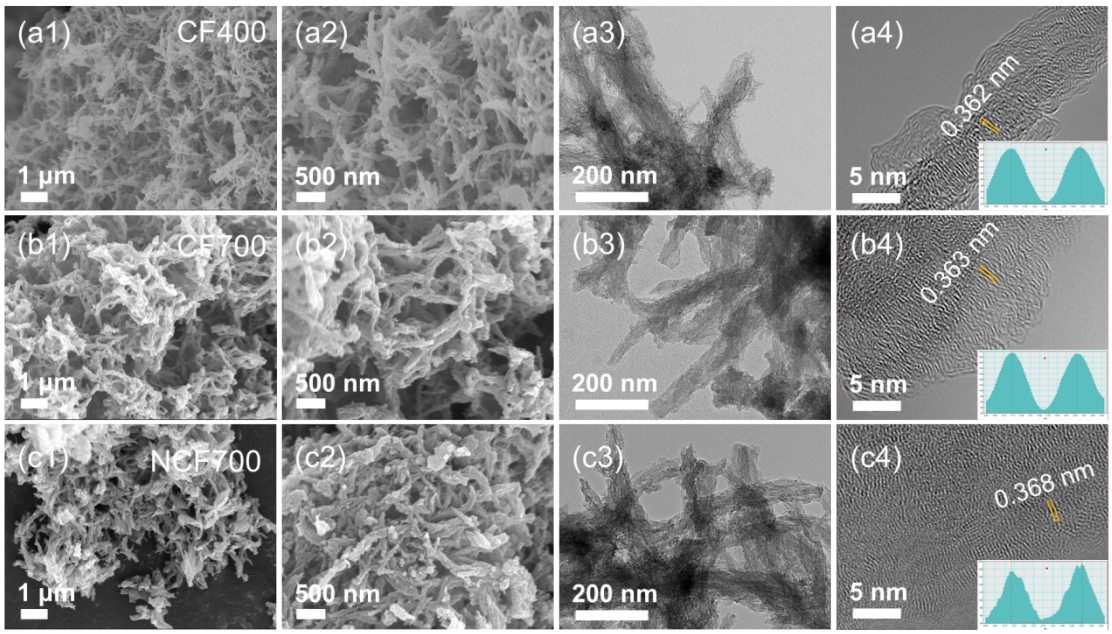


Fig. S2 SEM, TEM, and HRTEM of (a) CF400, (b) CF700, and (c) NCF700.

