Supplementary Materials

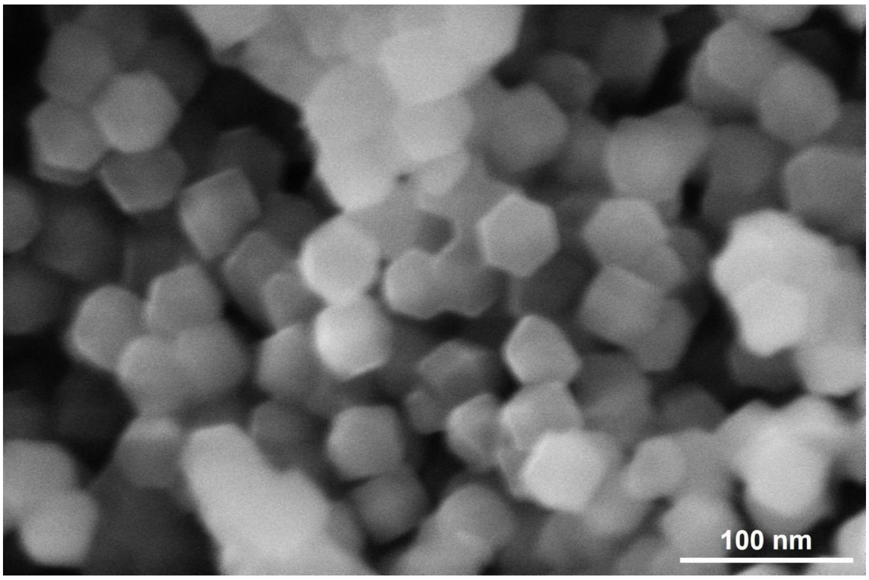
Axial chlorine-induced asymmetric cobalt single-atom coordination fields for boosting oxygen reduction reaction

Xi-Rong Jiang[1], Guo-Dong Xie[1], Jun-Hao Li[1], Wen-Jie Huang[1], Jun-Da Lu[1], Pan Xie[1], Yan Dong[1], Wen-Da Ma[1], Yi-Da Deng[1,2], Xue-Rong Zheng[1,2]

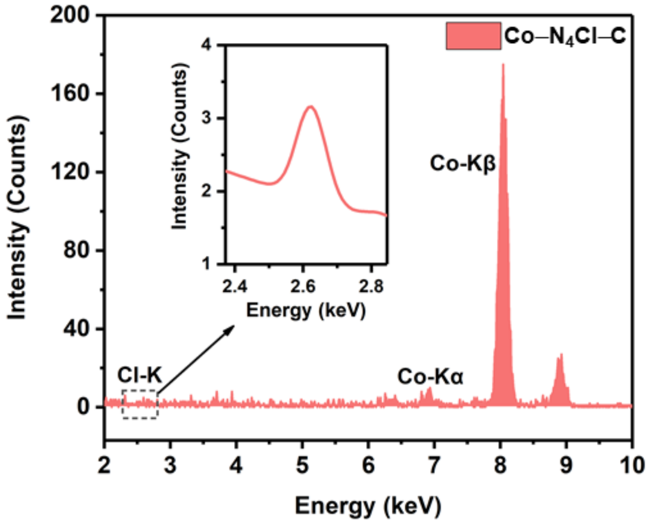
[1]State Key Laboratory of Marine Resource Utilization in South China Sea, School of Materials Science and Engineering, Hainan University, Haikou 570228, Hainan, China.
[2]School of Materials Science and Engineering, Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, China.

Correspondence to: Prof. Wen-Jie Huang, Prof. Xue-Rong Zheng, and Jun-Da Lu, State Key Laboratory of Marine Resource Utilization in South China Sea, School of Materials Science and Engineering, Hainan University, No. 58 Renmin Avenue, Haikou 570228, Hainan, China. E-mail: wj_huang@hainanu.edu.cn; xrzh@hainanu.edu.cn; lujundaacc@163.com

