

## Bi-functional air electrode developed from dual-MOFs strategy for high-performance zinc-air batteries

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### Supplementary information

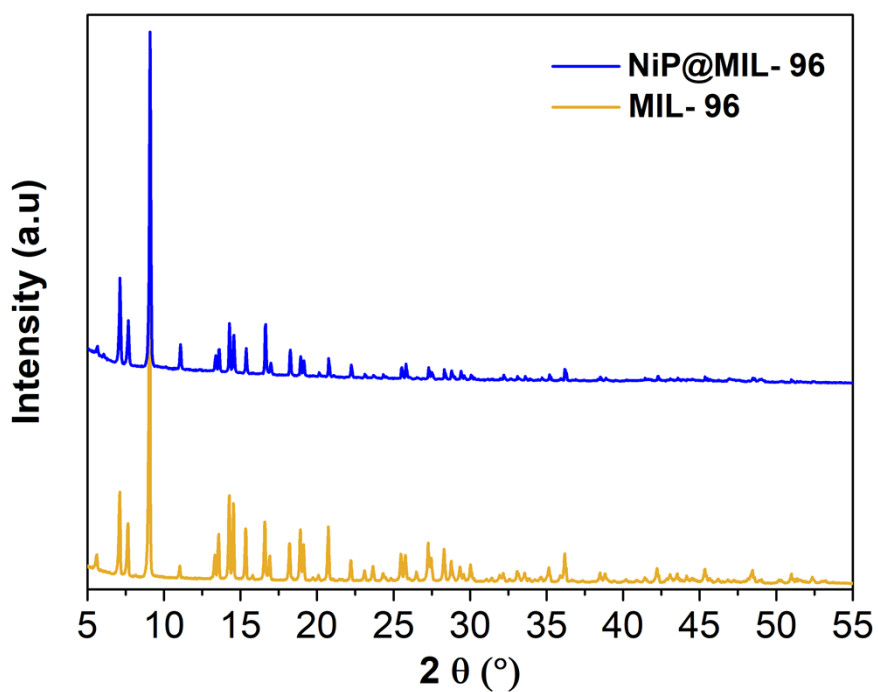


Fig.S1 XRD patterns of (a) MIL-96 and NiP-plated MIL-96

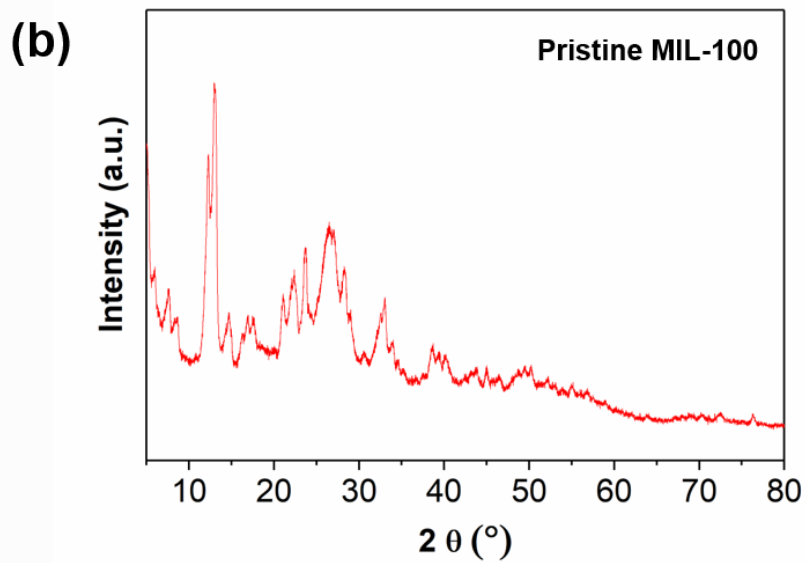
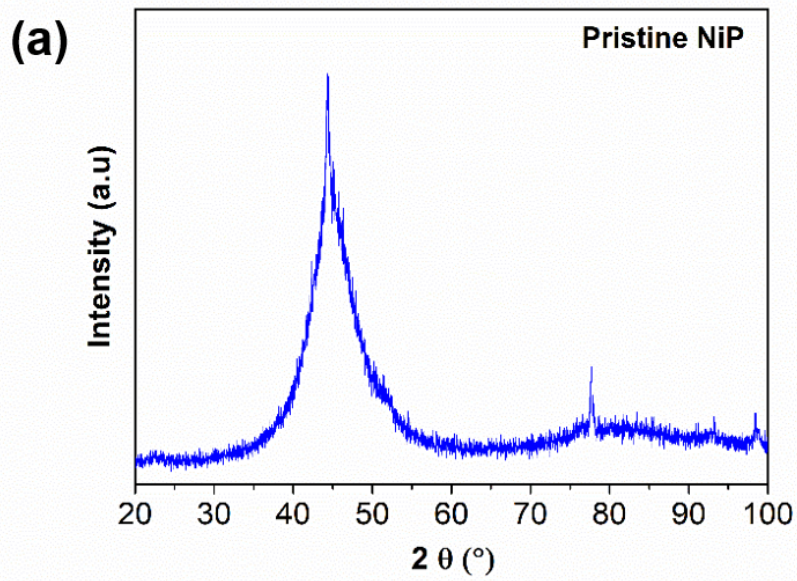