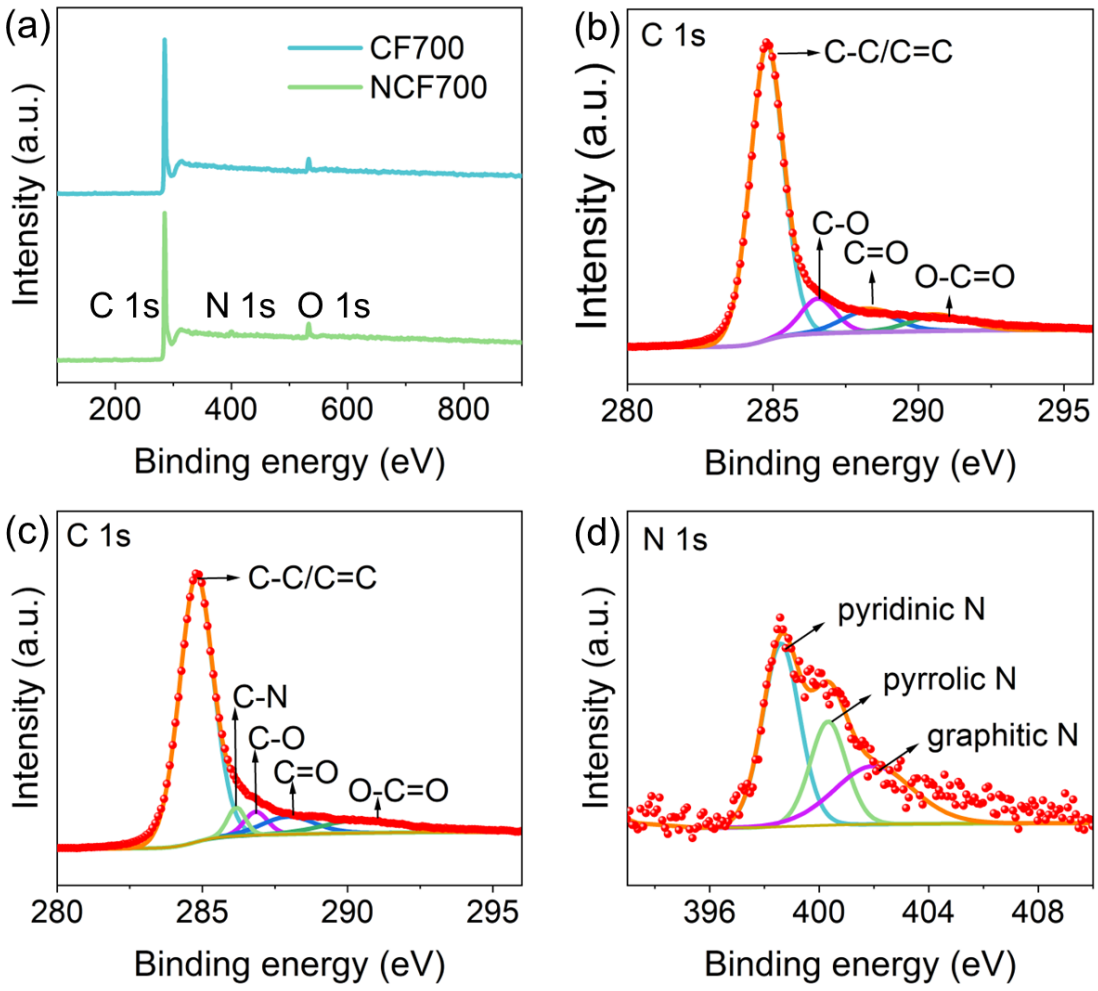


Fig. S3 (a) XPS survey spectra, The C 1s spectra of (b) CF700 and (c) NCF700, (d) high-resolution N 1s of NCF700.

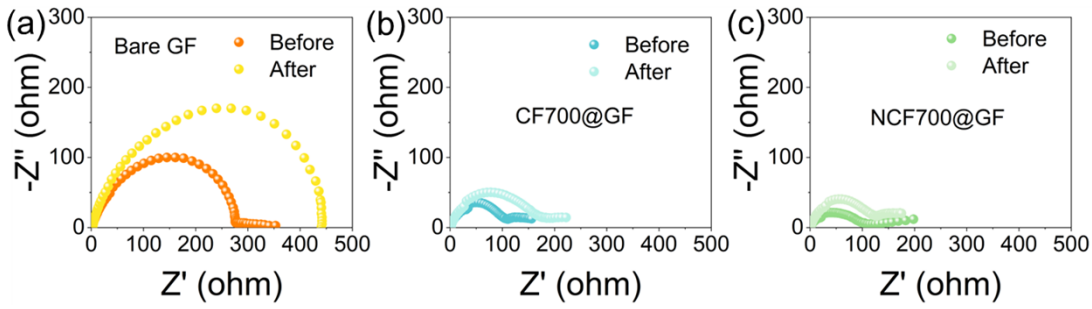


Fig. S4 Nyquist plots of symmetric cells with (a) bare GF, (b) CF700@GF and (c) NCF700@GF separators before and after CA measurement.

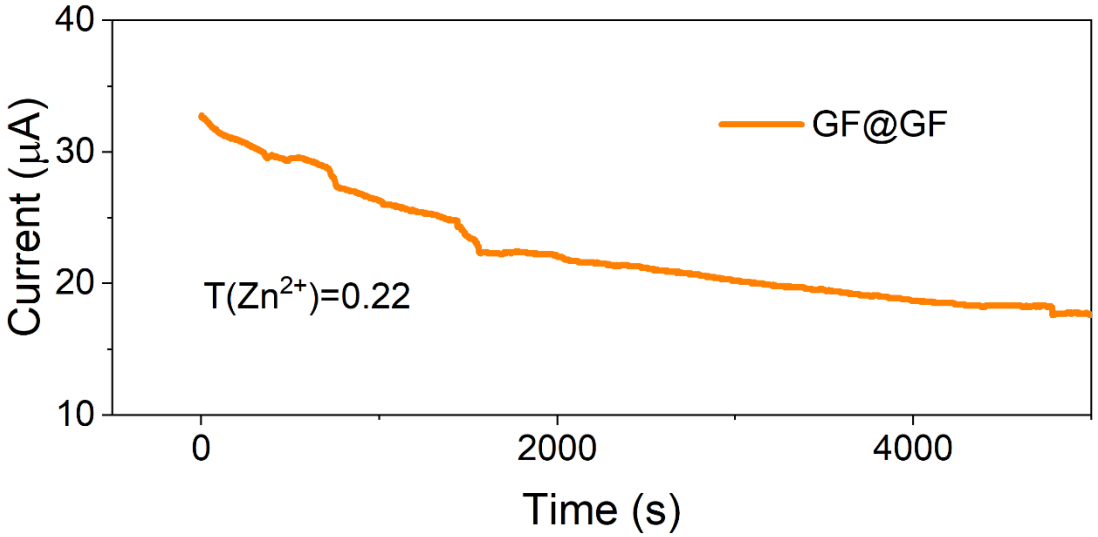


Fig. S5 Chronoamperometric curve of symmetric batteries with GF@GF separator.

