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# Monolithic Heteronanomat Paper Air Cathodes Toward Origami-Foldable/Rechargeable Zn–Air Batteries

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The ongoing surge in demand for flexible/wearable electronics spurs us to explore high-performance power sources with various form factors. Here we demonstrate monolithic heteronanomat (MH) paper air cathodes as a new electrode platform to enable the fabrication of origami-foldable zinc (Zn)–air batteries with reliable electrochemical rechargeability. The MH paper air cathodes consist of one-dimensional (1D) bifunctional catalyst mixtures (NdBa<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>O<sub>5+6</sub> double perovskite (NBSCF) nanofibers for the oxygen evolution reaction and nitrogen-doped carbon nanotubes (N-CNTs) for the oxygen reduction reaction), cellulose nanofibers (CNFs), and polytetrafluoroethylene (PTFE) nanoparticles, without the incorporation of conventional current collectors and gas diffusion layers. The CNFs and PTFE nanoparticles act as hydrophilic and hydrophobic binders, respectively, to construct three-dimensional (3D) bicontinuous electrolyte/air channels in the MH paper air cathodes. The well-developed electrolyte/air transport pathways, in combination with the rational design of the 1D bifunctional catalyst mixtures, enables the resultant Zn–air batteries (MH paper air cathode | CNF separator membrane | Zn–foil anode) to exhibit highly efficient charge/discharge performance and cyclability. In addition, the highly entangled network structure (based on a fibrous mixture of NBSCFs, N-CNTs, and CNFs) of the MH paper air cathode substantially improves its mechanical flexibility under various deformation modes, enabling the resultant Zn–air battery to be folded into a paper-airplane shape via origami folding.

# Introduction

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Forthcoming flexible/wearable electronics, the Internet of Things, and electric vehicles, which are expected to enable unforeseen ubiguitous interconnection via electronic transmission, have forced us to relentlessly pursue advanced power sources with reliable electrochemical performance and design flexibility.<sup>1-3</sup> Among various battery systems reported to date, rechargeable zinc (Zn)-air batteries4-6 have garnered considerable attention as a promising candidate beyond current state-of-the-art lithium (Li)-ion batteries because of their high energy density (1086 Wh kg<sup>-1</sup>, including oxygen), nontoxicity, environmental benignity, unlimited cathode reactant source (i.e., atmospheric oxygen), and high natural abundance of the electrode active materials.

Inspired by these advantageous features, researchers have devoted enormous effort to developing high-performance flexible Zn–air batteries.<sup>7-9</sup> Many of the previous studies have

focused on air catalysts.<sup>10, 11</sup> Typical fabrication approaches for flexible air cathodes have exploited direct synthesis of air catalysts on electron-conductive substrates (*e.g.*, metal foils or carbon-based substrates).<sup>12-14</sup> However, the air catalysts in flexible air cathodes have often shown insufficient bifunctional oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) catalytic activities and have also required harsh synthesis conditions, including high temperatures/pressures and acidic (or alkaline) solutions. In addition to the bifunctional air catalyst issue, the strong dependency of the cathodes' mechanical properties on the mechanical properties of their substrates has resulted in air cathode sheets that lack shape diversity and deformability, thus posing formidable challenges to their versatile application in flexible power sources.

To address the aforementioned longstanding challenges, specifically, the simultaneous achievement of bifunctional electrocatalytic activities and good mechanical flexibility, herein, intrigued by the exceptional compliance and deformability of paper, we present monolithic heteronanomat (MH) air cathodes as a new electrode platform to enable origami-foldable Zn-air batteries with reliable electrochemical rechargeability. The MH paper air cathodes comprise one-dimensional (1D) bifunctional catalyst mixtures, cellulose nanofibers (CNFs), and polytetrafluoroethylene (PTFE) nanoparticles, without the use of conventional current collectors and gas diffusion layers.