Fig. S2 XRD patterns of (a) pristine NiP-plating (b) pristine MIL-100

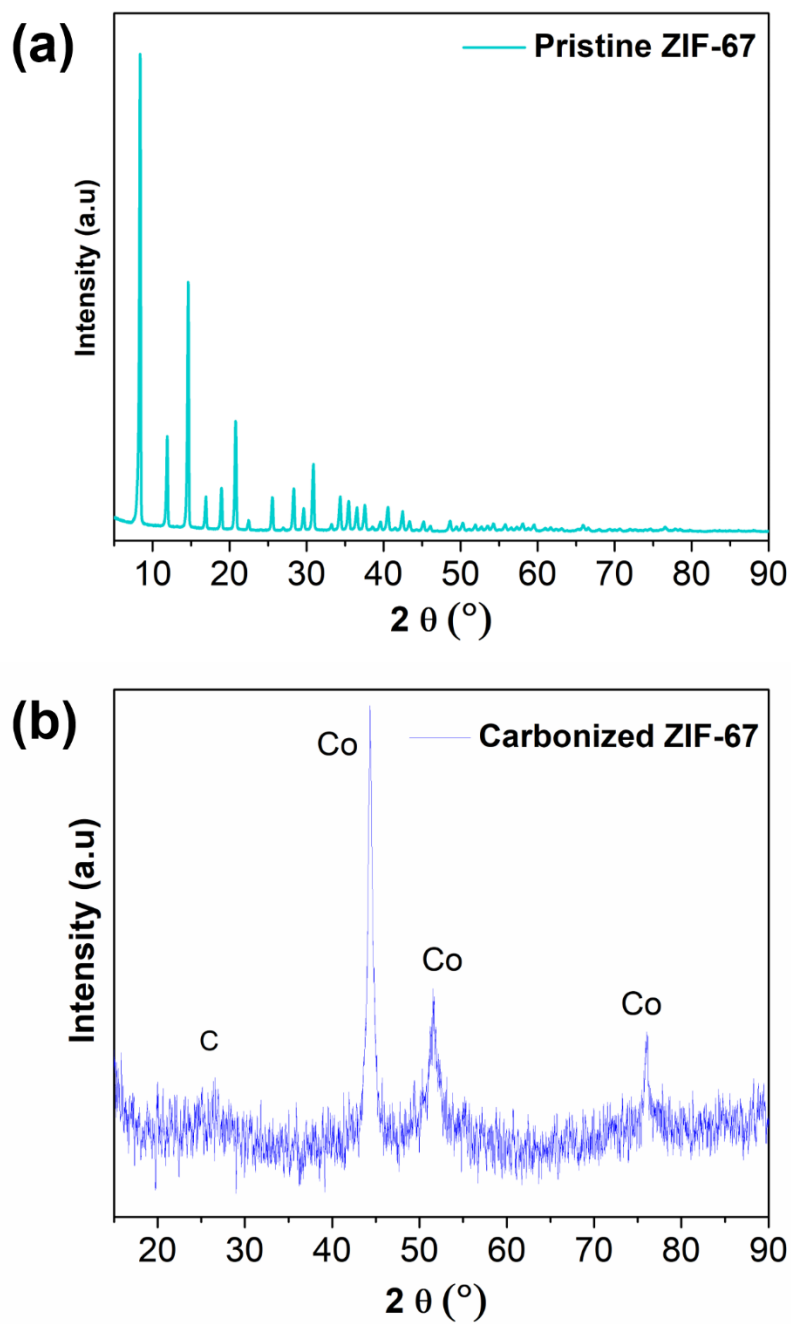
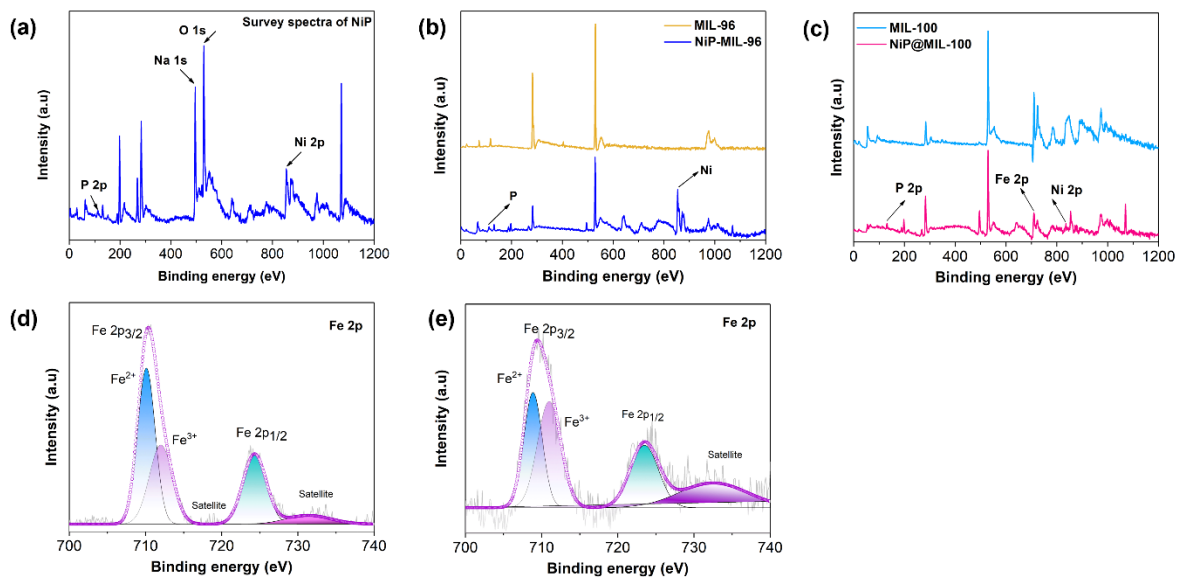


Fig.S3 XRD patterns of pristine ZIF-67 and (b) Carbonized ZIF-67 after the calcination of ZIF-67 at 750°C in the atmosphere of  $N_2$ .



