Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

FeCo alloy nanoparticle encapsulated in hollow N-doped carbon as bifunctional electrocatalyst for aqueous zinc-air batteries with low voltage gap

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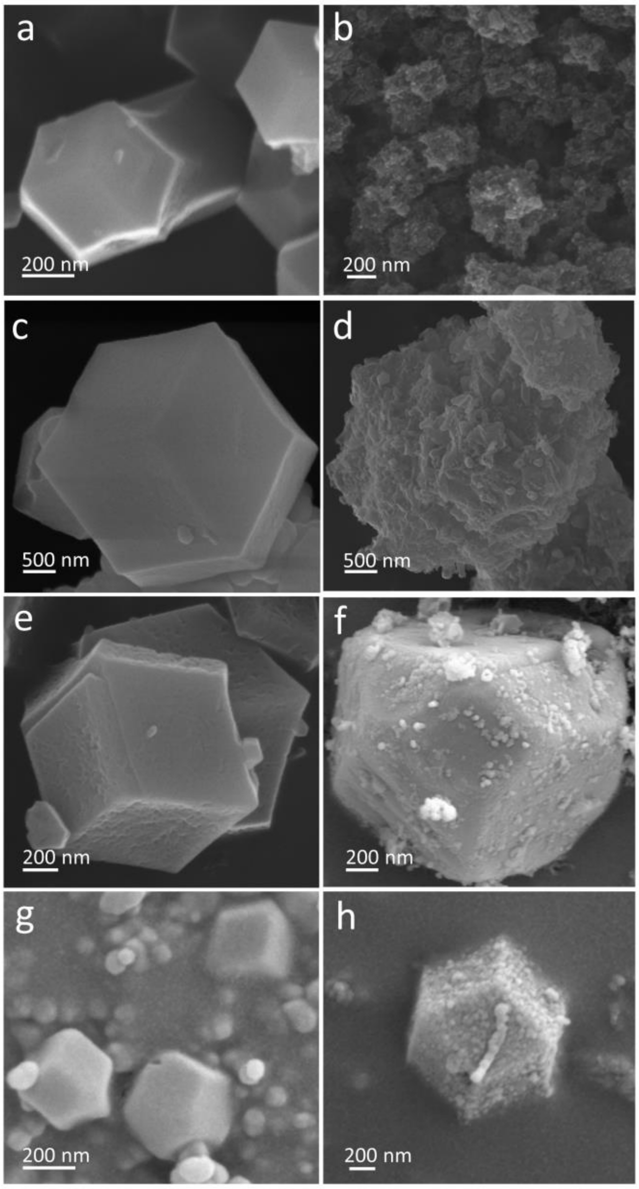

Figure S1. SEM images of (a) ZnFe-ZIF-0.1, (b) Fe_xCo_y@N-C-0.1, (c) ZnFe-ZIF-0.5, (d) Fe_xCo_y@N-C-0.5, (e) ZnFe-ZIF-0.3, (f) Fe@N-C, (g) ZnCo-ZIF, and (h) Co@N-C.

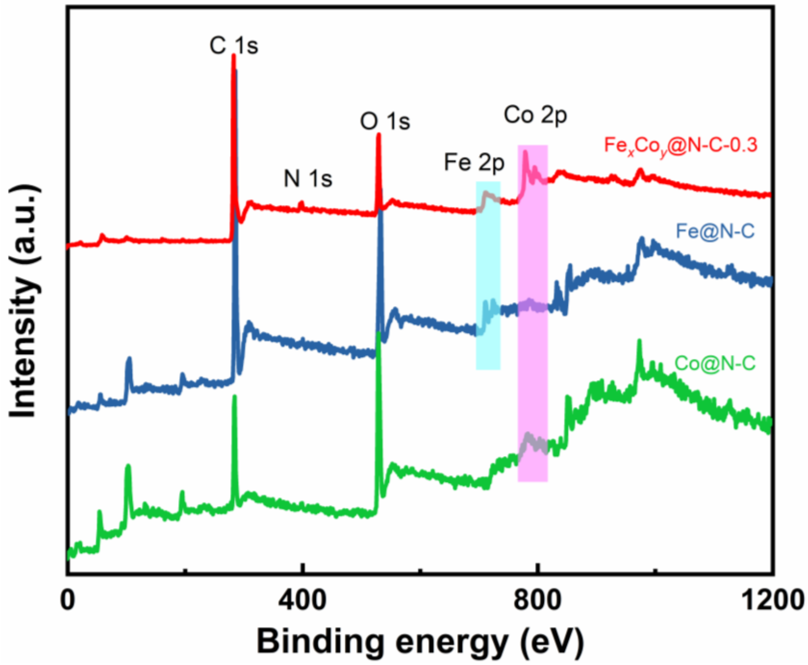

Figure S2. XPS spectrums of Fe_xCo_y@N-C-0.3, Fe@N-C and Co@N-C.

