

Supporting Information:

Developing NiMoO₄-Based Multifunctional Cathode for Hybrid Zinc Battery

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Experimental Section.

Chemicals and Materials: Nickel nitrate [Ni(NO₃)₂·6H₂O], sodium molybdate (Na₂MoO₄·2H₂O), anhydrous zinc acetate [Zn(CH₃COO)₂] and potassium hydroxide (KOH) were all purchased from Aladdin Industrial Corporation (Shanghai, China), and used as received without further purification. All aqueous solutions were prepared from deionized (DI) water (resistance: >18 MΩ cm).

Material Characterization:

The microstructure and composition of the NiMoO₄/NF was analyzed by field emission scanning electron microscope (FESEM, ZEISS Supra55), transmission electron microscope (TEM, Tecnai G2 F30), X-ray diffractometer (XRD, BPUKER/D2PHASER) with a Cu-Kα radiation and X-ray photoelectron spectrometer calibrated using C 1s peak at 284.8 eV (KRATOS AXIS Ultra DLD). Contact angle measurements were performed on a contact angle meter contact (Ossila).

Preparation of NiMoO₄/NF electrode:

Nickel foam (NF) was firstly treated with diluted hydrochloric acid solution for 30 min to remove oxide layer. After washed with DI water to remove excess hydrochloric acid, the cleaned NF was subjected to the growth of NiMoO₄ by hydrothermal method. Briefly, 3 mmol Ni(NO₃)₂·6H₂O and 3 mmol of Na₂MoO₄·2H₂O was dissolved in 60 mL DI water under stirring to obtain a light green solution. Such prepared solution together with the pretreated NF were put into a 100 mL Teflon-lined autoclave. The hydrothermal process was carried out at 120°C for 6 hours within an oven.

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After cooled naturally to room temperature, rinsed with DI water carefully and then vacuum dried. The obtained NiMoO₄ on NF (denote as Pre-NiMoO₄/NF) was then treated at 400°C at a heating rate of 5°C·min⁻¹ under N₂ atmosphere for 1h. After the heat-treatment, the sample was further coated with a conductive ink by simple drop-casting. The conductive ink was prepared by dispersion of 0.45g carbon black (CB) and 5g of 1wt.% polyvinylidene fluoride (PVDF) N-methylpyrrolidone (NMP) solution.

Preparation of multifunctional Co-NiMoO₄/NF electrode:

To construct multifunctional electrode with ORR properties based on NiMoO₄/NF, a reported ORR catalyst of C-CoPAN900 (Nanoscale 2015, 7, 1830) was coated on the NiMoO₄/NF by simple drop-casting method and the resulting electrode is denoted as Co-NiMoO₄/NF. The ORR catalyst ink used was composed of 20 mg catalyst and 2 mL Nafion dispersion (1 wt%, diluted by ethanol). The catalyst loading was controlled to be about 1 mg cm⁻². With such catalyst loading, the electrode not only can effectively promote ORR/OER for Zn-air function but also without significantly contributing to the capacity for the Ni-Zn function of the hybrid battery.^[8]

Preparation of hydrophobic air-permeable current collector for hybrid Zn-Ni/Zn-batteries:

To prevent electrolyte leakage, we employed hydrophobic and air-permeable nickel foam (NF) as the current collector and backing layer which was placed next to the multifunctional electrode of Co-NiMoO₄/NF. The hydrophobic and air-permeable NF was prepared by air spraying of mixing PTFE dispersion (30 wt% in DI water) and subsequent heat treatment at 300°C in for 1 hour.

Assembly of Zn-Ni batteries and hybrid Zn-Ni/Zn-airbatteries:

The nickel-zinc battery and hybrid battery were assembled using custom-made two-electrode cells as illustrated in Fig. S5 and Fig. 3a with the as-prepared cathodes accordingly. A polished zinc plate serve as the anode and an alkaline aqueous solution of 6M KOH containing 0.2 M Zn(CH₃COO)₂ was used as the electrolyte.