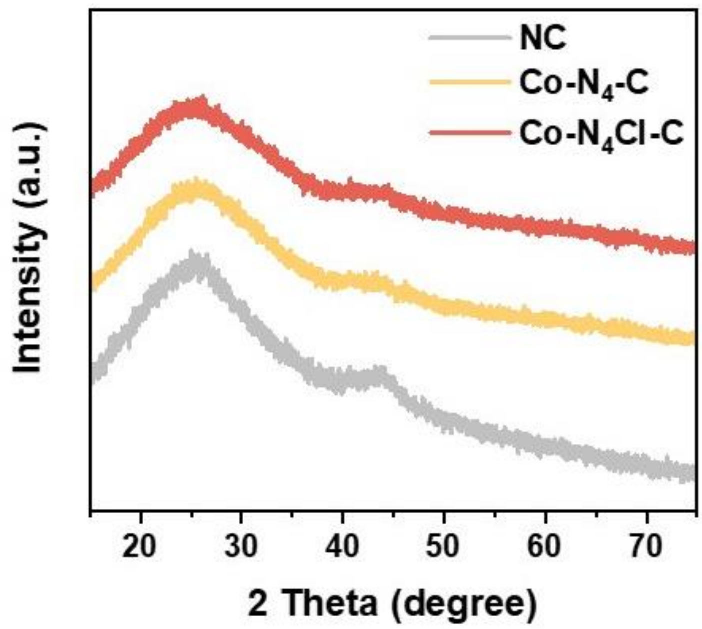
Supplementary figures



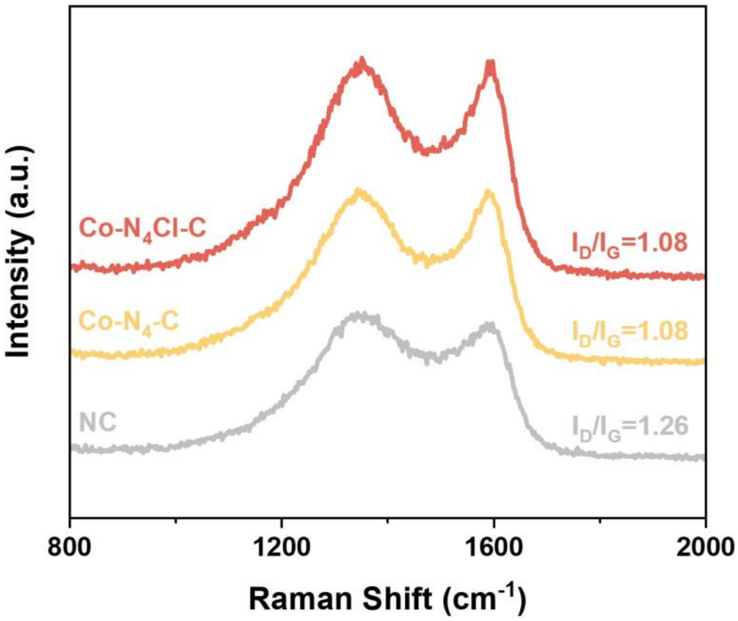
Supplementary Figure 1. SEM image of Co-ZIF-8 precursor.



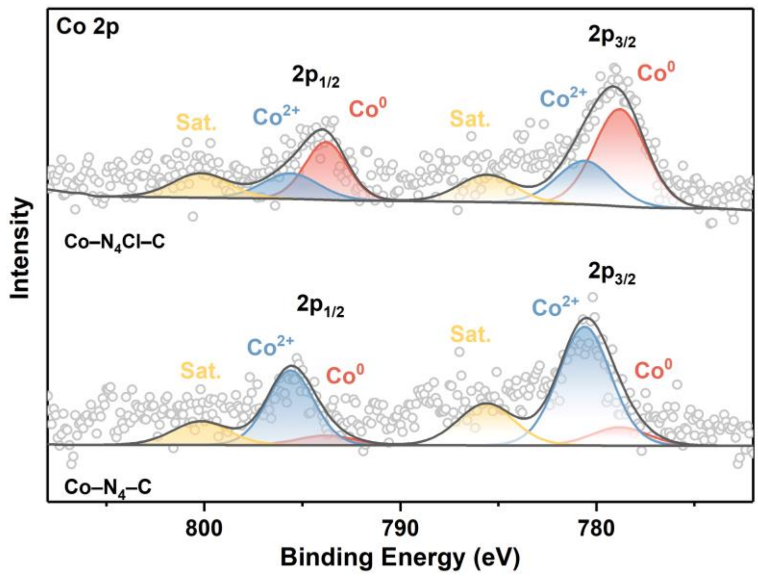
Supplementary Figure 2. The fitting curves of the energy dispersive spectroscopy spectrum of Co-N_4Cl-C catalyst.