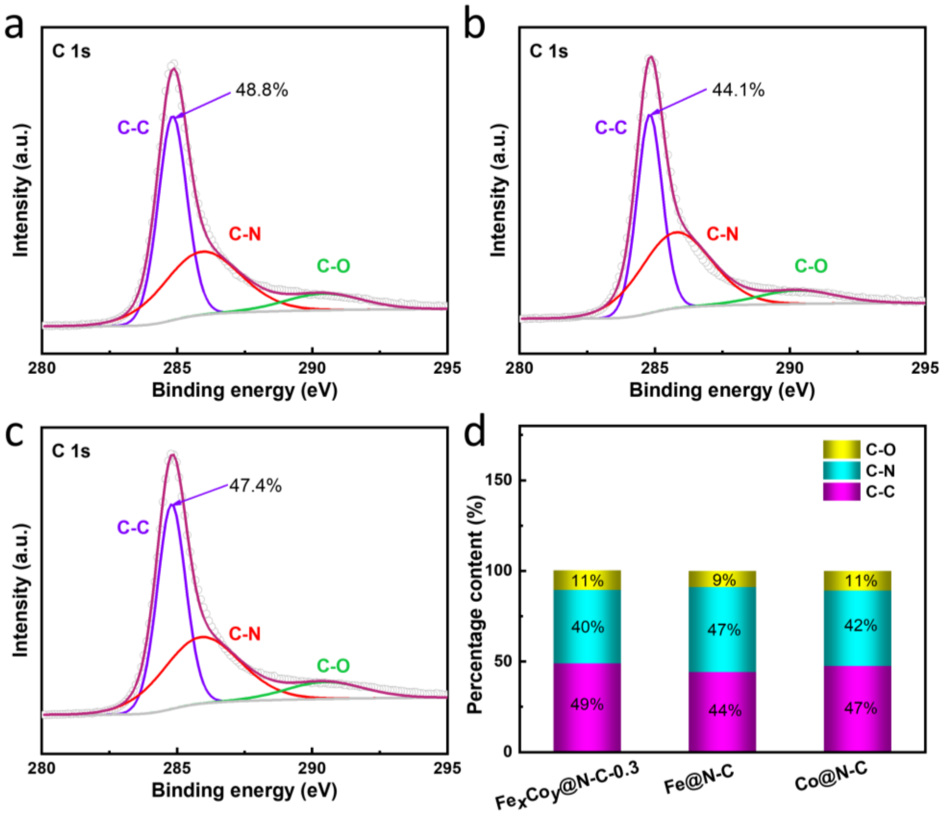

Figure S3. The C 1s XPS spectrums of (a) Fe_xCo_y@N-C-0.3, (b) Fe@N-C, and (c) Co@N-C. (d) Comparison of various C contents in Fe_xCo_y@N-C-0.3, Fe@N-C, and Co@N-C.