**Fig. S4** Survey spectra of (a) pristine NiP, (b) pristine MIL-96 and NiP@MIL-96 and (c) pristine MIL-100 and NiP@MIL-100, High-resolution deconvoluted XPS spectrum of Fe 2p of (d) pristine MIL-100 and (e) NiP@MIL-100

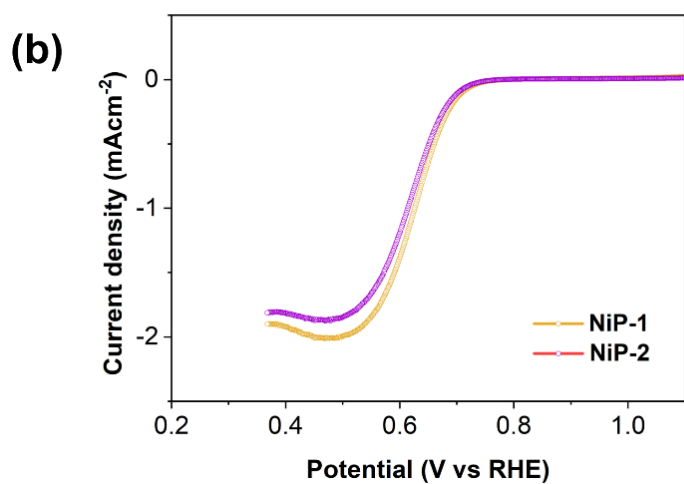
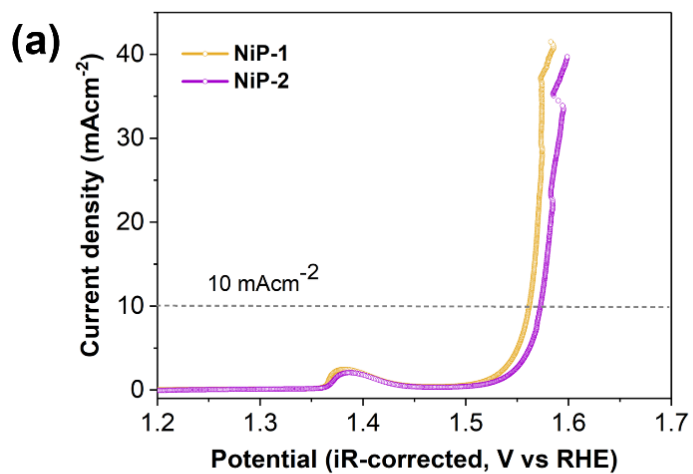


Fig. S5 (a) iR-corrected LSV curves of OER of NiP1 and NiP2 (b) LSV curves of ORR of NiP1 and NiP2

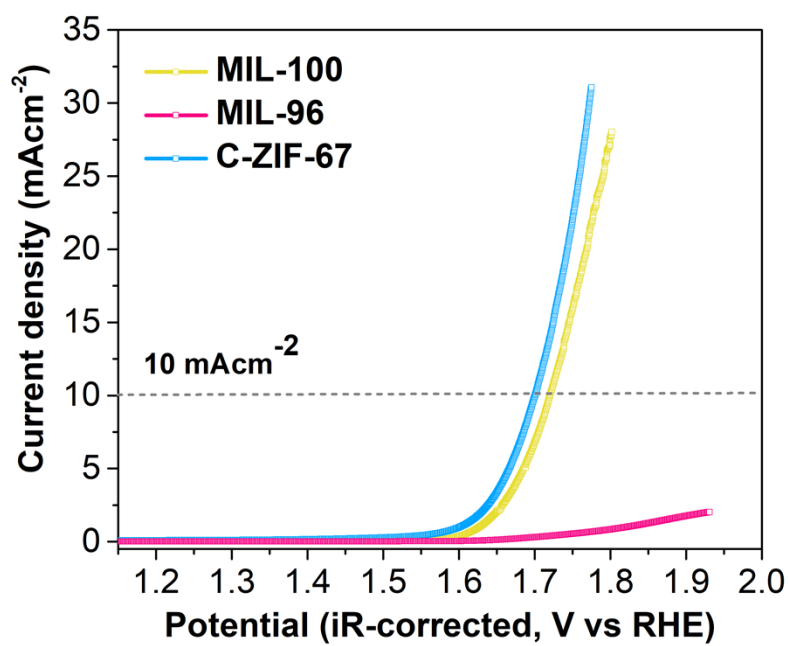


Fig. S6 iR-corrected LSV curves of OER of pristine MIL-96, MIL-100 and carbonized ZIF-67

