Electronic Supplementary Material (ESI) for Nanoscale.

# Supporting Information

# N-doped-carbon/cobalt-nanoparticles/N-doped-carbon multi-layer sandwich nanohybrids derived from cobalt-MOF of 3D molecular structure for bifunctional electrocatalysts toward on-chip solid-state Zn-air batteries

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# Experimental section

### Synthesis of cobalt-MOF {$[H_2N(CH_3)_2]4[Co_3(Hdpa)_2].3DMF$}:

A mixture of $H_6$dpa (48.4 mg, 0.10 mmol) [$H_6$dpa=3,4-di (3,5-dicarboxyphenyl) phthalic acid] and $Co(NO_3)_2 \cdot 6H_2O$ (43.7 mg, 0.15 mmol) was dissolved in DMF (2.5 mL) [DMF=dimethylformamide] in a screw-capped vial. After two drops of $HNO_3$ and 1.0 mL of $H_2O$ were added to the mixture, the vial was capped and placed in an oven at 110 ºC for 48 h. The resulting single crystals were washed to give compound 1. Anal. Calc. for $C_{65}H_{71}Co_3N_7O_{27}$: C,50.07; H,4.59; N,6.29. Found: C,49.86; H,4.71; N,6.53%. IR (KBr, $cm^{-1}$): 3422 (m), 3052 (w), 2800 (s), 2633 (m), 2150 (w), 1705 (m), 1633 (s), 1399 (m), 1232 (s), 1104 (m), 774 (s), 710 (m), 630 (w).

### Preparation of NdC-CoNPs-NdC-700, NdC-CoNPs-NdC-800 and NdC-700:

The prepared cobalt-MOF crystal sample (100 mg) was transferred into a railboat, then it was annealed in a tube furnace at a heating rate of 5 °C $min^{-1}$ under a stream of $Ar_2$. The carbonization was performed at 700 °C for 2 h. After naturally cooling back to room temperature, the black powder is obtained, marked as NdC-CoNPs-NdC-700. And the NdC-CoNPs-NdC-800 sample was prepared by the same method of NdC-CoNPs-NdC-700 except that the pyrolysis temperature was 800 degrees. For comparison, the N-doped-carbon laminated nanohybrids without cobalt nanoparticles labeled as NdC-700 was prepared by 0.5 mol hydrochloric acid to remove the cobalt nanoparticles of NdC-CoNPs-NdC-700.

### Fabrication and test of liquid rechargeable Zn-air batteries (ZABs):

The liquid ZAB was assembled with Zn-plate served as the anode and catalyst-coated carbon cloth (1 $cm^2$) served as the air electrode, the mixed solution of 6 M KOH and 0.2 M $Zn(CH_2COO)_2$ as electrolyte. Typically, 10 mg of catalyst was fully dispersed in a solvent consisting of 700 μL DI water, 240 μL isopropanol, and 60 μL Nafion solution by sonication for 2 h. Then, 100 μL catalyst ink was dripped on 1 $cm^2$ carbon cloth to achieve a catalyst loading amount of 1 mg/$cm^2$. ZABs tests were measurand with LAND Battery Testing System (LAND-CT2001A,China). Both the discharge/charge current and corresponding power densities were standardized to the active area of air cathode electrode.

**Synthesis of polyacrylamide-co-polyacrylic (PAM-co-PAA) acid solid polymer alkaline electrolyte:**

Based on previous research in our lab, the 0.05 g N, N'-methylenebis (acrylamide) (AR grade, Aladdin) and 0.05 mL N, N, N', N'-tetramethylethylenediamine (CP grade, Aladdin) were added in a mixed solution of 4.5 g acrylamide (AM, AR grade, Aladdin), then, 5 mL acrylic acid (AA, AR grade, Aladdin) dissolved in 50 ml DI water subsequently. This mixture was stirred with a magnetic stirrer until the reactant was dissolved completely. After the mixture being deoxygen for 30 min with nitrogen gas, 0.01 g initiator ammonium persulfate (APS) was added and stirred rapidly for 10 s. Taking the homogeneous solution (1 ml) into a cubic container and heating at 60 °C for 3 h, the polyacrylamide-co-polyacrylic acid) (PAM-co-PAA) gel film was obtained. Finally, the as-obtained PAM-co-PAA gel film was dried in a oven for 12 h at 80 °C to remove the water, and then soaked in a 20 mL mixture solution of 6 M KOH and 0.2 M Zn $(CH_2COO)_2$ for 24 h to form the PAM-co-PAA solid polymer alkaline electrolyte.