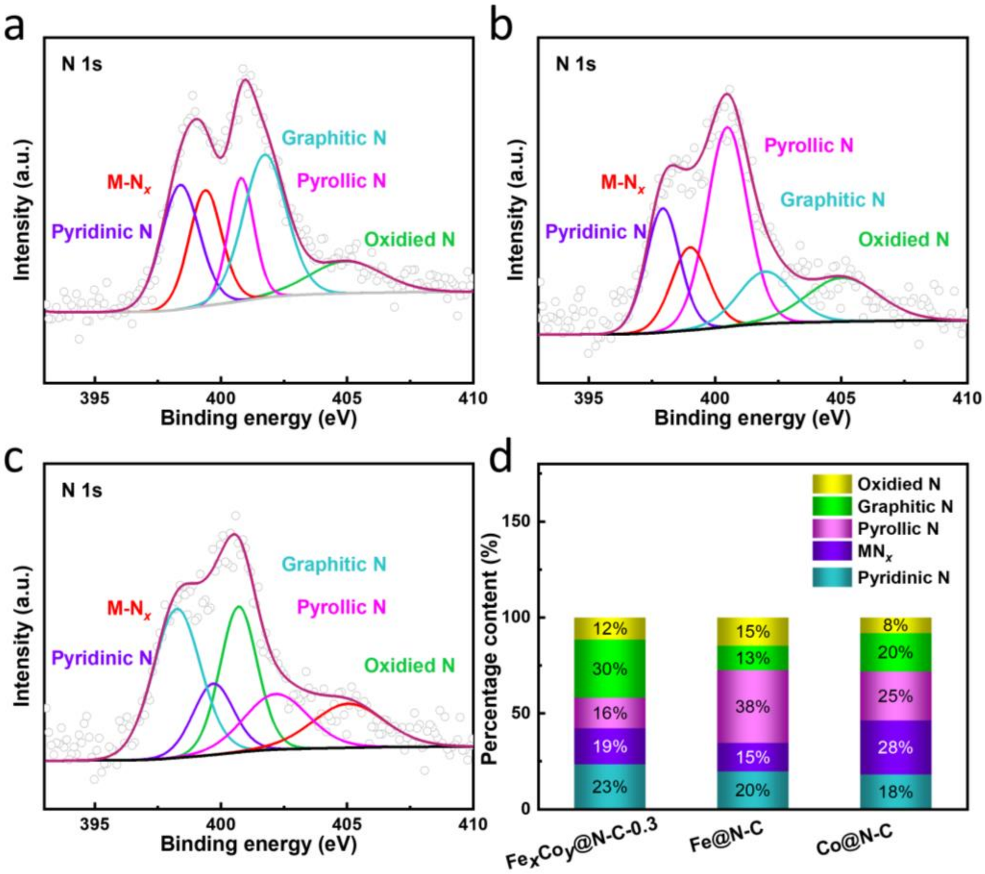

Figure S4. The N 1s XPS spectrums of (a) Fe_xCo_y@N-C-0.3, (b) Fe@N-C, and (c) Co@N-C. (d) Comparison of various N contents in Fe_xCo_y@N-C-0.3, Fe@N-C, and Co@N-C.

Table S1. Comparison of the ORR performance of as-prepared catalysts.

Catalyst	$E_{1/2}$ (V vs. RHE)	The Tafel slope (mV dec^{-1})
Fe_xCo_y@N-C-0.1	0.839	90.9
Fe_xCo_y@N-C-0.3	**0.842**	**88.1**
Fe_xCo_y@N-C-0.5	0.836	94.3
Fe@N-C	0.810	101.5
Co@N-C	0.803	118.2
Pt/C	0.809	100.7

Table S2. Comparison of ORR performance (vs. RHE) of Fe_xCo_y@N-C-0.3 with reported M-N-C catalysts in alkaline solution.

Catalysts	$E_{1/2}$ (V)	E_{onset} (V)	Ref.
Fe_xCo_y@N-C-0.3	**0.842**	**0.98**	**This work**
$Fe_8Co_{0.2}$-NC-800	0.820	/	*Nano-Micro Lett.* **2023**, 15, 26.
NP-Co_{SA}NC	0.860	/	*Energy Storage Materials* **2023**, 56, 165–173.
CoFe@NC/KB-800	0.845	0.95	*Chem. Eng. J.* **2022**, 427, 131614.
CoNi-CoN_4-HPC-900	0.820	1.03	*Nano Energy* **2022**, 99, 107325.
ZnCo-HNC	0.820	1.05	*Small* **2022**, 18, e2107141.
Co@NPC/C-MWCNTs	0.790	0.87	*Chem. Eng. J.* **2022**, 432, 134192.
CoNP@FeNC-0.05	0.850	1.02	*Nano-Micro Lett.* **2022**, 14, 162.
CoFe/S-N-C	0.855	/	*Chem. Eng. J.* **2022**, 429, 132174.
Co/CoFe@NC	0.840	0.97	*Nano-Micro Lett.* **2021**, 13, 126.
FeCo/N-HCSs	0.791	0.98	*Chem. Eng. J.* **2021**, 407, 127961.
Fe_1-HNC-500-850	0.842	0.93	*Adv. Mater.* **2020**, 32, 1906905.
Fe_3C-Co/NC	0.830	0.94	*Adv. Funct. Mater.* **2019**, 29, 1901949