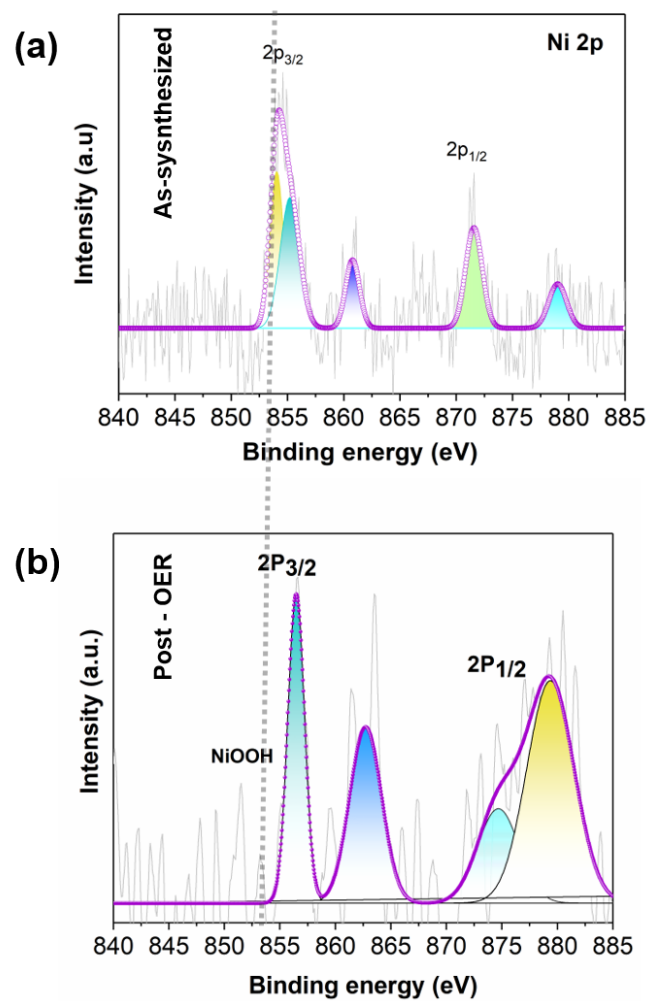


Figure S7. XPS characterization of Ni 2p in the NiP@MIL-100 (a) XPS spectra of the as-synthesized NiP@MIL-100, (b) XPS spectra of NiP@MIL-100 after OER activity, respectively.

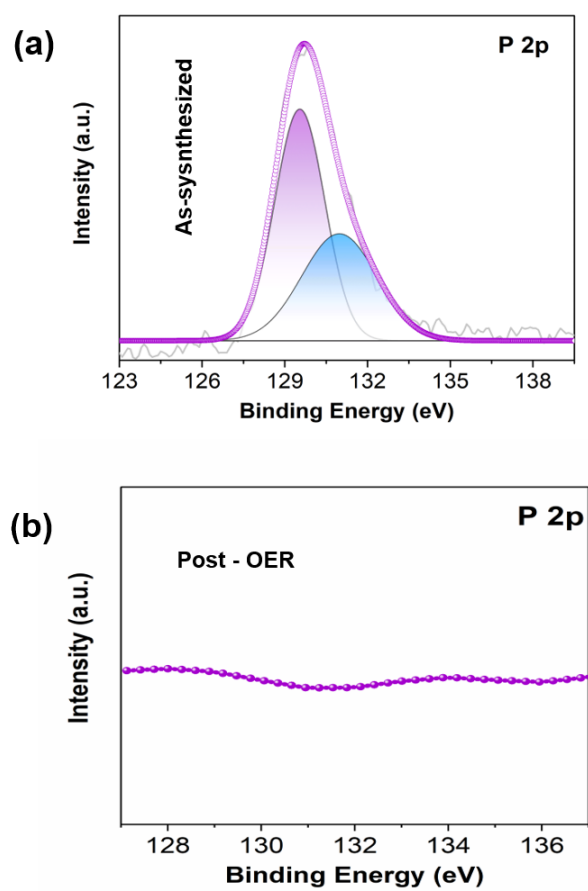
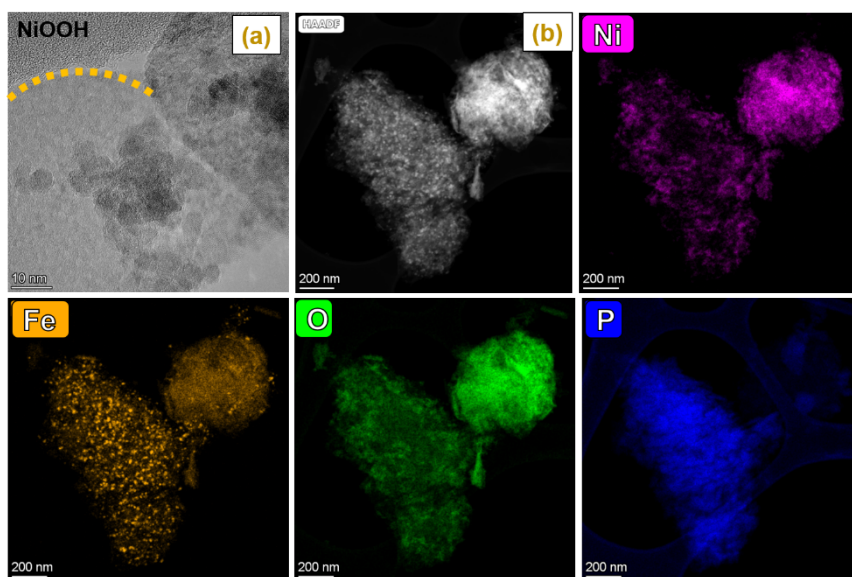


Figure S8. XPS characterization of P 2p in the NiP@MIL-100 (a) XPS spectra of the as-synthesized NiP@MIL-100, (b) XPS spectra of NiP@MIL-100 after OER activity, respectively.