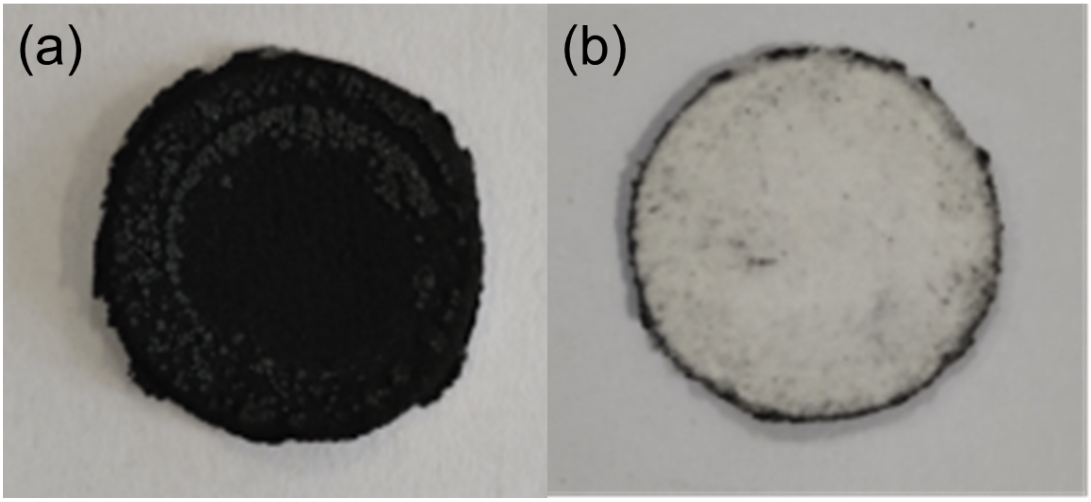


Fig. S6 digital photos of NCF700@GF FZM (a) and NCF700@GF (b) separator after 20 cycles at 4 mA cm^{-2} and 4 mAh cm^{-2}.

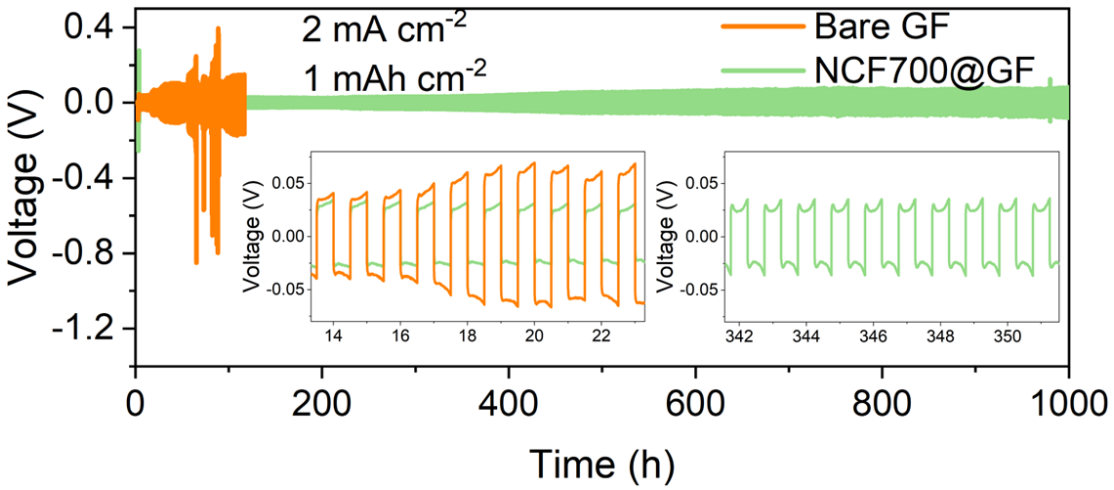
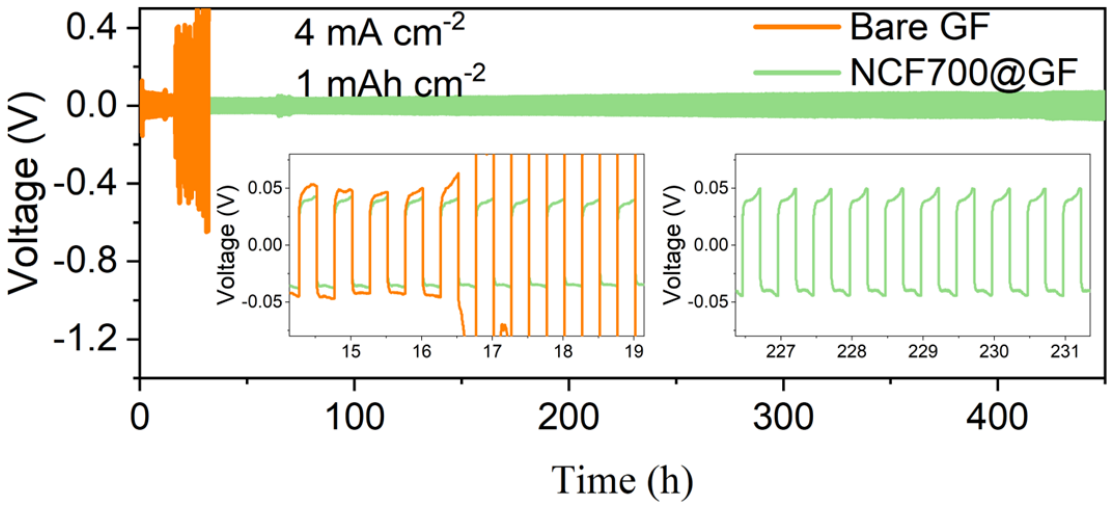