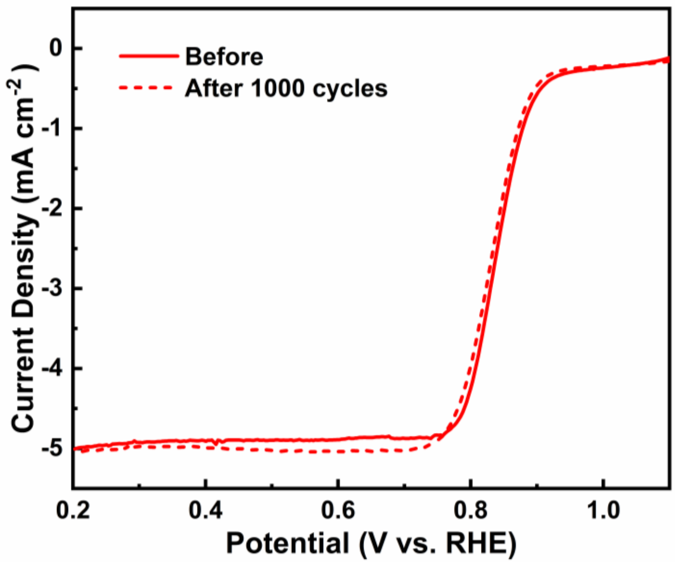

Figure S5. LSV curves of ORR obtained before and after CV tests of 2000 cycles for Fe_xCo_y@N-C-0.3.

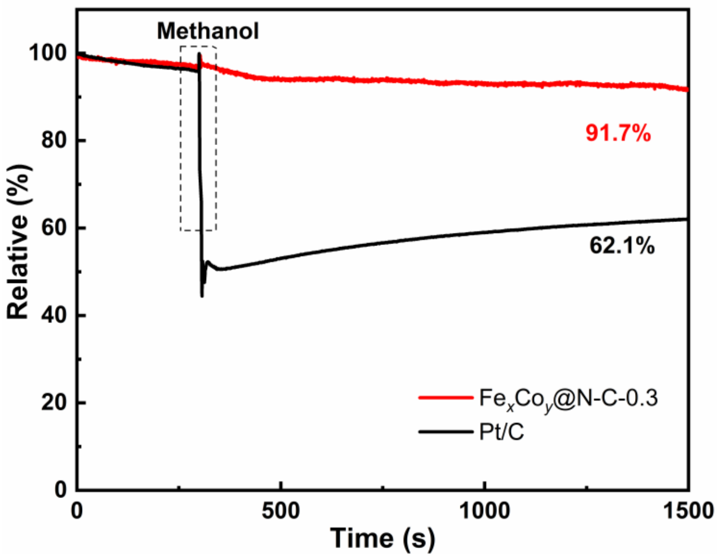

Figure S6. Methanol crossover tolerance test of Fe_xCo_y@N-C-0.3 and Pt/C.

Table S3. Comparison of the OER performance of as-prepared catalysts.

Catalyst	$E_{j=10}$ **(V vs. RHE)**	**The Tafel slope (mV dec^{-1})**
Fe_xCo_y@N-C-0.1	1.597	119.1
Fe_xCo_y@N-C-0.3	**1.528**	**87.7**
Fe_xCo_y@N-C-0.5	1.645	150.0
Fe@N-C	1.661	169.3
Co@N-C	1.637 (fast decay)	147.6
RuO_2	1.607	138.8

Table S4. Comparison of OER performance (vs. RHE) of Fe_xCo_y@N-C-0.3 with recently reported M-N-C catalysts in alkaline solution.