The 1D catalyst mixtures are composed of  $NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$  double perovskite (NBSCF) nanofibers

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as an oxygen evolution reaction (OER) catalyst and nitrogendoped carbon nanotubes (N-CNTs) as an oxygen reduction reaction (ORR) catalyst to ensure bifunctional electrocatalytic activities. Among various catalyst materials explored to date, perovskite oxides have recently attracted increasing attention as an appealing electrocatalyst because of their excellent catalytic activities, long-term cycling stability, and high conductivity.<sup>15</sup> Among them, the cation-ordered structure of NBSCFs has been extensively investigated because of its high electrical conductivity, fast OER kinetics, and good stability.<sup>16</sup> Meanwhile, N-CNTs are known to provide highly efficient ORR performance because of their catalytically active pyridinic-N species.<sup>17-19</sup> Therefore, combining NBSCFs with N-CNTs is expected to result in electrode materials with enhanced electrocatalytic activity through coupling of their effects.

CNFs, which are characterized by nanoscale dimensions, uniaxial directionality, and chemical functionalities,<sup>20-22</sup> are introduced as a hydrophilic binder to hold the 1D catalyst mixtures and promote the formation of aqueous electrolyte In addition, polytetrafluoroethylene channels. (PTFE) nanoparticles are incorporated to prevent electrolyte flooding and provide air routes in the MH paper air cathode. The simultaneous use of CNFs (as a hydrophilic binder) and PTFE (as a hydrophobic binder) enables the formation of well-developed three-dimensional (3D) bicontinuous electrolyte/air transport pathways. Meanwhile, the highly entangled network structure (based on a fibrous mixture of NBSCF, N-CNTs, and CNFs) of the MH paper air cathode exhibits substantially improved mechanical flexibility under various deformation modes.

Benefiting from the architectural uniqueness and rational design of the 1D bifunctional catalyst mixtures of the MH paper air cathodes, the resulting Zn–air batteries (MH paper air cathode | CNF separator membrane | Zn–foil anode, filled with aqueous alkaline electrolyte) demonstrate highly efficient discharge/charge performance at various current densities and stable capacity retention during cycling. Furthermore, paper-airplane-shaped Zn–air batteries were successfully fabricated *via* the so-called "origami folding" technique, demonstrating extreme foldability that far exceeds those achievable with conventional Zn–air batteries.

### Experimental

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#### Fabrication of NdBa<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>1.5</sub>Fe<sub>0.5</sub>O<sub>5+δ</sub> (NBSCF) nanofibers

The NBSCF nanofibers were fabricated *via* electrospinning method. The precursor solution was prepared with  $Nd(NO_3)_3 \bullet 6H_2O$  (99.9%, metal basis),  $Ba(NO_3)_2$  (99+%),  $Sr(NO_3)_2$  (99+%),  $Co(NO_3)_2 \bullet 6H_2O$  (98+%), and  $Fe(NO_3)_3 \bullet 9H_2O$  (98+%) (provided from Sigma-Aldrich). Those chemicals were dissolved in N,N-Dimethylformamide (DMF, 99.5%) solvent with proper molar ratio (Nd : Ba : Sr : Co : Fe = 2 : 1 : 1 : 3 : 1) as 100 mM concentration. The precursor solution was mixed with 13 wt% of polyvinylpyrrolidone (PVP, Mw = 1,300,000). A mixture solution was placed in a 30 mL syringe with a positively charged capillary tip with a diameter of 0.5 mm. The electrospun fibers

were collected on an aluminum (Al) foil placed on top of a metal collector. The applied voltage was 20 kV, the distance between the syringe needle tip and collector was 18 cm, and the flow rate of the solution was 1 mL h<sup>-1</sup>. The electrospun webs were dried at 70°C for 1 h in an air atmosphere. Then, the dried webs were sintered at 900°C for 4 h in an air atmosphere.

#### Fabrication of MH paper air cathodes

The MH paper air cathodes were fabricated through vacuum filtration of the cathode suspension. The cathode suspension was prepared by; (i) dispersing a predetermined amount of NBSCF, N-CNT (US Research Nanomaterials, Inc. C purity > 98%, N content = 3  $\sim$  5 wt%, length  $\sim$  35  $\mu m$ ), and wt% polytetrafluoroethylene (PTFE, Sigma-Aldrich, 60 dispersion in water) by ultrasonication in a sodium dodecyl sulfonate (SDS)/urea (Sigma-Aldrich)-dissolved aqueous solution; (ii) freezing the as-prepared suspension at -12°C; (iii) adding CNF suspension into the suspension followed by additional mixing. Details of the preparation procedure of the CNF suspension were described in previous publications.<sup>23</sup> After being vacuum-filtrated, the cathode mixture was rinsed with deionized water (DIW) and isopropyl alcohol to remove the dispersion agents of SDS/urea and then dried in a vacuum oven (at 60°C) overnight, yielding a self-standing MH paper air cathode. The composition ratio of 1D catalyst mixture (NBSCF/N-CNT = 5/5 (w/w))/CNF/PTFE in the air cathode was 40/25/35 (w/w/w).