Electrochemical measurement and battery testing:

The electrochemical performances were evaluated by cyclic voltammetry (CV), constant current charge-discharge (GCD), and alternating current impedance test (EIS) on an electrochemical workstation (CHI 660E). The continuous discharge-charge tests were carried out for evaluated the cycle performance and rate performance of the battery on a NEWARE battery testers in ambient air conditions (oxygen from air). For three-electrode system, the as-prepared electrodes, Hg/HgO, Pt sheet and 6M KOH were used as the working electrode, reference electrode, counter electrode and electrolyte, respectively.

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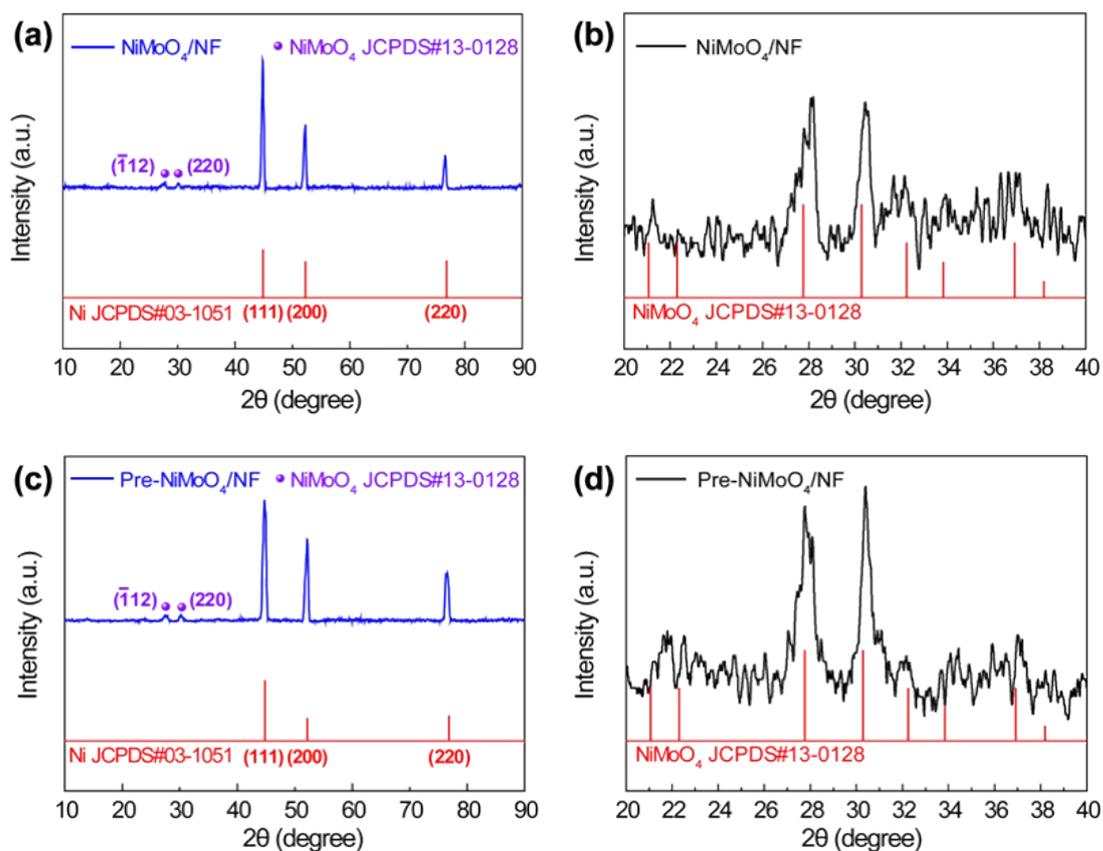


Fig. S1. (a) XRD evidence of NiMoO₄ grown on NF. (b) Detailed XPS spectra of Ni 2p and Mo 3d of NiMoO₄/NF. (c,d) XRD patterns of Pre-NiMoO₄/NF.