Fig. S7 Cycling performance of symmetric batteries based on bare GF and NCF700@GF at 2 mA cm^{-2}.



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125 Fig. S8 Cycling performance of symmetric batteries based on bare GF and
126 NCF700@GF at 4 mA cm^{-2}.

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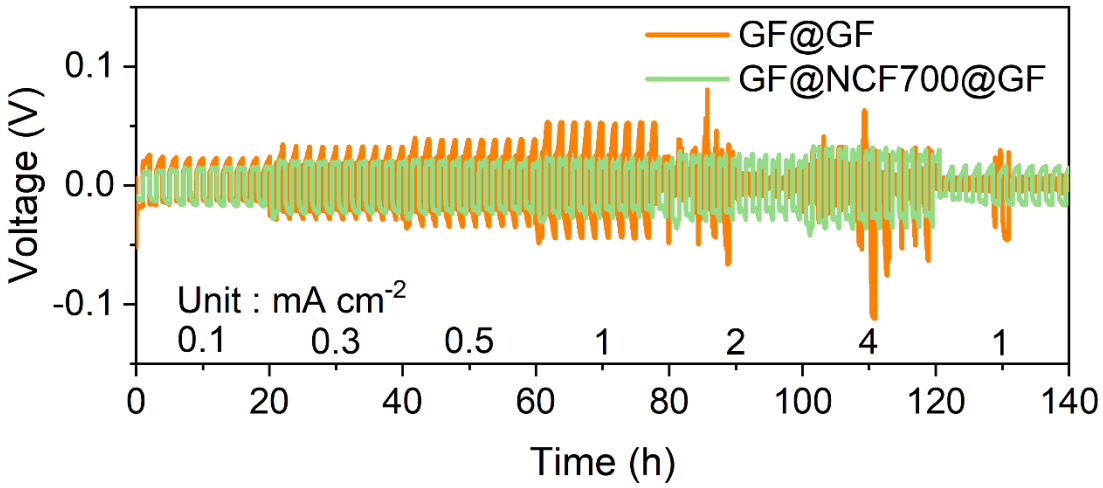


Fig. S9 The rate performance of symmetrical cells based on GF@GF and GF@NCF700@GF.