#### Preparation of Zn-air batteries

For coin-type Zn–air batteries, the basic electrochemical performances of the MH paper air cathode were characterized using a coin-type (CR2032) Zn–air battery (assembled with a Zn foil (Alfa Aesar, thickness ~ 100  $\mu$ m) anode, an alkaline electrolyte (6 M KOH and 0.2 M Zn(OAc)<sub>2</sub>), and a glass fiber separator membrane (EL-CELL, ECC1-01-0012)).

For pouch-type foldable Zn-air batteries, to explore the feasibility as a flexible power source, a pouch-type Zn-air battery (assembled with the as-prepared MH paper air cathode, a Zn foil anode, an alkaline electrolyte (6 м КОН and 0.2 м  $Zn(OAc)_2$ , and a CNF-based separator membrane<sup>24</sup>). The CNFbased separator membrane was fabricated by drying 0.5 wt% CNF suspension dispersed in DIW and then chemically crosslinking the dried membrane to ensure the physical stability against alkaline electrolyte. Chemical crosslinking was conducted with 10 wt% glutaraldehyde and 0.2 wt% hydrochloric acid in acetone solution at room temperature. The MH paper air cathode, CNF-based separator membrane, and Zn foil anode were stacked in-series and sealed with a paraffin film (thickness = 130  $\mu$ m, used as a packaging substance). The paraffin film adjacent to the air cathode possessed holes to allow air passage.

#### Structural/physicochemical characterizations

The crystalline structure of the NBSCF nanofibers was identified by X-ray diffraction (XRD, Bruker diffractometer with Cu K $\alpha$ 

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Fig. 1 Physicochemical/electrochemical characterization of NBSCF nanofibers and NBSCF/N-CNT mixtures. (a) XRD pattern and (b) N<sub>2</sub> adsorption–desorption isotherms of NBSCF nanofibers. (c) SEM images of NBSCF nanofibers. (d) ORR and (e) OER performance of N-CNT/NBSCF (vs. NBSCF, N-CNT, Pt/C (for ORR), and IrO<sub>2</sub> (for OER)) in 0.1 M KOH solution at 1600 rpm with a scan rate of 10 mV s<sup>-1</sup>.

radiation, D8 Advance) with a 20 range of 20° to 80°. The oxygen contents (5+ $\delta$ ) of the NBSCF nanofibers were assessed by the iodometric method at room temperature. The nitrogen adsorption-desorption measurements were carried out at -196°C with a BELSORP-Mini II (Bel Japan) instrument. The NBSCF nanofibers were degassed at 200°C for 24 h under N<sub>2</sub> flow before the measurements. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The Xray photoelectron spectroscopy (XPS) analyses were carried out with an ESCALAB 250XI from Thermo Fisher Scientific with a monochromated Al-Ka (ultraviolet He1, He2) X-ray source. The microstructure was examined by transmission electron microscopy (TEM, JEOL, JEM-2100F), field emission scanning electron microscopy (FE-SEM, HITACHI, S-4800), and energy dispersive X-ray spectroscopy (EDS, JEOL, JSM 6400). The water contact angle was measured by a drop shape analyzer with 3 μm of DIW. (KRUSS, DSA100).

## Electrochemical/mechanical characterizations

The potentiostat (VMP3, Biologic) was used to measure cyclic voltammetry (CV) and linear sweep voltammetry (LSV) with 1600 rpm controlled rotating disk electrode system (RRDE-3A, Biologic). A platinum wire and an Ag/AgCl electrode (saturated KCl filled) were used as the counter and reference electrodes, respectively. An aqueous solution of 0.1 M KOH was  $O_2$ -saturated for the electrolyte. The working electrodes were prepared by loading the catalyst inks onto the glassy carbon disk electrode. The catalyst loading density was 0.8 mg cm<sup>-2</sup> with disk electrode area of 0.1256 cm<sup>-2</sup>. 20 mg of catalyst was dispersed in 0.45 mL of ethanol, 0.45 mL of isopropyl alcohol, and 0.1 mL of 5 wt% Nafion solution (Sigma-Aldrich, 274704) to

prepare the catalyst ink. 5  $\mu L$  of catalyst ink was applied onto the glassy carbon (GC) disk electrode. The Pt/C (Alfa Aesar, 35849) and IrO\_2 (Alfa Aesar, 43396) were used as reference materials.