Catalyst	$E_{j=10}$ (V)	Tafel slope (mV dec^{-1})	Ref.
Fe_xCo_y@N-C-0.3	**1.528**	**87.7**	**This work**
$Fe_8Co_{0.2}$-NC-800	1.630	89.1	*Nano-Micro Lett.* **2023**, 15, 26.
Co@C-CoNC	1.638	73.0	*Nano-Micro Lett.* **2023**, 15, 48.
NP-Co_{SA}NC	1.550	/	*Energy Storage Materials* **2023**, 56, 165–173.
CoNi-CoN_4-HPC-900	1.700	153.0	*Nano Energy* **2022**, 99, 107325.
CoNP@FeNC-0.05	1.630	146.0	*Nano-Micro Lett.* **2022**，14，162
Co@N-HPC-700	1.710	168.5	*Chem. Eng. J.* **2022**, 433, 134469.
Fe_3C-Co/NC	1.570	49.0	*Adv. Funct. Mater.* **2019**, 29, 1901949.

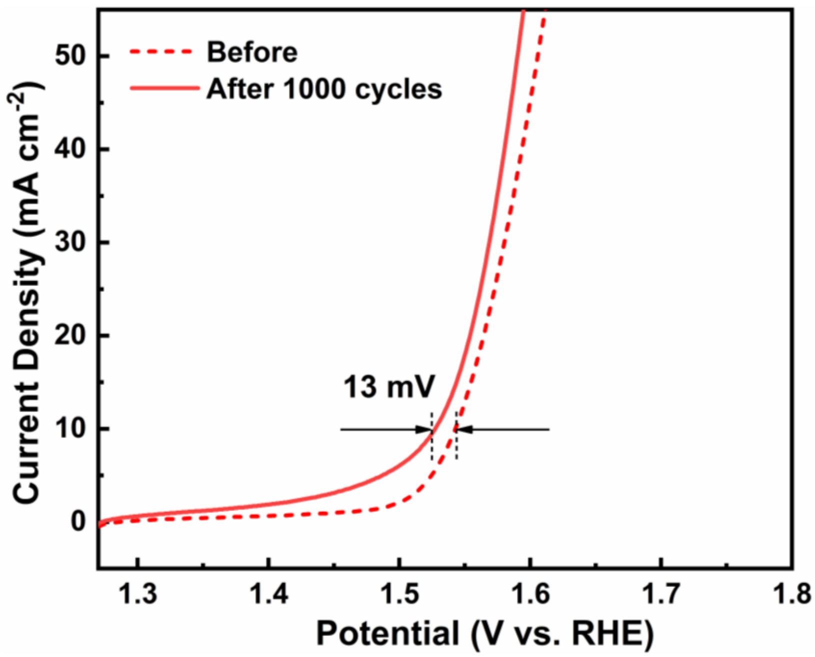

Figure S7. LSV curves of OER obtained before and after CV tests of 2000 cycles for Fe_xCo_y@N-C-0.3.

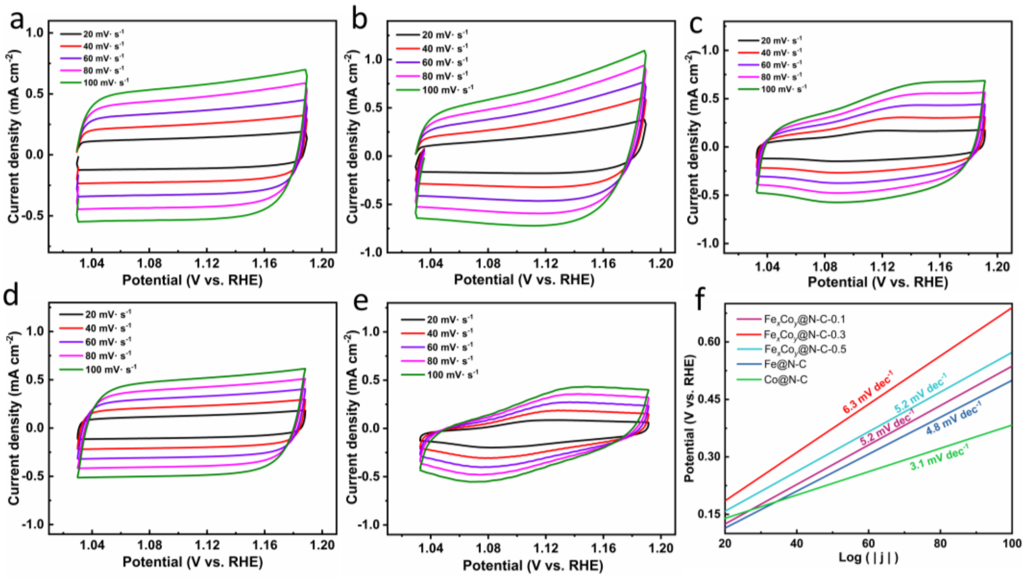

Figure S8. The CV tests at different scan rates of (a) Fe_xCo_y@N-C-0.1, (b) Fe_xCo_y@N-C-0.3, (c) Fe_xCo_y@N-C-0.5, (d) Fe@N-C, (e) Co@N-C-0.5, and (f) the corresponding C_{dl} value.

