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Axial Chlorine Induced Symmetry-breaking Iron Single-Atom Catalyst for Electrochemical Ammonia Synthesis

Jieying Wan^a, Ji Yang^{b*}, Na Yang^c, Yifei Sun^d, Chuansheng Hu^e, Yang Zhao^f, Xiaoyan Xu^f, Haifeng Qi^g, Xiaodong Li^a, Hao Zhang^{a*}

^aState Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China.

^bCollege of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

^cSchool of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, Sichuan China.

^dState Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005 P. R. China.

^eNational Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Hefei 230026, Anhui China.

^fDalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

^gMax Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Translational Research Hub, Cardiff University, Maindy Road, Cardiff CF24 4HQ, UK.

* Corresponding authors.

Email addresses: zhang_hao@zju.edu.cn; chem.yang@xmu.edu.cn

Keywords: Electrochemical Ammonia Synthesis, Nitrate reduction, Fe-N-C, Single-atom catalyst, Symmetry-breaking

Abstract

Electrochemical nitrate reduction reaction (NO_3^- RR) presents a sustainable method for ammonia synthesis. Single-atom catalysts possessing the symmetric planar four-ligand structure (M-N_4) serve as advantageous catalytic active sites for NO_3^- RR. However, the inherent extreme symmetry of the standard M-N_4 structure limits the reaction kinetics. Herein, we introduce a symmetry-breaking iron single-atom catalyst coordinated with axial chlorine on nitrogen-doped carbon (Cl-Fe-NC) for NO_3^- RR. Cl-Fe-NC exhibits a 99.4% ammonia Faradaic efficiency (FE) at -0.28 V vs. RHE with a $9396.7 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{cm}^{-2}$ yield rate at -0.68 V vs. RHE, remarkable surpassing Fe-NC ($<80\%$, $4330.9 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{cm}^{-2}$ at the same potential). Operando Synchrotron Radiation Fourier transform infrared (SR-FTIR) spectroscopy confirms that key intermediates, such as $^*\text{NO}$, $^*\text{NO-H}_x$, and $\sigma(\text{N-H})$, are formed. Density functional theory (DFT) calculations attribute the optimized free energy of NO_3^- RR intermediates to the axial chlorine design, reducing the potential determination step barrier energy by up to 0.66 eV. The presence of axial Cl atoms modulates the symmetry of the single Fe atom, enhancing the adsorption of nitrate ions and the enrichment of critical intermediates during NO_3^- RR, while inhibiting the hydrogen evolution reaction (HER). This discovery opens avenues for boosting electrochemical ammonia synthesis through precise modulation of atomic structures by doping heteroatoms for symmetry-breaking.

Introduction

Ammonia (NH_3) plays a vital role in various industries,^{1,2} including agriculture, textiles, pharmaceuticals, dyes and plastics.³⁻⁷ It is also increasingly recognized as a potential carbon-free energy carrier, boasting a high energy density (4.3 kWh kg^{-1}) and significant hydrogen storage capacity (17.7%).⁸⁻¹¹ However, the conventional Haber-Bosch ammonia synthesis process necessitates harsh operating conditions ($\sim 500^\circ\text{C}$, $150\text{--}300 \text{ atm}$),¹²⁻¹⁶ consuming $1\text{--}2\%$ of global energy and contributing up to 1% of CO_2 emissions.¹⁷⁻²¹ Electrochemical nitrogen (N_2) reduction reaction (NRR) presents a compelling alternative,²² utilizing water as a sustainable proton source of and renewable energy such as solar or wind for NH_3 synthesis under mild conditions.²³ Nevertheless, NRR suffers from a low NH_3 yield rate ($10^{-6}\text{--}10^{-4} \text{ mol h}^{-1} \text{cm}^{-2}$) due to the limited solubility of N_2 and the stability of the $\text{N}\equiv\text{N}$ bond (941 kJ mol^{-1}).

^{17,24} In contrast, nitrate (NO_3^-) offers excellent solubility and a significantly lower dissociation energy for $\text{N}=\text{O}$ (204 kJ mol^{-1}). ²⁵ Additionally, apart from naturally abundant sources such as flue gas and pollutant water, NO_3^- can be efficiently derived from air using technologies such as plasma conversion. ^{18,26–29} Recent studies have increasingly focused on addressing the bottleneck of nitrate reduction, including sustainable supply of nitrate and mass transfer limitations of nitrate at higher current density. ^{30,31} Therefore, electrochemical NO_3^- reduction reaction ($\text{NO}_3^- \text{RR}$) emerges as a prospective avenue for NH_3 production. ³²

Single-atom catalysts (SACs), particularly those comprising $\text{M-N}_x\text{-C}$ (where M represents Fe, Co, Cu, among others), have attracted significant attention due to the unparalleled atom utilization efficiency and unique electronic configurations. ^{5,25,33} Notably, research has revealed that the symmetric planar four-ligand structure (denoted as the M-N_4) constitutes the most effective catalytic active site within M-N_x systems. ^{4,34,35} Nevertheless, the standard arrangement of four coordinating nitrogen atoms surrounding the active metal center leads to a symmetrical electronic density distribution, impeding the adsorption and activation of intermediates, and subsequently constraining the kinetics of catalytic activity. ³⁶ Additionally, the competition between NO_3^- and proton (H^+) on the active site and the concurrent hydrogen evolution reaction (HER) significantly diminish the FE of NO_3^- to NH_3 conversion. ³⁷