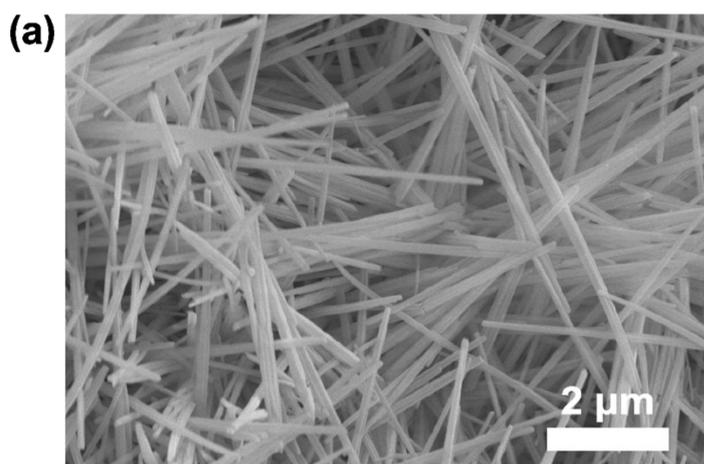


Fig. S2. (a) SEM image of Pre-NiMoO₄/NF.

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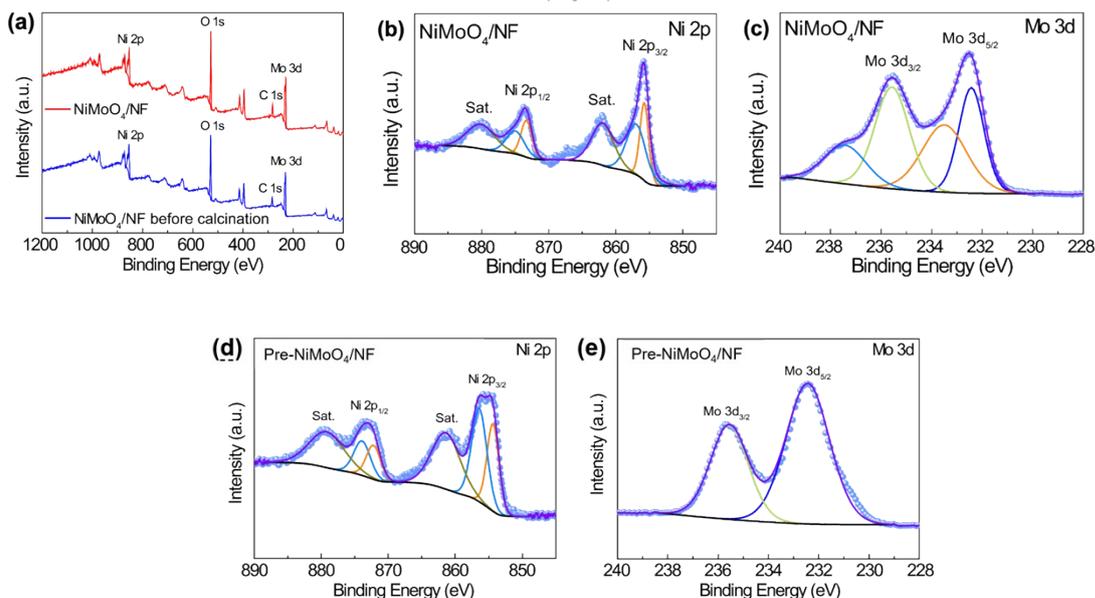


Fig. S3. (a) XPS full spectra of NiMoO₄/NF and Pre-NiMoO₄/NF before calcination. XPS spectra of Ni 2p and Mo 3d of (b, c) NiMoO₄/NF and (d, e) Pre-NiMoO₄/NF, respectively.