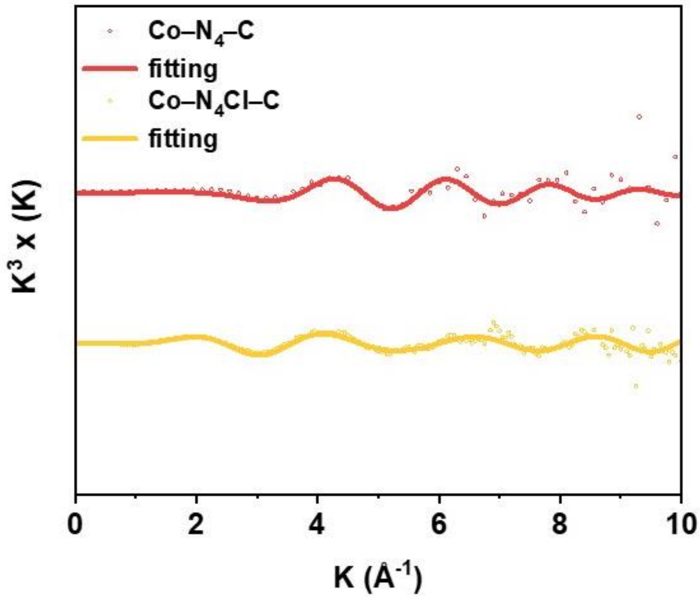
Supplementary Figure 3. XRD patterns of Co-N_4-C, Co-N_4Cl-C and NC catalysts.



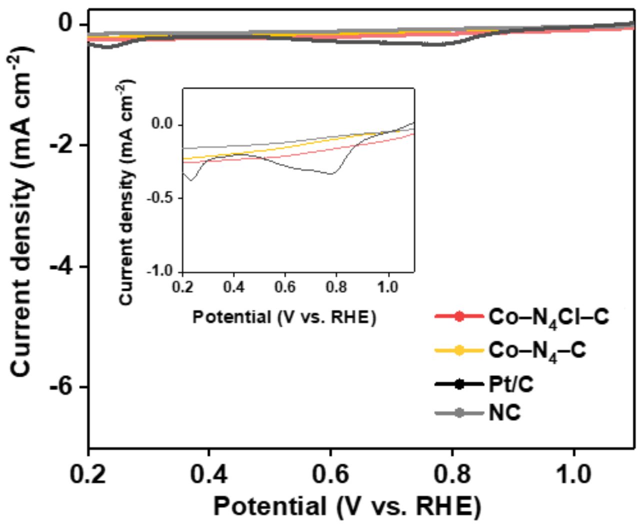
Supplementary Figure 4. Raman spectra of Co-N_4-C and Co-N_4Cl-C catalysts.



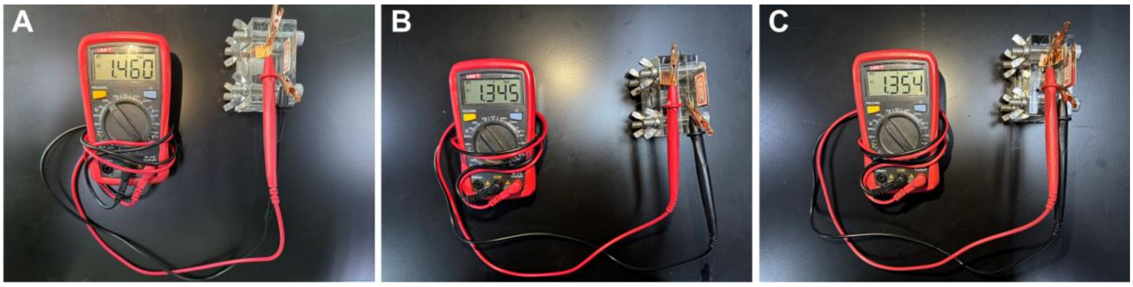
Supplementary Figure 5. Co 2*p* XPS spectra of Co-N_4-C and Co-N_4Cl-C catalysts.