**Fabrication and test of on-chip all-solid-state rechargeable Zn-air batteries:**

Based on previous research in our lab, first, finger-shaped Zn-foil (thickness of 0.03 mm) and carbon cloth were fabricated by a home-made interdigital cutting-mould. Then the as-prepared electrocatalyst ink was coated on the finger-shaped carbon cloth (loading amount of 1 mg/cm$^2$). Subsequently, the as-obtained interdigital anode/cathode electrodes were deployed on a solid alkaline gel electrolyte film supported by a bottom silicone encapsulation layer. After that, a top silicone encapsulation layer with air holes was overlaid on the well-deployed interdigital anode/cathode electrodes and adhered firmly to the bottom silicone encapsulation layer with semicured silicone serving as glue. After fully curing of the semicured silicone with thermal treatment in an oven of 50 °C for 30 min, a planar all-solid-state rechargeable Zn-air battery is successfully prepared and packaged, without peeling off.

**Materials and Characterization**

All reagents and solvents were commercially available and were used without further purification. In addition, the microstructure and phase composition of the as-obtained samples were characterized by Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan), Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), X-ray powder diffraction (XRD Bruker D8-ADVANCE) with an 18 kW advanced X-ray diffrac-tometer with Cu $K_\alpha$ radiation ($\lambda$=1.54056 Å), Raman spectroscopy (inVia-Reflex, Renishaw, UK), and Fourier transform infrared spectroscopy (VERTEX 801HYPERION2000, Bruker Optics, Germany). Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5°C/min. (XPS) was conducted with a Mg Ka achromatic X-ray source.

**Electrochemical characterizations**

The catalyst ink was prepared by dispersing catalyst (10 mg) and 50 μL Nafion (DuPont) into 700 μL DI water and 250 μL isopropanol by sonication. The electrochemical activities (CV, ORR and OER) of the catalysts were tested in a standard three electrodes system on a electrochemical workstation (CHI 760E) in 0.1 M saturated KOH electrolyte at room temperature. The working electrode was a glassy carbon rotating disk electrode (diameter 5 mm) which drop casted with the catalyst ink to a loading amount of 0.2 mg cm$^{-2}$. The counter electrode was a platinum electrode, and a saturated calomel electrode (SCE) as a reference electrode. All potentials here are converted to a reversible hydrogen electrode (RHE) scale, $E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{\theta}_{Ag/AgCl}$. The catalytic performance toward the ORR was measured from -0.8 to 0.2 V (vs. Ag/AgCl). The catalytic activity for OER was evaluated from 0 to 1.0 V (vs. Ag/AgCl). In comparison, commercial 20 wt% Pt/C catalyst ink (for ORR) and the $RuO_2$ catalyst ink (for OER) were prepared using the same procedure. The cyclic voltammetry (CV) measurements were performed at 20 mV s$^{-1}$ from -0.8 to 0 V (vs. Ag/AgCl) in $O_2$-saturated and $N_2$-saturated electrolyte, respectively. In order to test the electrochemical performances of the catalysts for ORR, the linear sweep voltammetry (LSV) carves were performed at a scanning rate of 5 mV s$^{-1}$ from -0.8 V to 0.2 V (vs. Ag/AgCl) at different rotation rates (400~2500 rpm) in $O_2$-saturated electrolyte. Rotating ring-disk electrode (RRDE: Pine Research Instrument, USA) voltammogram measurements for the calculation of the ORR electron transfer number were conducted on an RRDE configuration with a 320 μm gap Pt ring electrode. The electron transfer numbers (n) and peroxide yield ($HO_2^-$ %) can be obtained from the RRDE curve using the Eqs, respectively.

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \qquad HO_2^-\% = 200\frac{I_r/N}{I_d + I_r/N}$$

where $I_d$ is the disk current, $I_r$ is the ring current and N is the current collection efficiency of the Pt ring which was determined to be 0.37.

The double-layer capacitance (Cdl) values are calculated via the scan-rate-dependent CV curves based on the following equation. The Cdl value reflects the electrochemically active surface areas (ECSA) value, because the ECSA of an electrocatalyst is proportional to its Cdl value.

$$\mathrm{i} = \upsilon C_{\mathrm{dl}}$$

where i represents current density and $\upsilon$ represents the scan rate.

Electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency range from 100 kHz to 0.01 Hz.

**Crystallography**

The diffraction data was collected at 295(2) and 100(2) K for compound 1, with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were carried out utilizing SADABS routine.[1] The structures were solved by direct methods and refined using the SHELXTL 97 software.[2] Atoms were located from iterative examination of difference maps following least squares refinements of the earlier models. All the atoms except hydrogen atoms, which were fixed at calculated positions and refined by using a riding mode, were refined anisotropically until full convergence was achieved. It was necessary to constrain or restrain a number of bond lengths and angles in the structure in order get a stable refinement and chemically reasonable model. The microporous framework was occupied by extremely electron density, which could be assigned to be free materials. Because these guest materials in the crystal is highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE[3] subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules, and sets of solvent-free diffraction intensities were produced. The free materials were determined by combining single crystal structures, elemental microanalysis and TGA data. The crystallographic data for compound 1 are listed in Table S1.

| **Compound** | **1** |
|---|---|
| Empirical formula | $C_{65}H_{71}Co_3N_7O_{27}$ |
| Formula mass | 1559 |
| Crystal system | tetragonal |
| Space group | I-42d |
| *a* [Å] | 28.0519(10) |
| *b* [Å] | 28.0519(10) |

| | |
|---|---|
| $c$ [Å] | 9.7811(7) |
| α/(°) | 90 |
| β/(°) | 90 |
| γ/(°) | 90 |
| Dx, g cm$^{-3}$ | 0.995 |
| Nref | 3408 |
| V [Å$^3$] | 7696.8(7) |
| $Z$ | 4 |
| Tmin, Tmax | 0.786,0.827 |
| S | 1.091 |
| $\mu$ [mm$^{-1}$] | 0.695 |
| $F$ [000] | 2308 |
| Reflections collected | 3144 |
| Final $R$[a] indices [I>2σ(I)] | $R_1$ = 0.0477 |
| | $wR_2$ = 0.1213 |

**Table S1** Selected crystallographic data for compound **1**

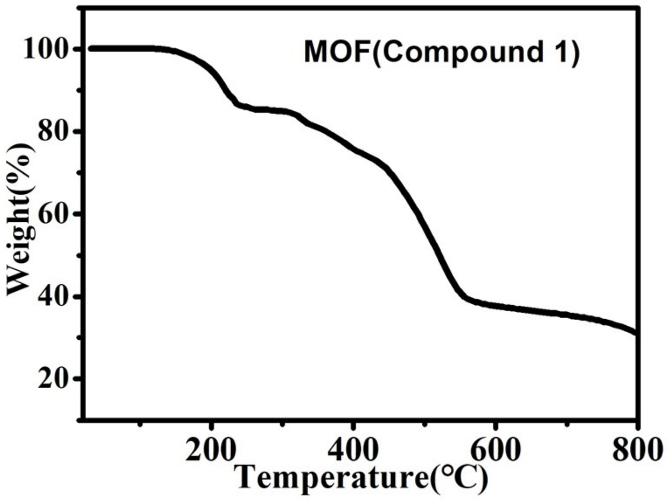


**Fig. S1**. The TGA diagram of MOF (compound **1**).

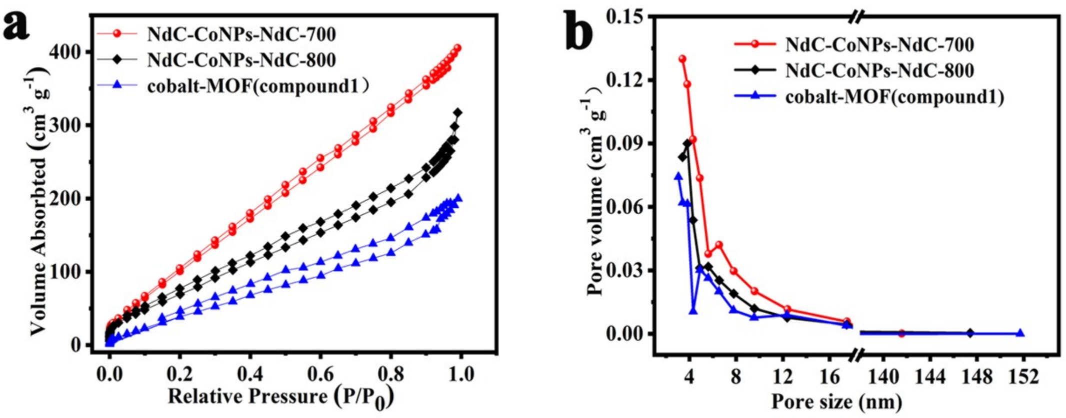


**Fig. S2**. (a) $N_2$ adsorption-desorption isotherms and (b) BJH pore-size distribution of the NdC-CoNPs-NdC-700, NdC-CoNPs-NdC-800, and Co-MOF precursor.