**Fig. S9** TEM and HAADF-STEM images of spent NiP@MIL-100 sample after OER and its corresponding element mapping images.

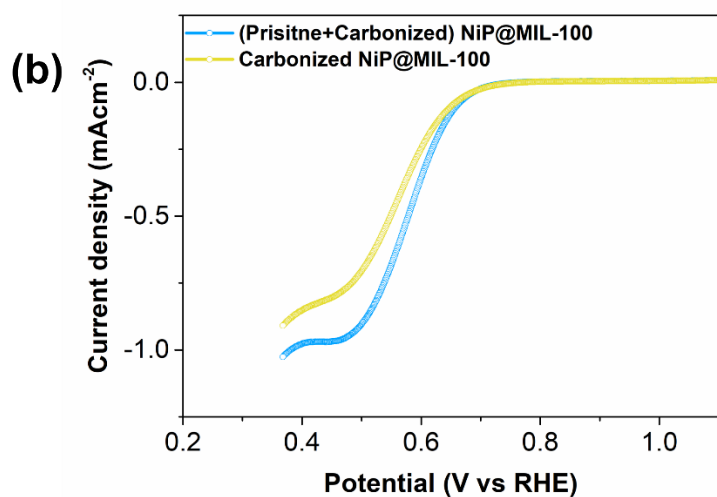
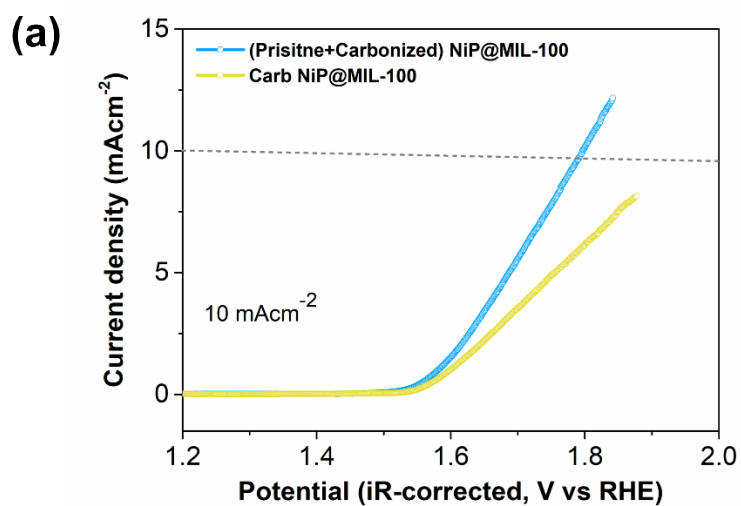


Fig. S10 (a) iR-corrected LSV curves of OER of carbonized NiP@MIL-100 and pristine +carbonized (50:50) NiP@MIL-100 catalysts in  $\text{O}_2$ -saturated 0.10 M KOH solution at 1600 rpm; (b) LSV curves of ORR of carbonized NiP@MIL-100 and pristine +carbonized (50:50) NiP@MIL-100 catalysts in  $\text{O}_2$ -saturated 0.10 M KOH solution at 1600 rpm

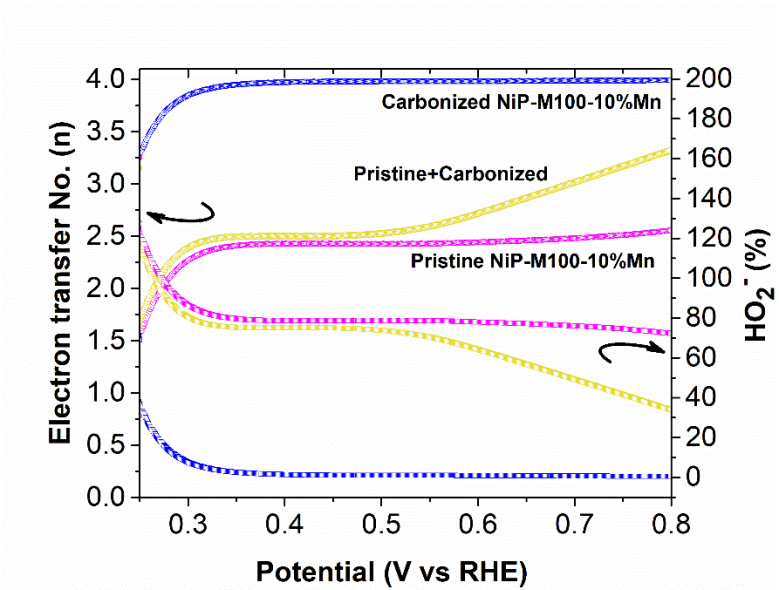


Fig. S11 Electron transfer number and percentage of HO<sub>2</sub><sup>-</sup> of pristine NiP@MIL-100, carbonized NiP@MIL-100 and pristine +carbonized (50:50) NiP@MIL-100 catalysts.