In this work, we introduce a symmetry-breaking strategy for the Fe-N_4 active site in $\text{NO}_3^- \text{RR}$ by coordinating axial chlorine to a Fe SAC on nitrogen-doped carbon (Cl-Fe-NC). In comparison to O ($2s^2 2p^4$), S ($3s^2 3p^4$), P ($3s^2 3p^3$), which have been investigated as doping heteroatoms ^{36,38–40}, Cl ($1s^2 2s^2 2p^6 3s^2 3p^5$) possesses more valence electrons and increases the density of states near the Fermi level ⁴¹. This characteristic is anticipated to significantly influence the adsorption and activation of intermediates during $\text{NO}_3^- \text{RR}$. The Cl-Fe-NC exhibits an FE of up to 99.4% for NH_3 at -0.28 V vs. reversible hydrogen electrode (RHE) in an alkaline solution. Furthermore, it achieves an exceptional NH_3 yield rate of $9396.7 \mu\text{g}_{\text{NH}_3} \text{ h}^{-1} \text{ cm}^{-2}$ at -0.68 V vs. RHE, significantly surpassing most reported $\text{NO}_3^- \text{RR}$ catalysts so far. Synchrotron radiation Fourier transform infrared (SR-FTIR) spectroscopy and density functional theory (DFT) calculations unravel that the introduction of Cl decreases the electron density of the Fe center, thereby increasing its oxidation state and inhibiting HER. Importantly, the axial coordinated Cl breaks the symmetry of the Fe-N_4 active site and therefore promotes the

adsorption and activation of intermediates during NO_3^- RR, leading to the superior NO_3^- RR performance.

Results and Discussion

Synthesis and characterization of Cl-Fe-NC SAC

The Cl-Fe-NC SAC was prepared using a facile pyrolysis strategy, involving mixing precursors, including FeCl_3 , $\text{NH}_2\text{OH}\cdot\text{HCl}$, and $\text{C}_6\text{H}_{12}\text{O}_6$, followed by pyrolysis at 800 °C to obtain the Cl-Fe-NC SAC (Methods).⁴² Fe-NC SAC (without chlorine) and NC (nitrogen-doped carbon) catalysts were also prepared using a similar method for comparison. Low-magnification transmission electron microscopy (TEM) images of Cl-Fe-NC SAC and Fe-NC SAC indicate a well-defined porous structure (Figure S1 in Supporting Information), with no nanoparticles observed on the carbon frameworks. Analysis of the pore structure using the N_2 sorption method indicates a Brunauer-Emmett-Teller (BET) surface area of 279.3 m^2/g for the Cl-Fe-NC SAC and 286.4 m^2/g for Fe-NC SAC (Figure S2). Powder X-ray diffraction (XRD) patterns of Cl-Fe-NC SAC and Fe-NC SAC show only low-crystallinity graphitic properties, suggesting the absence of metallic crystallites, without significant signal observed for metallic Fe species (Figure S3). Additionally, elemental maps of the Cl-Fe-NC SAC obtained from energy-dispersive X-ray spectroscopy (EDS) indicate a uniform distribution of Fe, N, Cl, and C elements throughout the N-doped carbon structure (Figure 1a-1b). Similarly, Fe-NC SAC presents an excellent dispersion of atomic species (Figure S4). Furthermore, high-angle annular dark-field scanning TEM (HAADF-STEM) images directly indicated the dispersion of isolated Fe atoms on the porous carbon, which are clearly identifiable as bright dots marked by red circles in Figure 1c. In various areas of Cl-Fe-NC SAC and Fe-NC SAC, no Fe clusters or nanoparticles are detected. (Figures S5-S6). Moreover, the Fe metal loading of Cl-Fe-NC SAC and Fe-NC SAC is estimated to be 1.7 wt% and 1.8 wt%, respectively, according to inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis.

The chemical and atomic structures of the catalysts were further analyzed using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). As shown in the N 2p XPS spectrum (Figure 1d), the high-resolution N 1s spectrum of the catalysts all exhibits five N peaks in the same types, attributed to Fe- N_x (399.7 eV), pyridinic-N (398.3 eV), pyrrolic-N (400.6 eV), graphitic-N (401.7 eV), and oxidized-N (403.6 eV).⁴¹ The high-resolution Cl 2p

XPS spectrum of Cl-Fe-NC SAC and Fe-NC SAC reveals the presence of Fe-Cl (198.09 eV: $2p_{3/2}$ and 199.8 eV: $2p_{1/2}$) and C-Cl (202.2 eV) bonds (Figure 1e). Additionally, the Fe 2p spectrum of Cl-Fe-NC SAC (Figure 1f) displays four peaks at 710.8 eV, 715.1 eV, 724.4 eV, and 730 eV, corresponding to the Fe $2p_{3/2}$ orbitals of Fe^{2+} and Fe^{3+} , and the $2p_{1/2}$ band with Fe^{2+} and Fe^{3+} species, respectively.³⁶ This confirms the coexistence of Fe^{2+} (42.3%) and Fe^{3+} (57.7%). In addition, the XPS spectrum of Fe-NC SAC (Figure 1f) reveals approximately 56.6% of Fe^{2+} and 43.4% of Fe^{3+} . These results demonstrate that the introduction of Cl into the Fe-NC system results in an increase in the valence state of Fe in Cl-Fe-NC SAC, indicating electron transfer to Cl and a slight increase in the oxidation state of Fe.