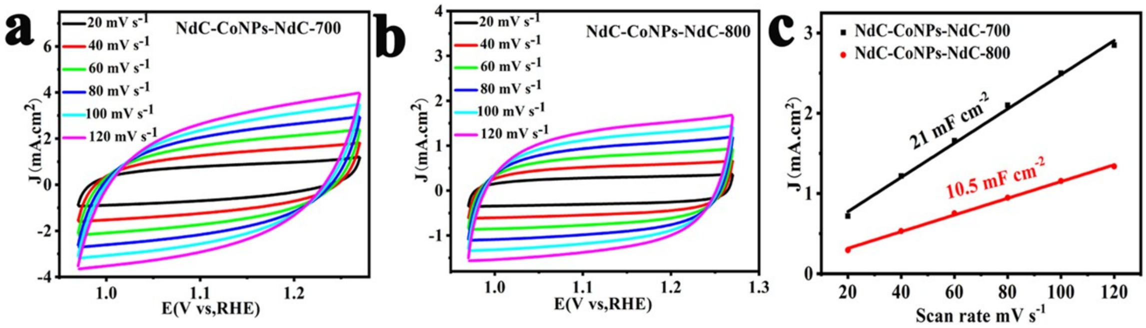


**Fig. S3**. CV curves in the double-layer region of the electrodes loaded with (a) the NdC-CoNPs-NdC-700 and (b) NdC-CoNPs-NdC-800 in $O_2$-saturated 0.1 M KOH electrolyte at different scan rates; (c) Current density at 1.30 V vs scan rate for the samples and the calculated $C_{dl}$ values.

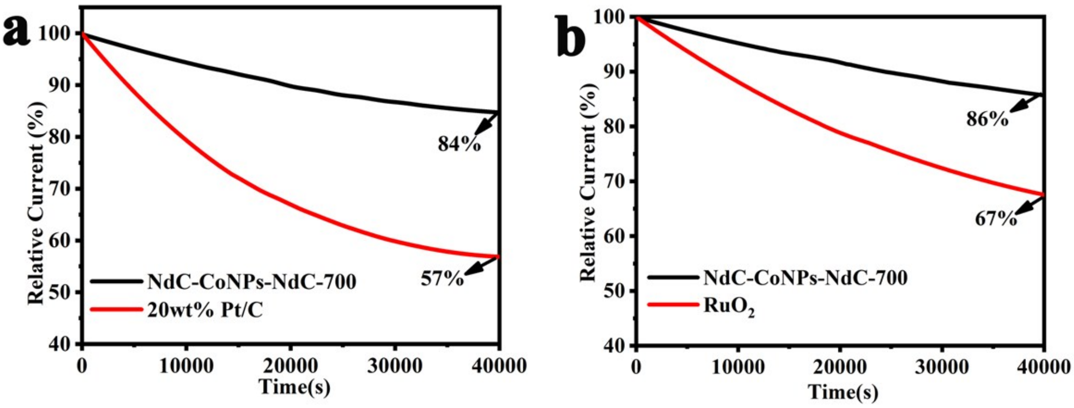


**Fig. S4**. (a) The ORR durability evaluated by i-t chronoamperometric response of NdC-CoNPs-NdC-700 and commercial 20wt% Pt/C sample; b) The OER durability evaluated by i-t chronoamperometric response of NdC-CoNPs-NdC-700 and commercial RuO$_2$ sample.