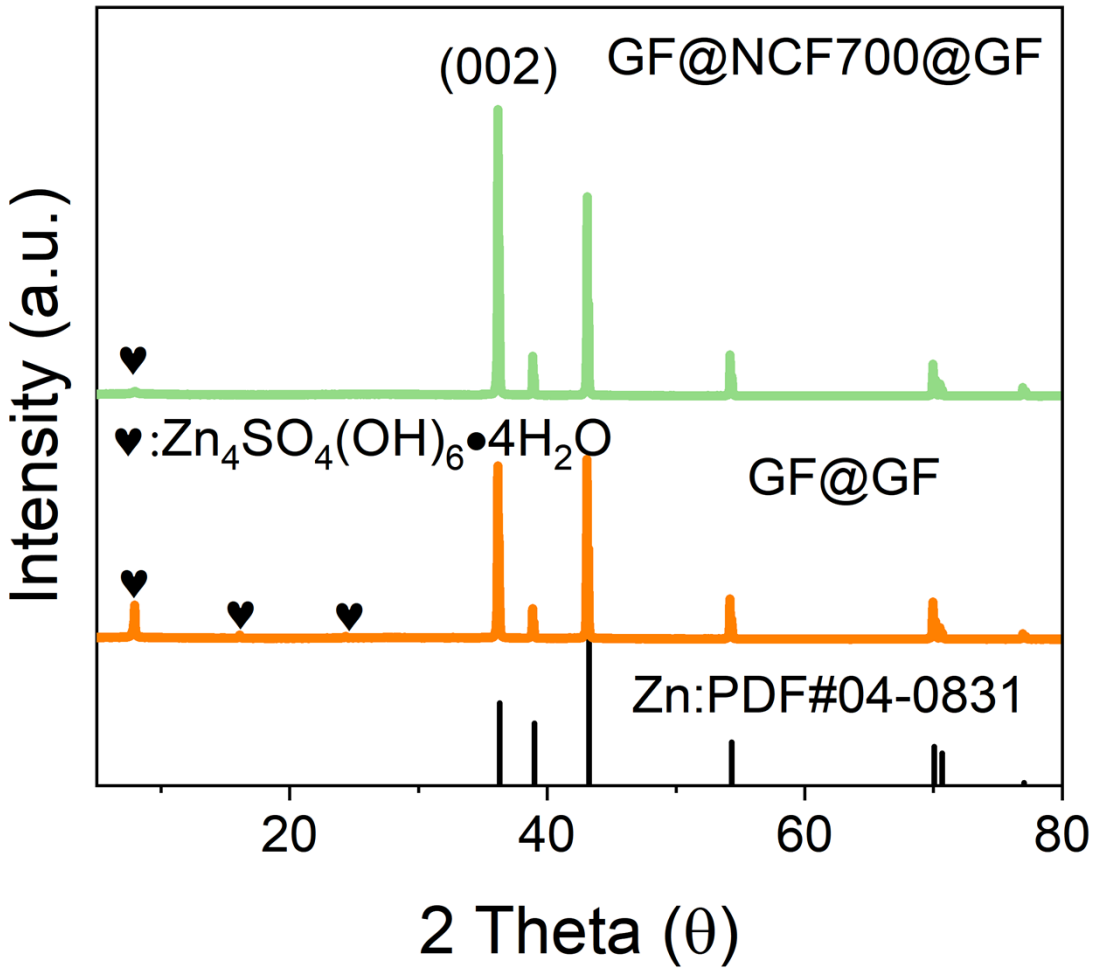


Fig. S10 XRD patterns of Zn anode based on GF@GF and GF@NCF700@GF after 20 cycles..