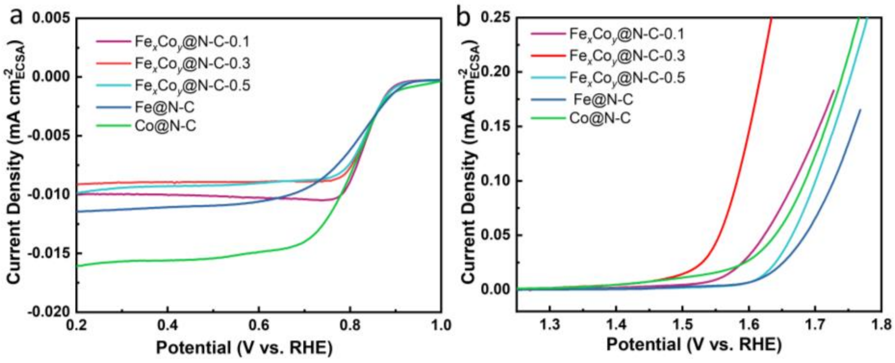

Figure S9. The specific activity based on ECSA for (a) OER and (b) HER.

Table S5. Comparison of the reversible potential difference (ΔE) (vs. RHE) of Fe_xCo_y@N-C-0.3 with recently reported M-N-C catalysts in alkaline solution.

Catalyst	***ORR*** $E_{1/2}$ **(V)**	***OER*** $E_{j=10}$ **(V)**	ΔE **（V）**	**Ref.**
Fe_xCo_y@N-C-0.3	**0.842**	**1.528**	**0.686**	**This work**
$Fe_8Co_{0.2}$-NC-800	0.820	1.630	0.810	*Nano-Micro Lett.* **2023**, 15, 26.
NP-Co_{SA}NC	0.860	1.550	0.790	*Energy Storage Materials* **2023**, 56, 165–173.
CoFe@NC/KB-800	0.845	1.615	0.770	*Chem. Eng. J.* **2022**, 427, 131614.
CoNi-CoN_4-HPC-900	0.820	1.700	0.880	*Nano Energy* **2022**, 99, 107325.
CoNP@FeNC-0.05	0.850	1.630	0.780	*Nano-Micro Lett.* **2022**, 14, 162.
Co/CoFe@NC	0.840	1.540	0.700	*Nano-Micro Lett.* **2021**, 13, 126.
FeCo/N-HCSs	0.791	1.522	0.731	*Chem. Eng. J.* **2021**, 407, 127961.
Fe_3C-Co/NC	0.830	1.570	0.740	*Adv. Funct. Mater.* **2019**, 29, 1901949

Table S6. Performances of recently reported aqueous ZABs based on M-N-C catalysts.

Catalyst	OCP(V)	Peak power density (mW cm^{-2})	The voltage gap (V)	Stability	Ref.
Fe_xCo_y@N-C-0.3	**1.45**	**191.00**	**0.73**	**345 h at 5 mA cm^{-2}**	**This work**
$Fe_8Co_{0.2}$-NC-800	~1.43	124.90	/	311 h at 5 mA cm^{-2}	*Nano-Micro Lett.* **2023**, 15, 26.
Co@C-CoNC	1.53	162.8	~0.85	100 h at 2 mA cm^{-2}	*Nano-Micro Lett.* **2023**, 15, 48.
NP-Co_{SA}NC	1.42	158.10	0.88	80 h at 10 mA cm^{-2}	*Energy Storage Materials* **2023**, 56, 165–173
FeCo-DACs/NC	1.50	175.00	~0.91	240 h at 10 mA cm^{-2}	*Adv. Mater.* **2022**, 34, 2107421.
Co/$ZnCo_2O_4$@NC-CNTs	1.47	305.00	0.92	103 h at 20 mA cm^{-2}	*Nano Energy* **2021**, 82, 105710.
Co/CoFe@NC	1.49	146.60	0.74	~360 h at 20 mA cm^{-2}	*Nano-Micro Lett.* **2021**, 13, 126.
CoNC-NB2	1.50	246.00	~1.00	140 h at 2 mA cm^{-2}	*Small* **2020**, 16, 2001171.
H-Co@FeCo/N/C	1.45	125.20	1.00	200 h at 2 mA cm^{-2}	*Appl. Catal. B Environ.* **2020**, 278, 119259.
CoNi-SAs/NC	1.45	101.40	0.82	~32 h at 5 mA cm^{-2}	*Adv. Mater.* **2019**, 31, 1905622.
Fe/Co-N/S-Cs	~1.40	102.63	0.69	~30 h at 5 mA cm^{-2}	*Appl. Catal. B Environ.* **2019**, 241, 95-103.