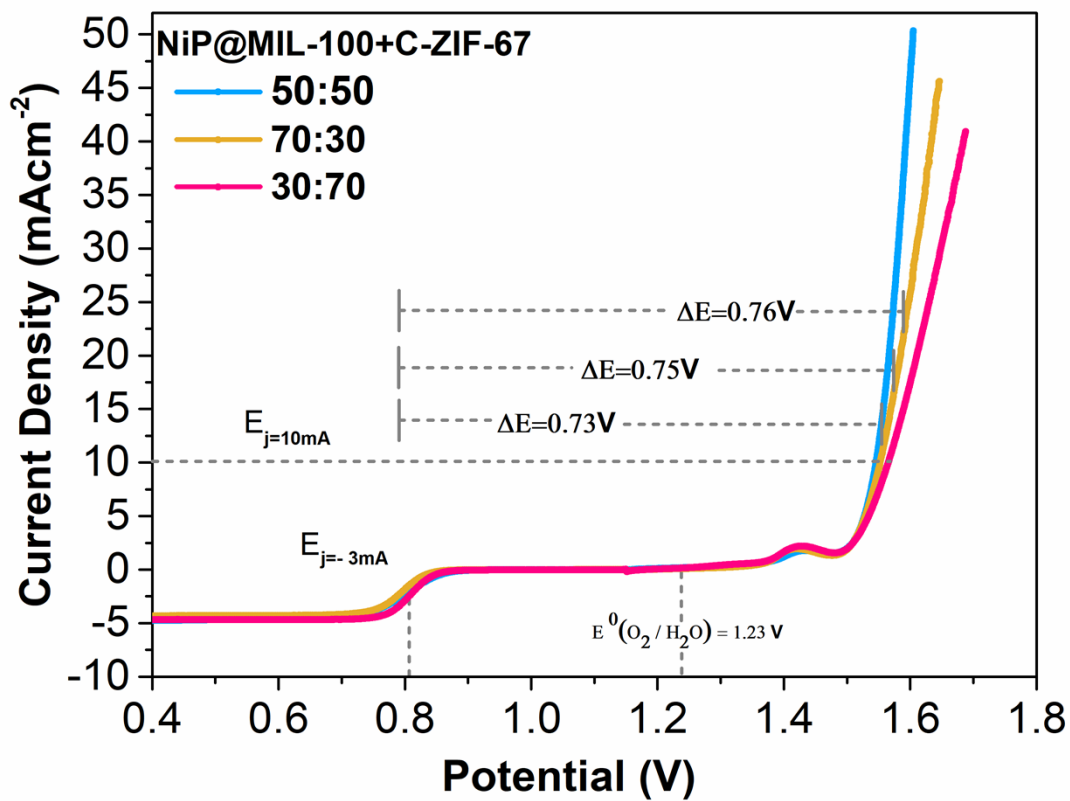


Fig. S12 Overall polarization curves of C-ZIF-67+NiP@MIL-100 at different ratios in 0.1 M KOH

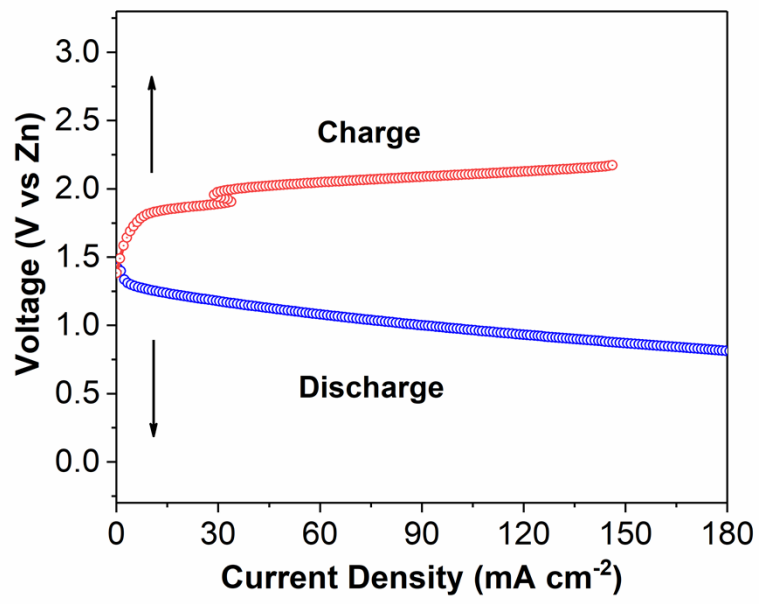


Fig. S13 Discharge and charge polarization curves

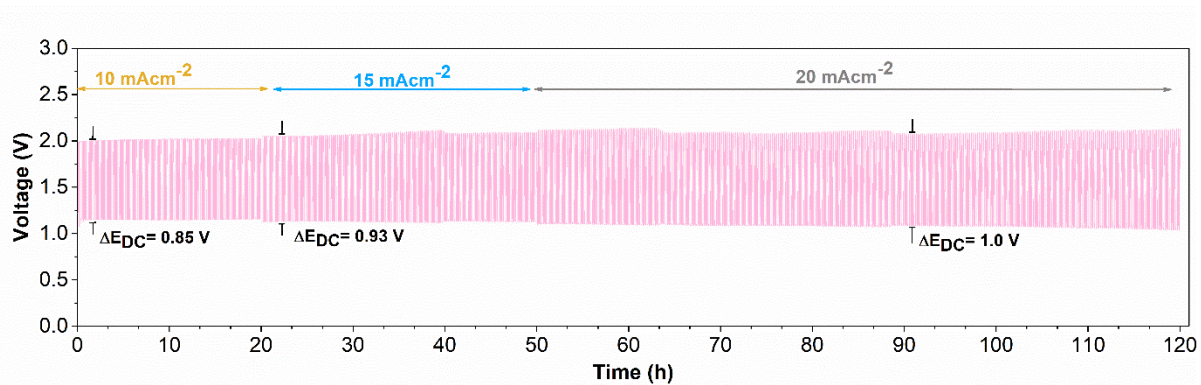


Fig. S14 Galvanostatic charge/discharge test for rechargeable zinc-air battery based on pristine NiP@MIL-100+ carbonized ZIF-67 tested for cyclic stability at 10, 15 and 20 mA cm<sup>-2</sup>