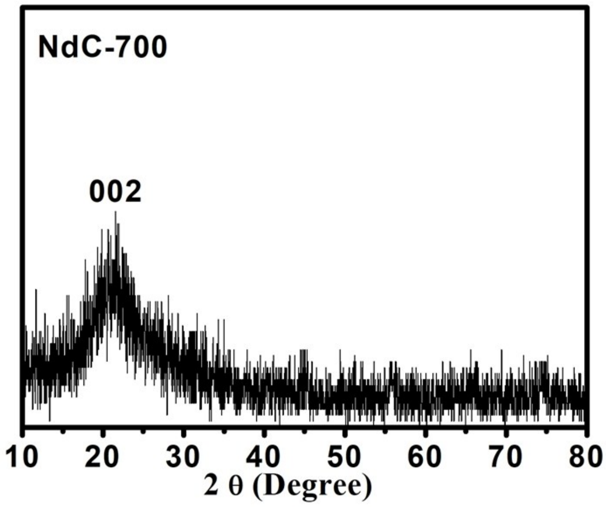


**Fig. S5** The XRD pattern of the NdC-700 contrast sample with acid to remove Co nanoparticles of NdC-CoNPs-NdC-700.

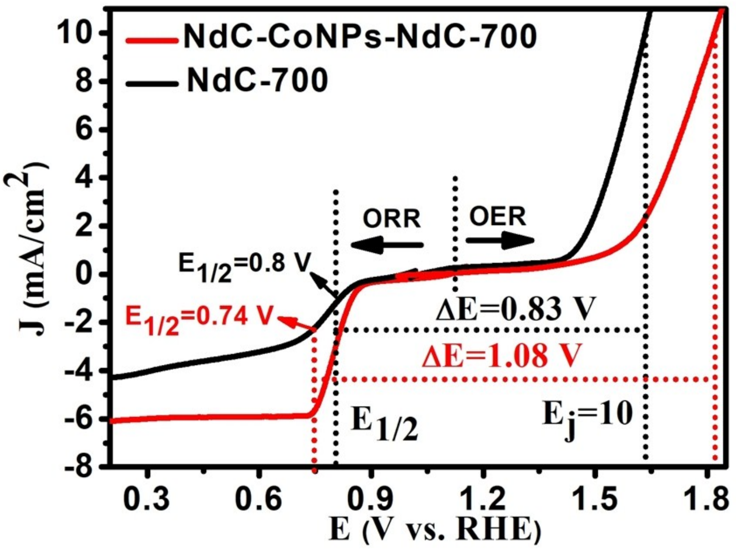


**Fig. S6** The overall LSV curves of the NdC-CoNPs-NdC-700 and NdC-700 contrast sample with acid to remove Co nanoparticles in the whole ORR and OER region in 0.1 M KOH.