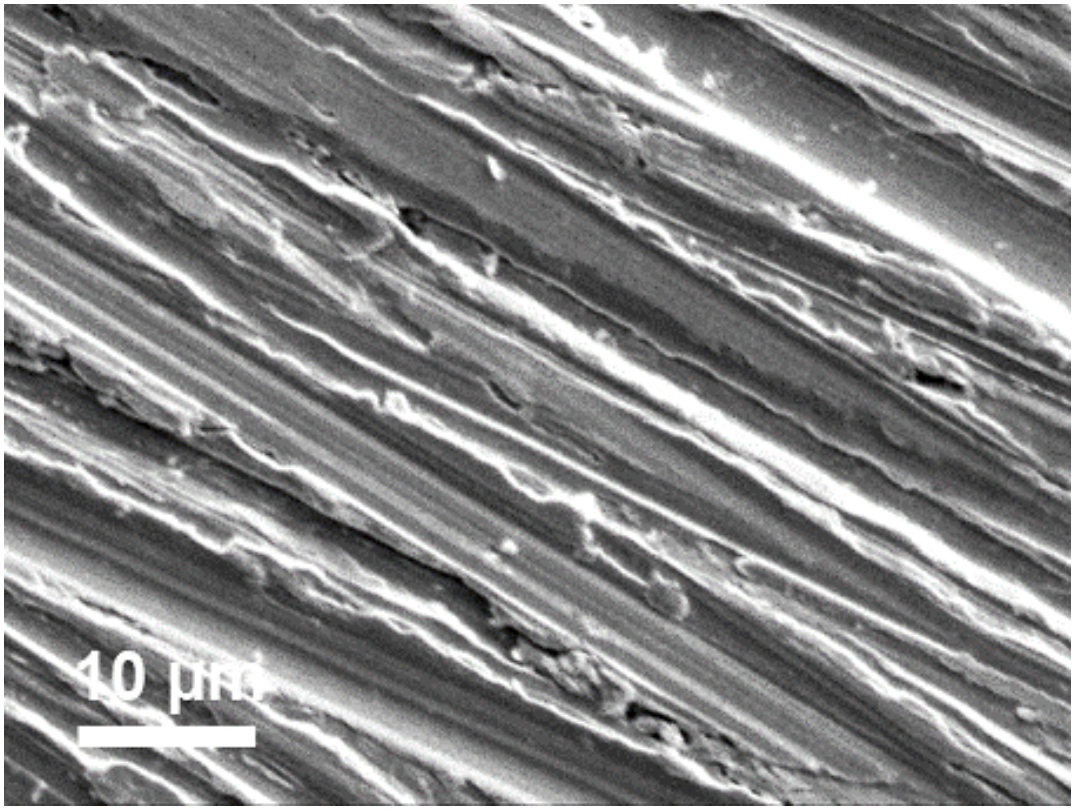
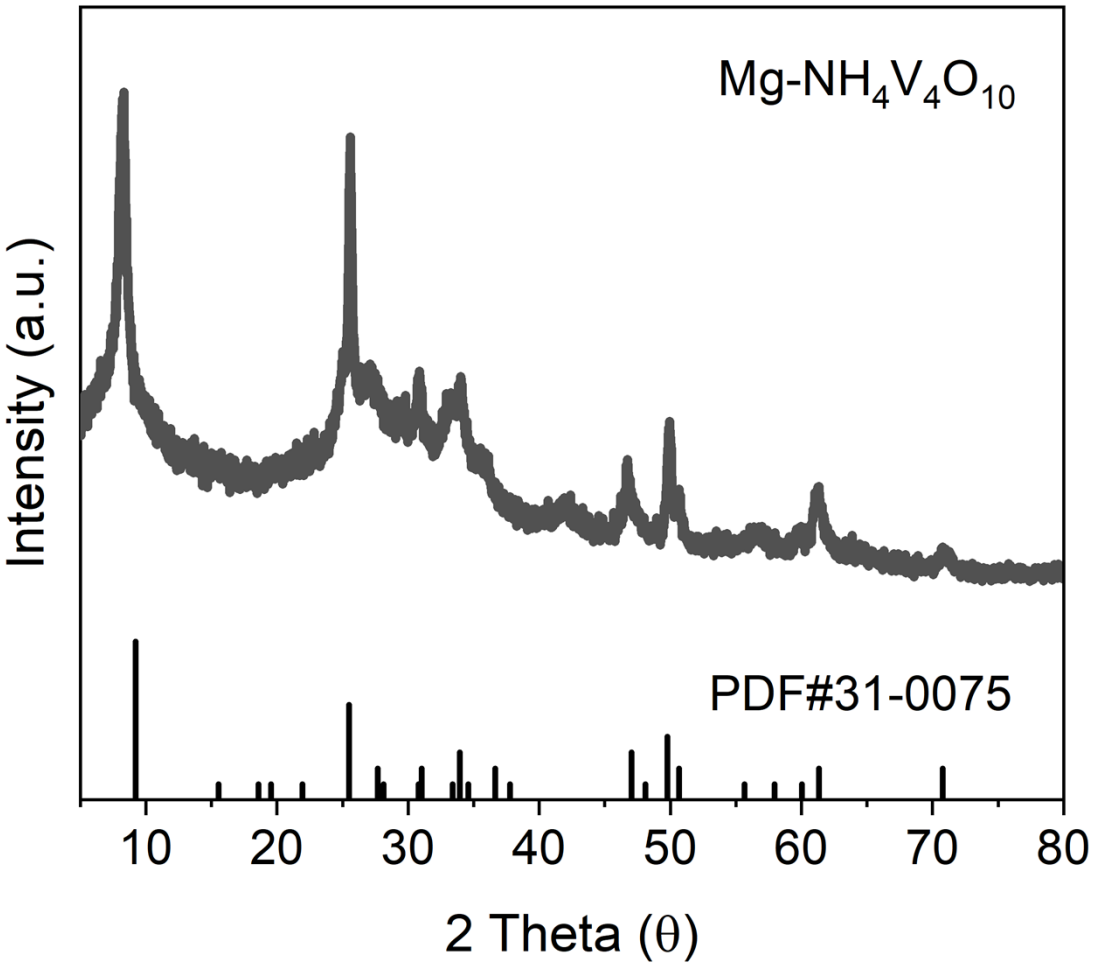


Fig. S11 SEM image of Zn foil before cycling.