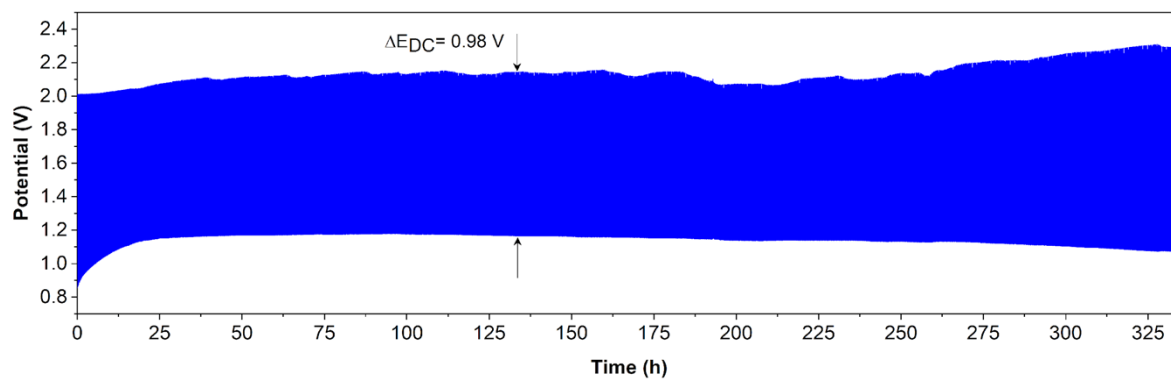


Fig. S15 Rechargeable zinc–air battery test. galvanostatic charge/discharge test based on pristine NiP@MIL-100 catalysts tested for cyclic stability at  $5 \text{ mA cm}^{-2}$ .

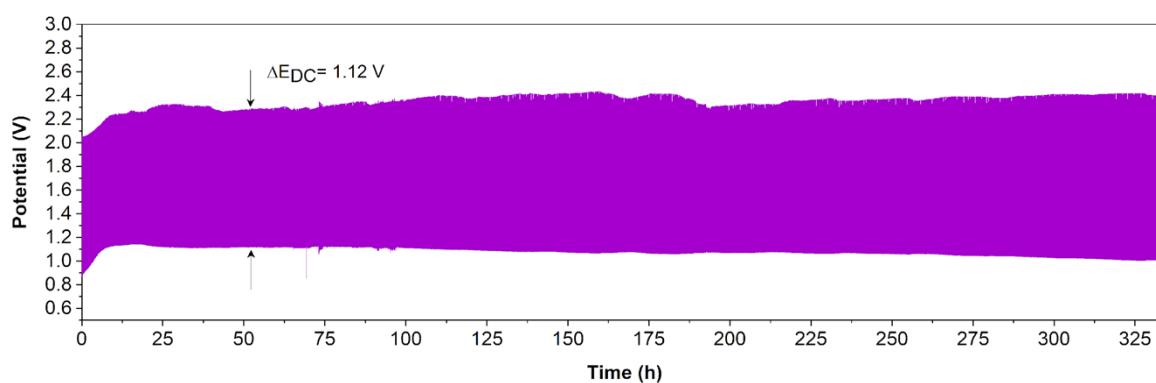


Fig. S16 Rechargeable zinc–air battery test. galvanostatic charge/discharge test based on carbonized NiP@MIL-100 catalysts tested for cyclic stability at  $5 \text{ mA cm}^{-2}$ .

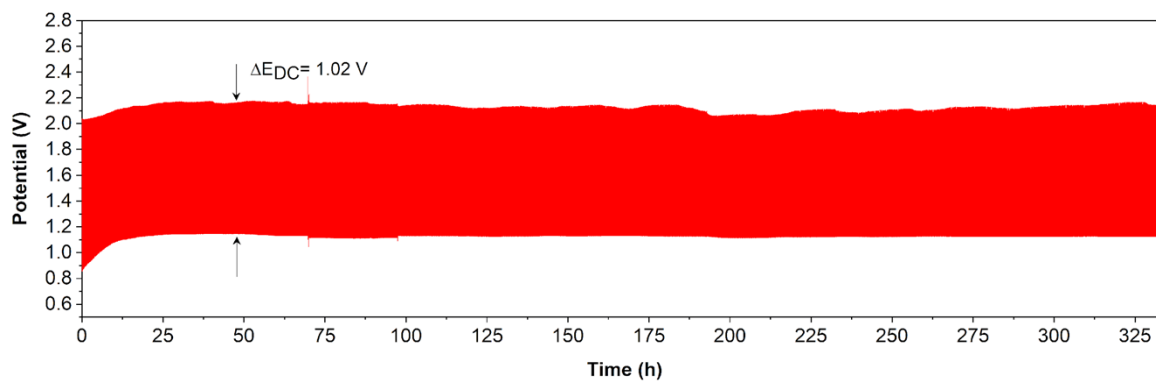


Fig. S17 Rechargeable zinc–air battery test. galvanostatic charge/discharge test based on pristine+carbonized (50:50) NiP@MIL-100 catalysts tested for cyclic stability at  $5 \text{ mA cm}^{-2}$ .