The full discharge was conducted by chronopotentiometry at a current of 1 mA cm<sup>-2</sup> until a cell voltage decrease to zero. The galvanostatic discharge/charge cycling tests were conducted, and each cycle period was 10 min (5 min discharge followed by 5 min charge) in the voltage range of 0.0 (discharge cutoff) – 2.4 V (charge cutoff). The electrochemical impedance spectroscopy (EIS) data were recorded (maintaining at 1.2 V for each single cell) at an applied voltage of 10 mV in the frequency range  $10^{-2}$  to  $10^{5}$  Hz.

The mechanical flexibility of the MH paper air cathodes was quantitatively investigated using a universal tensile tester (Petrol LAB, DA-01) under the bending modes. The change in the electrical resistance of the cathodes was monitored as a function of bending (bending radius = 3 mm and deformation rate = 200 mm min<sup>-1</sup>). The Zn–air batteries were subjected to mechanical deformation under various folding modes, wherein an *in-situ* analysis of their discharge/charge profiles was conducted.

# **Results and discussion**

## Preparation and Characterization of NBSCF and N-CNT Bifunctional Catalyst mixtures

The NBSCF nanofibers were synthesized *via* an electrospinning method followed by a sintering process at 900°C for 4 h, as schematically depicted in Fig. S1<sup>+</sup>. The crystal structure of the

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NBSCF nanofibers was confirmed by X-ray diffraction (XRD) analysis (Fig. 1a). The XRD pattern indicates that perovskitestructured NBSCF nanofibers were successfully synthesized without any detectable impurity phase. Furthermore, the characteristic peaks of the NBSCF nanofibers were indexed as tetragonal  $(P4/mmn)^{25, 26}$  with lattice parameters of a = 3.859 Å and c = 7.716 Å confirmed by Rietveld refinement. The NBSCF nanofibers showed a type-IV N<sub>2</sub> adsorption–desorption isotherm, and the specific surface area of NBSCF was 5.9 m<sup>2</sup> g<sup>-1</sup> (Fig. 1b). Fig. 1c shows the morphology of the NBSCF nanofibers, whose diameter was approximately 100–200 nm. These results demonstrate the successful preparation of the NBSCF nanofibers *via* the electrospinning method.

As a next step, we prepared NBSCF/N-CNT catalyst mixtures for an air electrode catalyst. The structure of the NBSCF/N-CNT mixtures was characterized by high-angular annular dark-field (HAADF) TEM imaging and energy-dispersive spectroscopy (EDS) elemental mapping (Fig. S2<sup>+</sup>). The NBSCF/N-CNT catalyst mixtures exhibit a well-dispersed web-like morphology because of the fibrous feature of the NBSCF nanofibers and N-CNTs.

To deduce the optimal ratio of the NBSCF/N-CNT mixtures, we carried out rotating ring-disk electrode (RRDE) measurements to evaluate their ORR and OER catalytic activities (Fig. S3a and S3b<sup>+</sup>). The samples with different composition ratios are abbreviated as N:C = n:m (where n is the ratio of NBSCF and mis the ratio of N-CNTs). The NBSCF/N-CNT mixture with a 5:5 ratio (N:C = 5:5) exhibited the best ORR and OER performance. The ORR onset potential of the optimized NBSCF/N-CNT mixture was -0.78 V (vs RHE) at -1 mA cm<sup>-2</sup>, which is lower than that of Pt/C (0.90 V vs RHE), as shown in Fig. 1d. Interestingly, the current density of the NBSCF/N-CNT mixture is comparable to that of Pt/C at high voltage. The ring currents of the samples are shown in Fig. S3c and S4b<sup>+</sup>; these values were used to calculate the number of transferred electrons in Fig. S3d and S4c<sup>+</sup>. In addition, the percentages of peroxide species  $(HO_2^-)$  are plotted in Fig. S3e and S4d<sup>+</sup>.