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143 Fig. S12 XRD pattern of MNVO.

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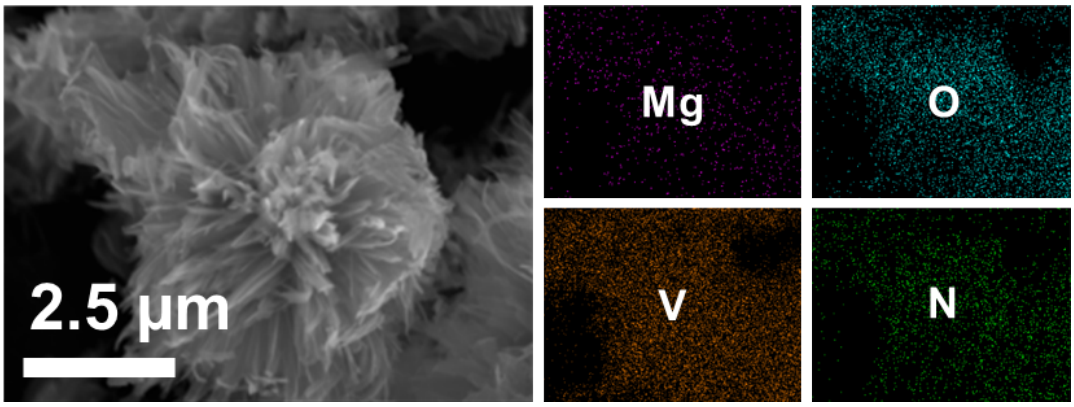


Fig. S13 SEM image and corresponding EDS mapping of MNVO.

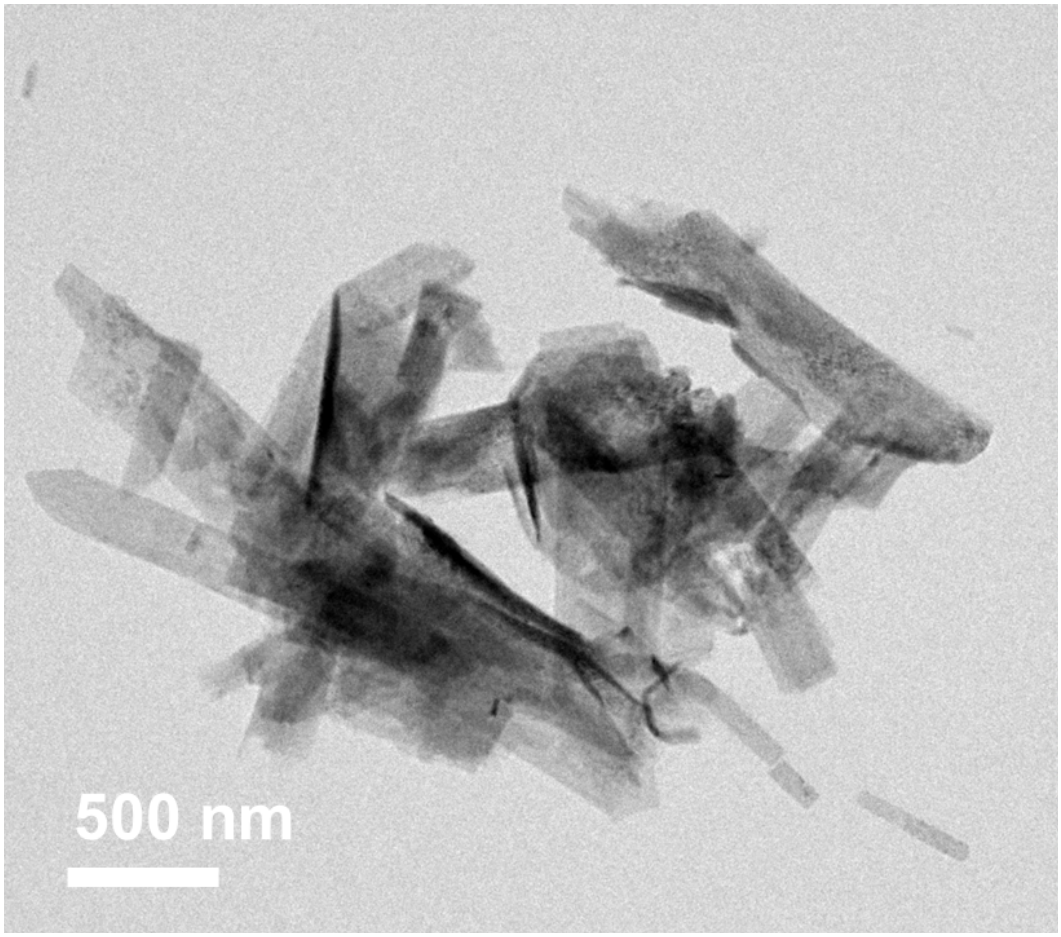


Fig. S14 TEM image of MNVO.