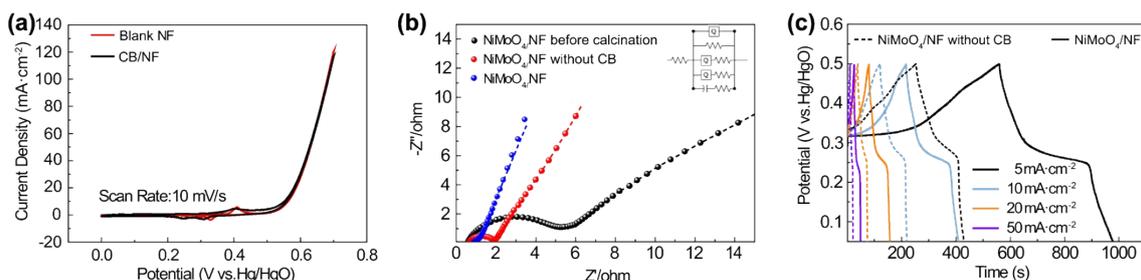


Fig. S4. (a) CV curves of blank NF and CB/NF at 10 mV/s. (b) Nyquist plots of NiMoO₄/NF before calcination (Pre-NiMoO₄/NF), NiMoO₄/NF without CB and NiMoO₄/NF. (c) charge-discharge curves of NiMoO₄/NF without CB (dashed lines) and NiMoO₄/NF (solid lines), respectively.

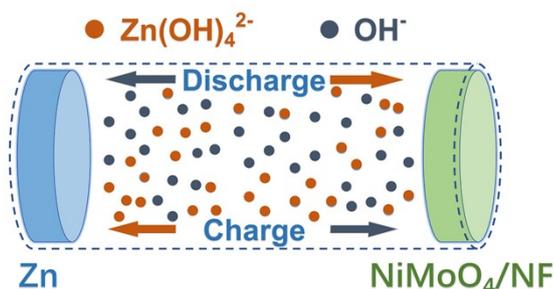


Fig. S5. Schematic illustration of Zn-Ni battery configuration with NiMoO₄ as the electrochemically active material.

The redox reaction of Mo does not occur during electrochemical measurement (Fig.2a), so the redox behaviour of Mo has no contribution to the tested capacity.

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This is well consistent with the previous reports about NiMoO₄ as electrode materials.^{s1} And the possible electrode reactions for the Zn-Ni battery can be described as follows:

- *Positive electrode:* $\text{NiMoO}_4 + \text{OH}^- \leftrightarrow \text{NiMoO}_4(\text{OH}) + \text{e}^-$
- *Negative electrode:* $\text{Zn}(\text{OH})_4^{2-} + 4\text{e}^- \leftrightarrow \text{Zn} + 4\text{OH}^-$
- *Full cell:* $2\text{NiMoO}_4 + \text{Zn}(\text{OH})_4^{2-} \leftrightarrow 2\text{NiMoO}_4(\text{OH}) + \text{Zn} + 2\text{OH}^-$