The number of transferred electrons (*n*) shown in Fig. S4c<sup>+</sup> was calculated by Equation (1):

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$
(1)

where  $I_d$  and  $I_r$  are the disc current and ring current, respectively, with an experimentally determined collection efficiency (*N*) of 0.41.<sup>27</sup> The calculated number of transferred electrons of the NBSCF/N-CNT mixture was approximately 3.42–3.75.

The hydrogen peroxide yields were calculated by the equation

$$HO_2^-(\%) = 200 \times \frac{I_{r/N}}{I_d + I_{r/N}}$$
 (2)

The measured  $HO_2^-$  yields are less than 12–29% for the NBSCF/N-CNT mixture over the potential range from -0.4 to -0.9 V.<sup>28, 29</sup> The ORR performance of the NBSCF/N-CNT mixture at 10 mA cm<sup>-2</sup> in alkaline solutions was compared with those of previously reported electrocatalysts, as shown in Fig. S5a and Table S1<sup>+</sup>. To investigate the electrocatalytic activity of the catalysts for the OER, linear sweep voltammetry (LSV) was

performed with NBSCF/N-CNT and commercial In  $\Omega_{22}$  the electrodes were immersed in a 0.1 M KOFF electrolyte Solution, and LSV was conducted at a scan rate of 10 mV s<sup>-1</sup> (Fig. 1e). As shown in Fig. S5b and Table S2<sup>+</sup>, the OER onset potential of NBSCF/N-CNT (1.67 V) was lower than that of the best OER catalysts reported to date <sup>28-32</sup>, such as IrO<sub>2</sub> (1.75 V), Mn<sub>3</sub>O<sub>4</sub>/CoSe<sub>2</sub> (1.68 V), MnO<sub>x</sub> thin film (1.77 V),  $\alpha$ -MnO<sub>2</sub>-SF (1.72 V), Mn<sub>x</sub>O<sub>y</sub>/NC (1.68 V), and LaCoO<sub>3</sub> (1.69 V) at 10 mA cm<sup>-2</sup>. These RRDE results confirm that the outstanding improvement of the catalytic activity is mainly attributable to the coupled effect of the NBSCF nanofibers and N-CNTs.

A previous study<sup>33, 34</sup> reported that pyrrolic N in N-doped carbon enhances the catalytic activity of double perovskites. . In specific, the ORR activity was improved by O<sub>2</sub> strongly adsorbed to the active sites of the catalyst that can reduce the bond length of N-O and Co-O at the binding sites. Additionally, the OER activity was improved by the increased covalency between transition metals and lattice oxygen in NBSCF induced by the electron transfer of N-CNT.<sup>35-39</sup> Specifically, the O species are strongly bonded to active sites at the N-edge of carbon and to Co of the perovskite surface. X-ray photoelectron spectroscopy revealed that the adsorption of O species (C-O-H) onto the NBSCF/N-CNT mixture was promoted, as compared with the result for a control sample (NBSCF/MWCNT) (Fig. S6<sup>+</sup>). This benign affinity of the NBSCF/N-CNT mixtures for oxygen reactants contributed to the enhanced ORR/OER performance (Fig. S7†).

#### Structural uniqueness and mechanical/electrochemical properties of MH paper air cathodes

The fabrication of the MH paper air cathode through vacuum filtration of the cathode suspension, along with a photograph of the cathode, is schematically depicted in Fig. 2a. The addition of a dispersing agent (SDS/urea = 5/5 (w/w)) enabled a satisfactory dispersion state of the cathode suspension (Fig. S8a<sup>+</sup>). Notably, such a good dispersion state was maintained over 12 h. The resulting MH paper air cathode exhibited a monolithic structure (inset of Fig. 2b). Notably, neither traditional current collectors nor gas diffusion layers were included in the MH paper air cathode. The 1D cathode components (i.e., NBSCFs, N-CNTs, and CNFs) are spatially intermingled, yielding a highly entangled network structure (Fig. 2b). When the CNFs were excluded, we failed to fabricate a self-standing air cathode (Fig. S9<sup>+</sup>), demonstrating the important role of the CNFs as a 1D binder for the catalyst mixtures. This all-fibrous structure of the MH paper air cathode is beneficial for constructing a highly porous structure. The interstitial voids of the MH paper air cathode should function as electrolyte- and air-conducting channels after being filled with aqueous electrolyte and air, respectively. The hydrophobic PTFE nanoparticles were added to prevent the air cathode from being completely soaked with the aqueous electrolyte, thereby securing air channels.