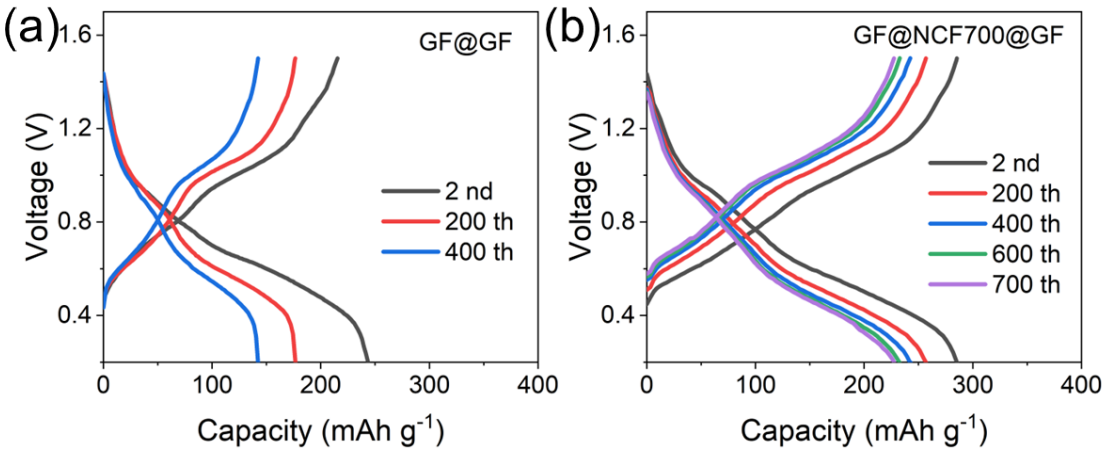
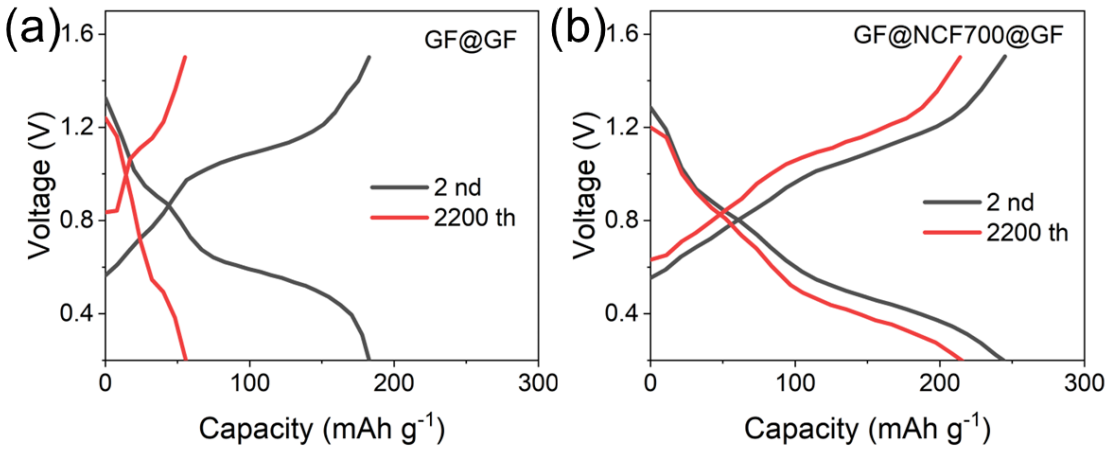


Fig. S15 Galvanostatic charge-discharge curves of (a) Zn||GF@GF||MNVO and (b) Zn||GF@NCF700@GF||MNVO full cell at 1 A g^{-1}.



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159 Fig. S16 Galvanostatic charge-discharge curves of (a) Zn||GF@GF||MNVO and (b)
160 Zn||GF@NCF700@GF||MNVO full cell at 3 A g^{-1}.

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References

1 L. Li, Y. Li, Y. Ye, R. Guo, A. Wang, G. Zou, H. Hou and X. Ji, *Acs Nano*, 2021, **15**, 6872-6885.

2 X. Wang, Y. Wang, A. Naveed, G. Li, H. Zhang, Y. Zhou, A. Dou, M. Su, Y. Liu, R. Guo and C. C. Li, *Adv. Funct. Mater.*, 2023, **33**, 2306205.