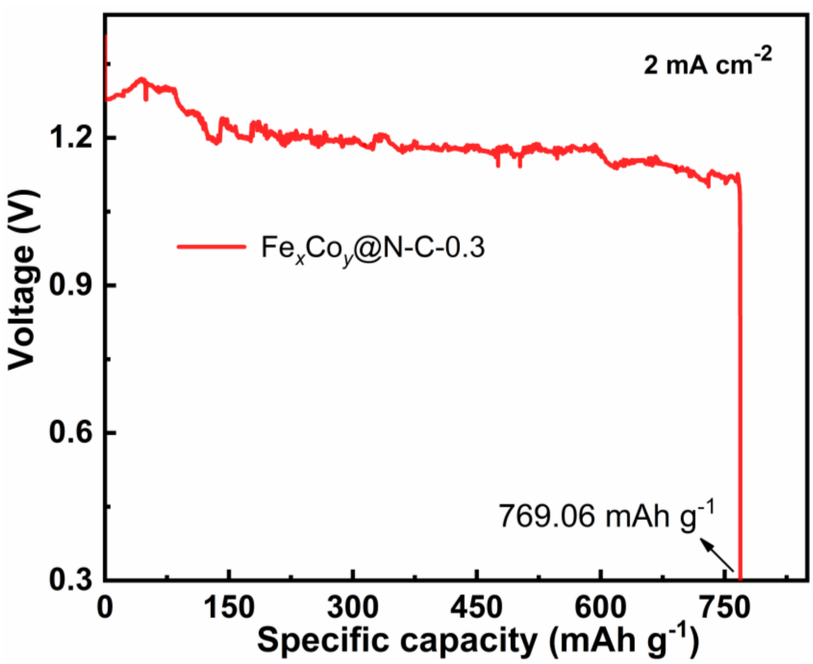

Figure S10. The specific capacity curve of the flexible ZABs based on Fe_xCo_y@N-C-0.3.

Table S7. Performances of recently reported flexible ZABs based on M-N-C catalysts.

Catalyst	OCP (V)	Stability	Ref.
Fe_xCo_y@N-C-0.3	**1.40**	**50 h at 5 mA cm^{-2}**	**This work**
$Fe_8Co_{0.2}$-NC-800	~1.39	/	*Nano-Micro Lett.* **2023**, 15, 26.
NP-Co_{SA}NC	1.32	5 h at 2 mA cm^{-2}	*Energy Storage Materials* **2023**, 56, 165–173.
CoNi-CoN_4-HPC-900	1.50	~27 h at 5 mA cm^{-2}	*Nano Energy,* **2022**, 99, 107325.
CoFe/N-HCSs	1.40	10 h at 1 mA cm^{-2}	*Chem. Eng. J.* **2021**, 407, 127961.
CoFe@NO-CNT	1.45	56 h at 2 mA cm^{-2}	*Electrochimica Acta* **2021**, 388, 138587.
Co/CoFe@NC	1.48	~92 h at 5 mA cm^{-2}	*Nano-Micro Lett.* 2021, 13, 126.
Co/$ZnCo_2O_4$@NC-CNTs	1.30	~20 h at 5 mA cm^{-2}	*Nano Energy* **2021**, 82, 105710.
CoFe/N-HCSs	1.40	10 h at 1 mA cm^{-2}	*Chem. Eng. J.* **2021**, 407, 127961
Co-NCNT	1.42	30 h at 2 mA cm^{-2}	*Carbon Energy* **2020**, 2, 461-471.