We investigated the dispersion uniformity of the MH paper air cathode by analyzing a cross-sectional EDS image (Fig. S10<sup>+</sup>). The characteristic elements originating from the NBSCF/N-CNT catalyst mixtures, CNFs, and PTFE nanoparticles—Nd, Ba, Sr, Co,

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**Fig. 2 Fabrication and characterization of MH paper air cathodes.** (a) Schematic of the fabrication procedure for the MH paper air cathode, along with its photograph. (b) Crosssectional SEM image showing the highly entangled network structure of the 1D cathode components. The inset shows a low-magnification image. (c) Change in the relative sheet resistance (R/R<sub>0</sub>, R<sub>0</sub> = sheet resistance prior to the bending deformation) as a function of deformation cycles under different deformation modes (bending radius = 3 mm and deformation rate = 200 mm min<sup>-1</sup>, five-folded zig-zag shape). (d) Photographs showing the mechanical flexibility; HM paper air cathode vs. control samples (commercial air cathode and carbon paper). (e) Discharge profiles of the MH paper air cathodes (with vs. without PTFE nanoparticles). Insets are photographs showing the water contact angle of the cathodes. (f) EIS spectra of the MH paper air cathodes as a function of their CNF content, along with the proposed equivalent circuit model. (g) Initial discharge voltages of the MH paper air cathodes (CNF content = 25 vs. 40 wt%) after exposure to ambient conditions for 8 h. Inset shows the corresponding discharge voltage profiles as a function of time.

and Fe from NBSCFs, N from N-CNTs, C and O from CNFs, and F from PTFE—are uniformly distributed in the through-thickness direction. Given that the N-CNTs can function as an electronconducting channel as well as an ORR catalyst, the uniform distribution of the N-CNTs is expected to facilitate electron conduction in the MH paper air cathode, without the use of an additional electron-conducting additive or even metallic current collectors. One major concern with electrodes without metallic current collectors or polymer binders is insufficient mechanical/dimensional tolerance under external deformation.<sup>21, 40, 41</sup> The mechanical flexibility of the MH paper air cathode was quantitatively estimated under various deformation modes. Fig. 2c shows that the electrical resistance of the MH paper air cathode remained almost constant after 1000 bending cycles (bending radius = 3 mm and deformation rate = 200 mm min<sup>-1</sup>) and even when bent into a five-folded zigzag shape. This result is further highlighted by a comparative analysis with a commercial air cathode (MEET Co., Ltd.) and a typical carbon paper commonly used for catalyst evaluation (Fig. 2d). Notably, the MH paper air cathode was knotted

without inducing structural defects or delamination. By contrast, the commercial air cathode, consisting of laminated multilayers (*i.e.*, a catalyst layer, a gas diffusion layer, and a current collector), was delaminated and eventually broke before the completion of 20 bending cycles. Similarly, the carbon paper was easily ruptured upon exposure to the deformation stress. These results show that the highly entangled network structure based on the fibrous mixture of NBSCFs, N-CNTs, and CNFs plays an important role in the exceptional deformability of the MH paper air cathode.

A prerequisite condition enabling facile ORR and OER performance in the bifunctional air cathodes is to secure the triphase (catalyst surface/electrolyte/air) interfaces.<sup>42</sup> To this end, the rational design of the structure and components in the air cathode is highly needed. To fulfill this requirement, we incorporated PTFE nanoparticles (for air pathways) and CNFs (for aqueous electrolyte channels) into the MH paper air cathode. Fig. 2e shows the full discharge profiles of coin-type cells. The air cathode containing PTFE nanoparticles exhibited a more stable and higher discharge plateau (discharge voltage





Fig. 3 Origami-foldable/rechargeable Zn-air batteries. (a) OCV profile of the 90° bent Zn-air battery. Inset shows its photograph. (b) Cell overpotentials reflecting the discharge-<br/>charge rate capability as a function of current density (1–20 mA cm<sup>-2</sup>). (c) Galvanostatic discharge-charge cycle profile at a current density of 1 mA cm<sup>-2</sup>. Insets show the magnified<br/>view of the initial and end parts. (d) Galvanostatic discharge-charge cycle profiles (before folding vs. folded state). Inset shows a photograph of the folded Zn-air battery. (e)<br/>Photograph of the paper-airplane-shaped Zn-air battery featuring the multifolded state. The inset shows its backside view. (f) Photograph showing the successful operation of an LED<br/>lamp<br/>poweredbytwopaper-airplane-shaped<br/>Zn-airZn-airbatteriesconnectedinseries.