**Table S1 BET surface area, pore volume and pore size of different materials.**

<b>Catalyst</b>	<b>Surface area (m<sup>2</sup>/g)</b>	<b>Pore volume (cm<sup>3</sup>/g)</b>	<b>Pore size (nm)</b>
MIL-96	619.5	0.2180	1.74
NiP@MIL-96	11.2	0.0054	0.27
MIL-100	1,594.7	0.3676	1.77
NiP@MIL-100	6.1	0.0005	0.98



**Table. S2 Peak positions of the samples before and after NiP-plating**

Samples	Peak position of elements (eV)				
	Ni		P		Fe
	Ni <sup>δ+</sup>	Oxidized Ni	P <sup>δ-</sup>	Oxidized P	Fe <sup>2+</sup>
Pristine NiP	853.82	855.15	130.5	132.4	-
NiP@MIL-96	853.80	855.14	130.5	132.35	-
MIL-100		-		-	710.1
NiP@MIL-100	854.75	855.3	129.6	131.2	708.6

**Table S3 Performance comparison of OER, ORR and Zinc-air battery performance of recently published work.**

<b>Catalysts</b>	<b>Peak power density (mW cm<sup>-2</sup>)</b>	<b>Onset Potential V</b>	<b>E<sub>1/2</sub> V</b>	<b>E<sub>j=10</sub> V</b>	<b>ΔE= E<sub>j=10</sub>-E<sub>1/2</sub> V</b>	<b>Tafel slope mvdec<sup>-1</sup></b>	<b>Stability (h)</b>	<b>References</b>
NiP@MIL-100+C-ZIF-67	203	0.94	0.83	1.52	0.69	62	500	This study
109CoNC SAC	162	1.05	0.86	1.65	0.79	-	80	1
NCA/Fe <sub>SA+NC</sub>	236	1.12	0.92	1.57	0.65	71.5	300	2
Fe <sub>1.2</sub> (CoNi) <sub>1.8</sub> S <sub>6</sub> MES	124	-	0.80	1.48	0.68	53.0	140	3
Fe, Ni@N-MWCNTs	114.9	0.84	0.71	1.54	0.83	40.0	170	4
Pt-NiO@Ni SP	188	1.04	0.90	1.55	0.65	97.3	200	5
CoP/CoO@MNC-CNT	152.8	0.921	0.84	1.50	0.66	89.3	500	6
Cu-Co/NC	295.9	0.97	0.85	1.49	0.64	60.4	500	7
Co-CoO/NPCF	214.1	0.91	0.843	1.59	0.75	43.8	200	8
CrMnFeCoNi	116.5	0.88	0.78	1.50	0.72	38	240	9
Co@C-CoNC	162.8	0.99	0.906	1.64	0.74	73	100	10
Fe SAs HS	170	1.0	0.86	1.57	0.71	68.8	70	11
NixP-NP-C900	266	0.90	0.76	1.78	1.02	205	20	12
S-CFZ	180	0.84	0.82	1.53	0.71	-	500	13
Co1-N3PS/HC	176	1.0	0.92	-	-	-	50	14
SA&NP-FeCo-NTS	108	0.98	0.85	1.58	0.73	109	250	15

CoFeN-NCNTs//CCM	145	0.89	0.84	1.57	0.73	49	500	16
NiFe <sub>3</sub> @NGHS-NCNTs	126.5	-	0.83	1.62	0.79	-	166	17
Co/CoSe@NC	148	0.9	0.81	1.56	0.75	78	125	18
Co/CeO <sub>2</sub> -NCNA@CC	123	-	0.77	1.58	0.81	-	380	19
FeNP@Fe-N-C	106.5	0.92	0.84	1.55	0.71	216	68	20
CC3	85	0.97	0.83	1.62	0.79	102	120	21
S-NiFe-LDH/NG	165	0.85	0.70	1.47	0.77	41	120	22
Ni-Fe-S/xNCQDs	94	0.97	0.85	1.53	0.68	86	240	23
Fe-FNC	226	0.85	0.80	-	-	-	140	24
Fe/12Zn/Co-NCNTs	166	1.0	0.88	1.57	0.69	93	320	25
Fe <sub>3</sub> Co/DSA-NSC	240	0.96	0.88	1.45	0.57	62	60	26
Fe <sub>3</sub> C/N,S-CNS	163	0.98	0.86	-	-	77	750	27
FeNi <sub>3</sub> @NWC	143	-	0.84	1.52	0.68	-	266	28
Co@NSC	141	0.91	0.86	1.57	0.71	181	94	29
FeNi LDH-TpF6	118	-	-	-	-	-	800	30
CoCu/N-CNS	104.3	0.92	0.84	1.48	0.64	99	400	31
NPPC	173.8	0.97	0.87	-	-	-	300	32
FeCoP2-CN <sub>C</sub>	76.9	0.91	0.85	1.53	0.68	124	45	33

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