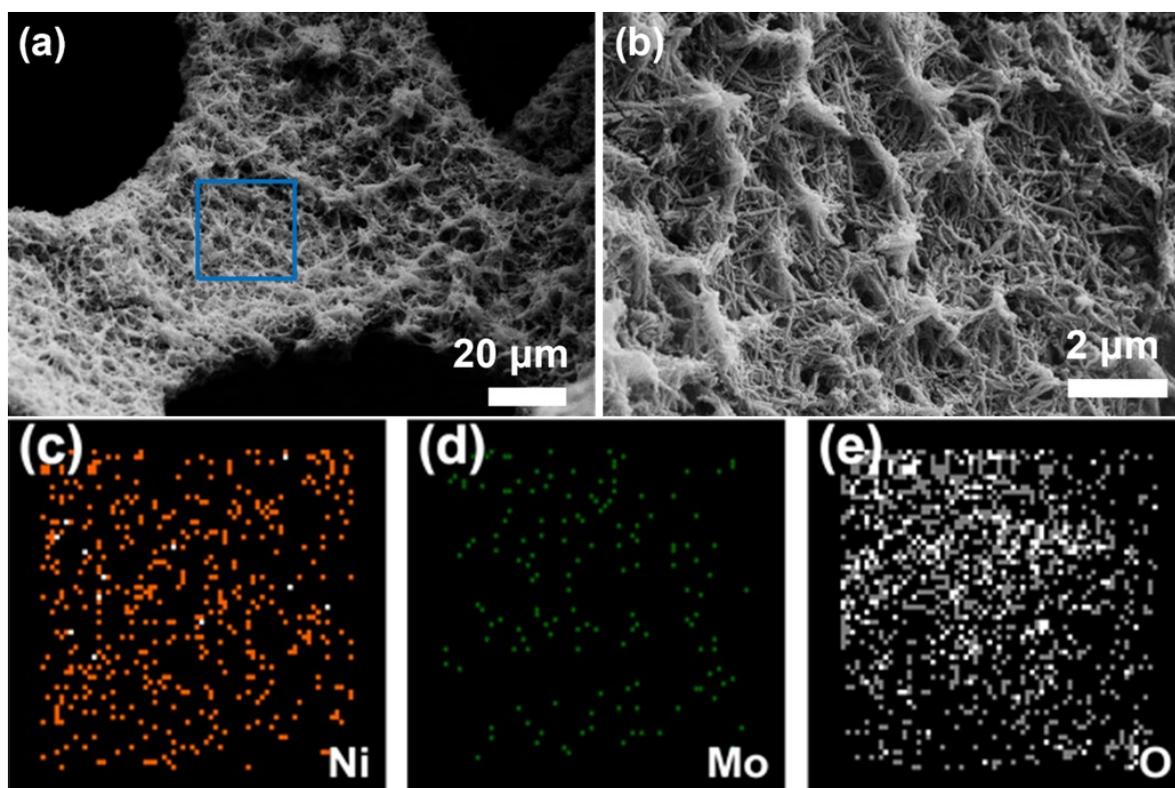


Fig. S6. a) A SEM image of the NiMoO₄/NF without CB after long cycling in Zn-Ni battery. b-e) SEM image and elemental mappings of the enlarged area corresponding to the blue square in (a).

One can readily conclude that the NiMoO₄ NW arrays tend to interconnect with each other and form networks with porous structures after the cycling test. The elemental mappings show that the chemical composition of the NiMoO₄ NWs has not changed, Ni, Mo and O are evenly distributed on the electrode surface.

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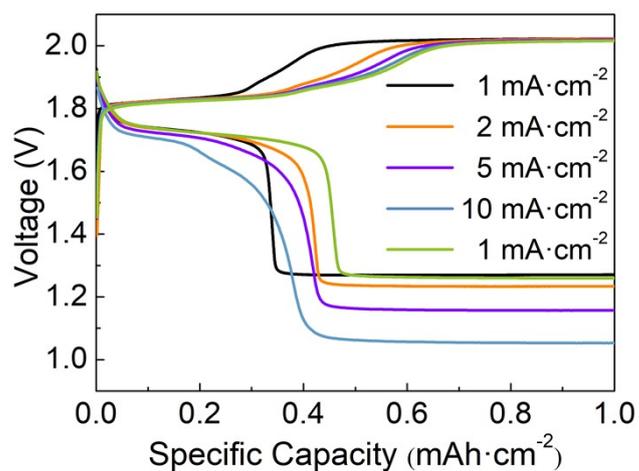


Fig. S7. Charge-discharge profile of hybrid battery at different current densities
Charge-discharge profile of hybrid battery with Co- NiMoO₄/NF electrode at different current densities.

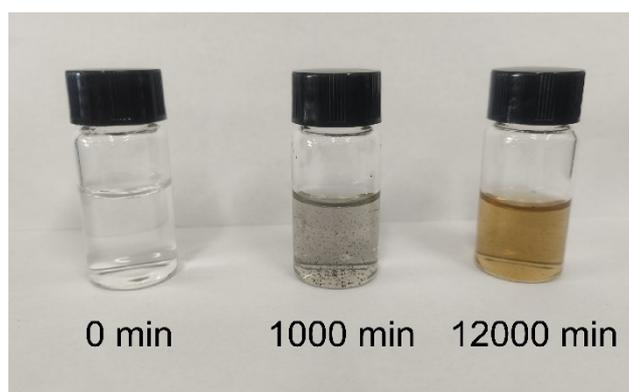


Fig. S8. Photos of the extracted electrolyte from the hybrid battery after cycling for different periods.

References:

- [8] B. Li, X. Ge, F. W. T. Goh, T. S. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, *Nanoscale*, 2015, **7**, 1830.
- [S1] Zhou, S. Zeng, D. Zheng, Y. Zeng, F. Wang, W. Xua, J. Liu, X. Lu, *Chem. Eng. J.*, 2020, **400**, 125832.