~1.2 V at 1 mA cm<sup>-2</sup>) than the control air cathode (without the PTFE nanoparticles), thus providing a longer discharge time. Previous studies 43 have reported that the hydrophilicity/hydrophobicity of air cathodes should be tuned to improve the discharge performance of air batteries. The control air cathode was excessively hydrophilic (as shown in the inset (bottom image) of Fig. 2e). Consequently, the air cathode may suffer from electrolyte flooding, gradually blocking the oxygen supply toward the air catalysts and resulting in a large overpotential during the ORR. In comparison, the MH paper air cathode with added PTFE nanoparticles exhibited increased hydrophobicity (inset (top image) of Fig. 2e), which contributed to the construction of air pathways in the cathode.

The effect of CNFs on the formation of the electrolyte channel in the MH paper air cathode was investigated. Fig. 2f shows the electrochemical impedance spectroscopy (EIS) results for cathodes with different CNF contents, along with the proposed equivalent circuit model. The charge-transfer resistance  $(R_{ct})$  is affected by the transport of reactants to the electrode surface during the redox reaction.44 The wellbalanced pathways of air and aqueous electrolyte promote the formation of tri-phase interfaces in the air cathode, resulting in a decrease of the R<sub>ct</sub>. Notably, the air cathode with 25 wt% CNFs exhibited the lowest  $R_{ct}$  (~27  $\Omega$ ). The lower CNF content (e.g., 14 wt%) rendered the resulting air cathode relatively hydrophobic (Fig. S11a<sup>+</sup>), yielding a larger  $R_{ct}$  (~77  $\Omega$ ), possibly because of the blockage of electrolyte channels. By contrast, the excess increase of the CNF content to 40 wt% caused a lack of hydrophobicity (Fig. S11b<sup>+</sup>), leading to electrolyte flooding in the air cathode and to an increase of the  $R_{ct}$  (~143  $\Omega$ ).

Because Zn-air batteries are half-open systems, electrolyte evaporation for the air cathodes warrants attention.<sup>45-47</sup> To

investigate the influence of electrolyte evaporation on cell performance, we measured the initial discharge voltages of the MH paper air cathodes after the corresponding Zn-air batteries had been exposed to ambient conditions for 8 h (Fig. 2g). The 40 wt% CNF-containing air cathode failed to exhibit normal discharge behavior, likely because serious evaporation of the aqueous electrolyte resulted in a loss of ionic conductivity in the cathode. The excessive content of hydrophilic fibers in air cathodes tends to cause rapid drying of the aqueous electrolyte via the capillary effect.48 Notably, the electrode with a CNF content of 25 wt% exhibited a higher initial discharge voltage, demonstrating the importance of well-tuned hydrophilicity/hydrophobicity. These initial discharge voltage profiles are well consistent with the change in electrolyte content of the MH paper air cathodes, which was estimated during the aforementioned evaporation test (Fig. S12<sup>+</sup>).

#### Origami-Foldable/Rechargeable Zn–Air Batteries

The MH paper air cathodes were assembled with Zn–foil anodes, alkaline electrolyte (6  $\,M$  KOH and 0.2  $\,M$  Zn(OAc)<sub>2</sub>, amount = 50  $\mu$ L cm<sup>-2</sup>)-soaked CNF-based separator membranes to develop origami-foldable/rechargeable Zn–air batteries (Fig. S13<sup>+</sup>). The resulting Zn–air battery exhibited a normal and stable open-circuit voltage (OCV) of 1.44 V over 720 min even in the 90° bent state (Fig. 3a). The discharge/charge rate capability of the Zn–air battery was examined as a function of current density (1–20 mA cm<sup>-2</sup>). Fig. 3b shows that the cell overpotential tends to increase with increasing current density, as initially expected. A narrow discharge–charge voltage gap (0.7 V) was observed at a current density of 1 mA cm<sup>-2</sup>, demonstrating the efficient bifunctional electrocatalytic