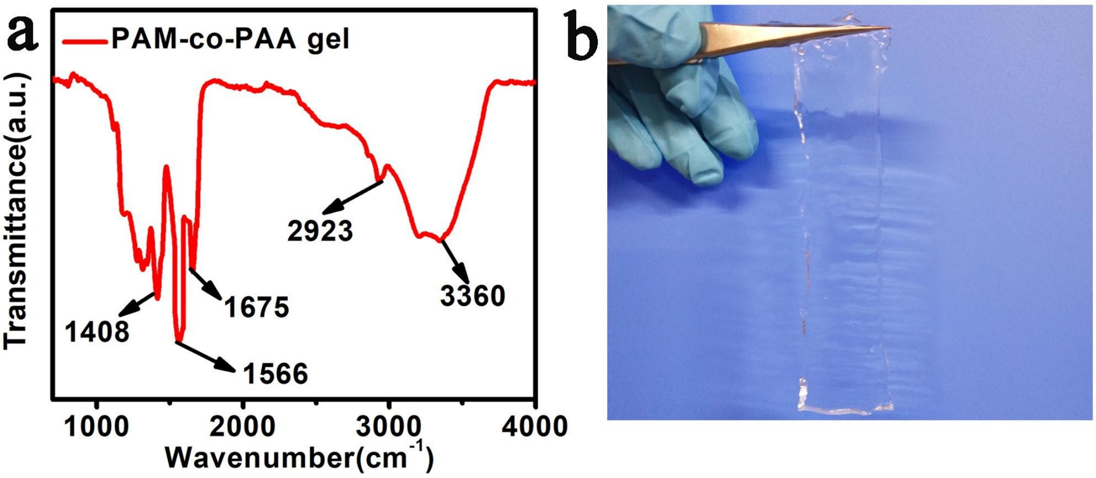


**Fig. S7**. (a) FTIR spectra of PAM-co-PAA gel and (b) corresponding photos.

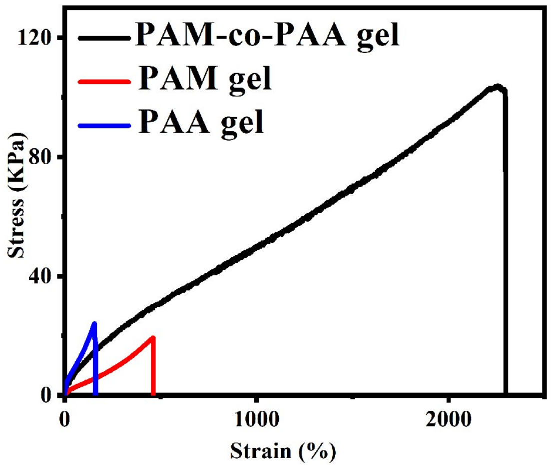
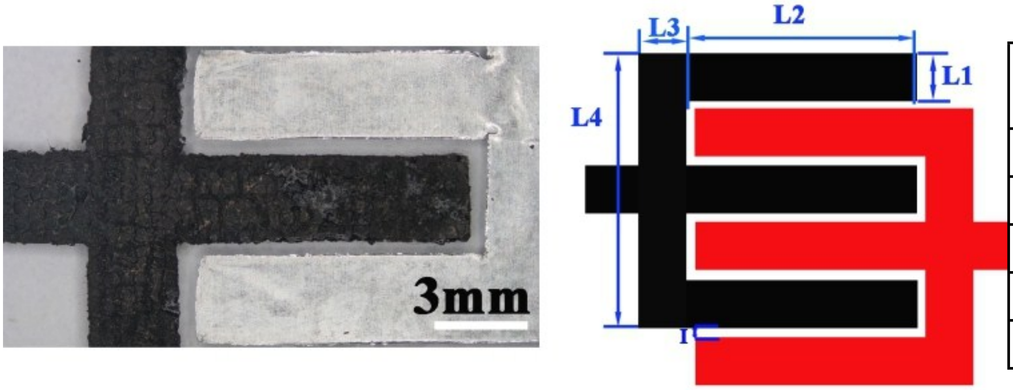


**Fig. S8**. The stress-strain profiles of PAM, PAA and PAM-co-PAA hydrogels.



| MZAB | Dimension parameters |
|---|---|
| L1 | 3.0 mm |
| L2 | 10.5 mm |
| L3 | 3.0 mm |
| L4 | 15.1 mm |
| I | 0.6 mm |

**Fig. S9**. Typical optical microscope photograph of the symmetrical interdigital electrodes of a single OAR-ZAB unit, and actual geometric parameters.

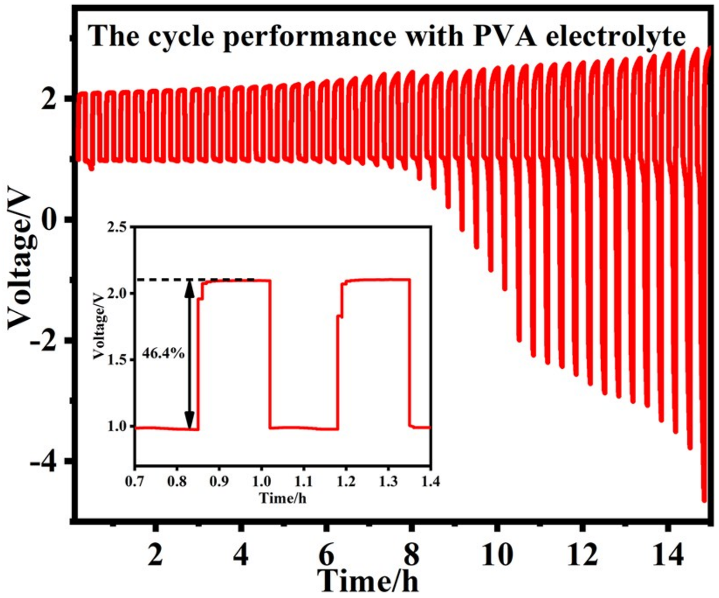


**Fig. S10**. Galvanostatic discharge/charge cycling curves of OAR-ZABs based on conventional PVA/1M KOH alkaline gel electrolytes at constant current density of 5 mA cm$^{-2}$.

[1] Bruker. SADABS, SMART and SAINT. Bruker AXS Inc., Madison, Wisconson, USA, **2002**.

[2] G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, **1997**.

[3] A. L. Spek, *Acta Crystallogr., Sect. A*. **1990**, *46*, C34.