Supplementary Figure 6. Extended X-ray absorption fine structure (EXAFS) fitting curves of the K-edge of Co-N_4-C and Co-N_4Cl-C catalysts at the *k*-space.

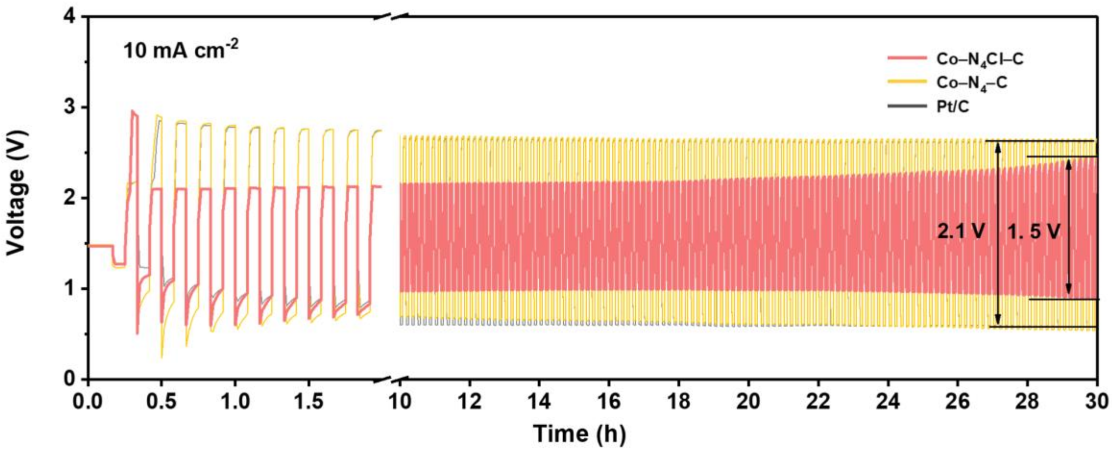


Supplementary Figure 7. Oxygen reduction reaction polarization curves of Co-N_4-C, Co-N_4Cl-C, Pt/C, and NC at a scan rate of 5 mV·s^{-1} under a rotation speed of 1,600 rpm in N_2-saturated 0.5 M NaCl electrolyte containing 1 M KOH.



Supplementary Figure 8. Photographic images of the open circuit voltage for (A) Co-N_4Cl-C-, (B) Co-N_4-C-, and (C) Pt/C-based SWZABs.

The Co-N_4Cl-C-based seawater-based zinc-air battery (SWZAB) exhibits an open-circuit voltage of 1.460 V, surpassing that of SWZABs driven by Co-N_4-C (1.345 V) and Pt/C (1.354 V). These values are in good agreement with the results measured using a workstation.



Supplementary Figure 9. Cycling performance of Co-N_4Cl-C-, Co-N_4-C- and Pt/C-based SWZABs at 10 mA·cm^{-2}.

Supplementary tables

Supplementary Table 1. Comparison of inductively coupled plasma OES spectrometer (ICP-MS) analysis for Co and Zn element in Co-N_4-C and Co-N_4Cl-C

Characterization	**ICP-MS (wt.%)for Zn**	**ICP-MS (wt.%)for Co**
Co-N_4-C	0.002	1.27
Co-N_4Cl-C	0.002	1.44

Trace amounts of Zn in the ICP-MS analysis indicate that Zn is effectively removed in Co-N_4-C and Co-N_4Cl-C.

Supplementary Table 2. Structural parameters extracted from quantitative EXAFS curve-fitting of samples using the ARTEMIS module of IFEFFIT

Sample	**Path**	***N***	**R (Å)**	**σ^2 (10^{-3}Å^2)**	**ΔE_0 (eV)**	**R-factor**
Co-N_4Cl-C	Co-N	3.6±0.5	2.03±0.01	1.58±0.04	-2.552±0.7	0.008
	Co-Cl	0.9±0.2	2.26±0.01	5.40±0.06		
Co-N_4-C	Co-N	4.1±0.3	1.88±0.01	9.84±0.04	-1.31±0.2	0.008

[a] ***N***, coordination number; [b] **R**, distance between absorber and backscatter atoms; [c] **σ^2**, Debye-Waller factor to account for both thermal and structural disorders; [d] **ΔE_0**, inner potential correction; [e] **R-factor** (%) indicates the goodness of the fit.