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reaction of the MH paper air cathode. The power density of the Zn-air battery was recorded as 18.59 mW cm<sup>-2</sup> at 20 mA cm<sup>-2</sup>. We speculate that the well-balanced electrolyte/air flow (as described in Fig. 2e–g), in combination with the N-CNT networks acting as electron conduction channels (Fig. 2b and c), is responsible for the efficient bifunctional ORR/OER kinetics of the MH paper air cathode.

Fig. 3c shows the galvanostatic discharge–charge cycling behavior of the Zn–air battery at a current density of 1 mA cm<sup>-2</sup> for 10 min per cycle. The cycling performance was observed over 900 min, with no obvious voltage fading fading (the discharge voltage was maintained around 1.0 V). The slight increase in the overpotential after 600 min may be due to the evaporation of the aqueous electrolyte. This good cycling performance was also observed at higher current densities (2 – 10 mA cm<sup>-2</sup>) (Fig. S14<sup>+</sup>).

Driven by the highly entangled network structure of the MH paper air cathode, the resulting Zn-air battery enabled a wide range of form factors suitable for various flexible applications. The Zn-air battery showed stable discharge-charge voltage profiles at a current density of 1.0 mA cm<sup>-2</sup> under the fully folded state; these profiles did not substantially differ from those of the unfolded Zn-air battery (Fig. 3d). To further highlight the mechanical deformability and design diversity of our Zn-air battery, we fabricated a paper-airplane-shaped Znair battery using origami folding techniques. The form of a paper airplane was chosen as a representative example to demonstrate an extremely folded state of the battery. Fig. 3e shows photographs of the paper-airplane-shaped Zn-air battery featuring the multifolded state. The origami foldingbased stepwise fabrication procedure of the paper-airplaneshaped Zn-air battery is depicted in Fig. S15<sup>+</sup>. Two of the Zn-air batteries were connected in series and successfully operated a light-emitting diode (LED) lamp (Fig. 3f).

The aforementioned results demonstrate that our MH paper air cathode represents a remarkable advancement in the flexibility and shape diversity of Zn–air batteries. The superiority of our Zn–air battery over previously reported flexible Zn–air batteries was described in terms of the mechanical deformability and electrochemical performance (Table S3<sup>+</sup>). To the best of our knowledge, this works represents the first report of an origamifoldable Zn–air battery with reliable electrochemical rechargeability.

# Conclusions

In summary, we have demonstrated the MH paper air cathode as an unprecedented electrode architecture to develop origami-foldable/rechargeable Zn–air batteries. The MH paper air cathode featuring a highly entangled network structure was composed of 1D catalyst mixtures (NBSCF nanofibers as an ORR catalyst, N-CNTs as an OER catalyst and for electronic channels), CNFs, and PTFE nanoparticles. Both the NBSCF nanofibers and N-CNTs in the 1D catalyst mixtures showed an intimate affinity toward oxygen reactants, benefiting the bifunctional electrocatalytic performance. The elaborate combination of hydrophilic CNFs and hydrophobic PTFE led to the formation of

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3D bicontinuous electrolyte/air transport pathways in the MH paper air cathode. This architectuPal: 104អំរដ្ឋមន្ត្រីទទំរុំ<sup>68</sup>រក៍ combination with the rational design of the 1D catalyst mixtures, brought a substantial improvement in the bifunctional electrocatalytic activity and cycling retention. The highly entangled network structure (based on the fibrous mixture of NBSCFs, N-CNTs, and CNFs) of the MH paper air cathode played an important role in enhancing the mechanical flexibility under various deformation modes. Paper-airplaneshaped Zn-air batteries were fabricated via origami folding and exhibited extreme foldability that is difficult to achieve with conventional Zn-air battery technologies. We envision that the MH paper air cathode strategy holds promise as a versatile and scalable electrode platform for advanced metal (e.g., Li, Mg, and Al, in addition to Zn)-air batteries that are rapidly emerging as "beyond-Li-ion electrochemistry" systems.

# **Conflicts of interest**

There are no conflicts to declare.

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