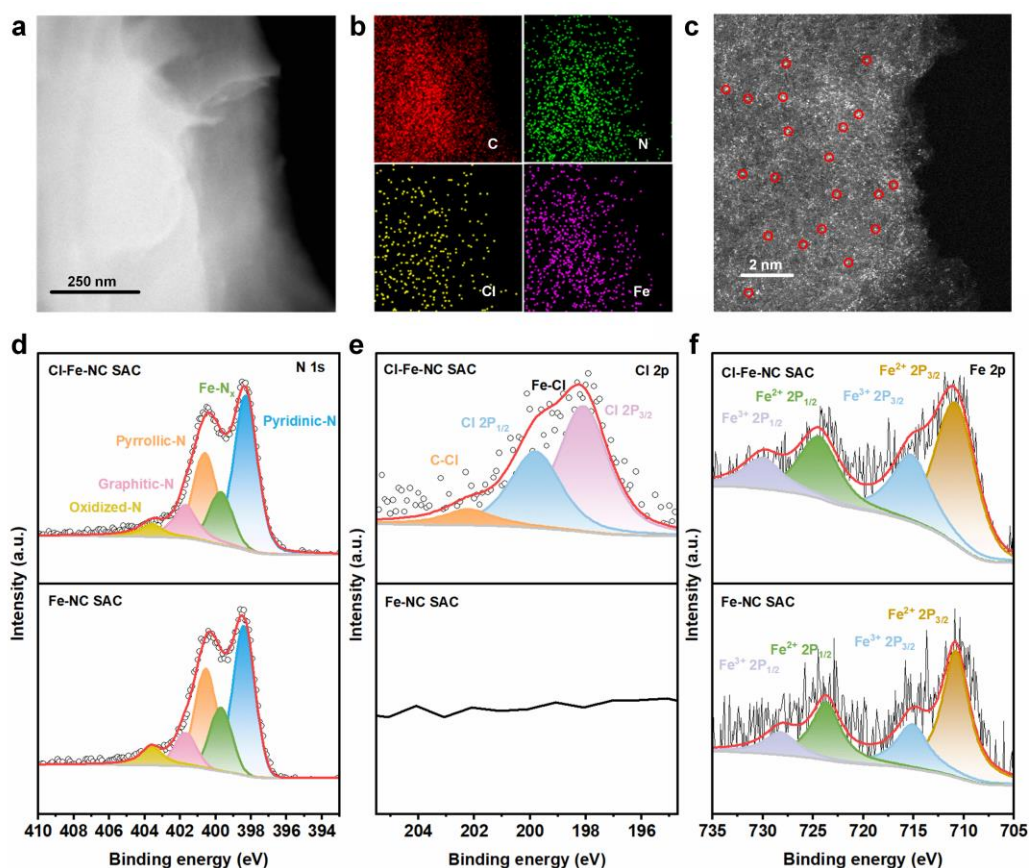


Figure 1 (a) Scanning transmission electron microscopy (STEM) image and (b) corresponding element maps of C, N, Cl, and Fe. (c) Atomic-resolution HAADF-STEM image. XPS characterization of Cl-Fe-NC SAC: (d) spectrum in the N 1s region fit to contributions of different N species, (e) spectrum in the Cl 2p region fit to contributions of different oxidation states of Cl, and (f) spectrum in the Fe 2p region fitted to contributions of different oxidation states of Fe.

Local electronic and atomic structure of Cl-Fe-NC SAC

To delve deeper into the interfacial structure and coordination environment for Fe species at

the atomic scale, Fe K-edge X-ray absorption near-edge structure (XANES) analysis of Cl-Fe-NC SAC was performed (Methods), revealing a lower pre-edge energy of Fe₂O₃ (+3 oxidation state), yet higher than that of Fe (0 oxidation state), FeO (+2 oxidation state), and Fe-NC SAC. This suggests that the oxidation state of Fe single atoms falls between Fe²⁺ and Fe³⁺, surpassing that of Fe-NC SAC (Figure 2a), a finding consistent with XPS. Furthermore, it elucidates that the isolated single Fe atoms of Cl-Fe-NC SAC carry partially positive charges, mainly attributed to the electronic effects from the axial Cl.^{36,41,43}

The corresponding Fourier-transferred (FT) *k*³-weighted extended X-ray absorption fine structure (EXAFS) spectrum (Figure 2b) was examined to glean further insights into the local coordination structure. It shows one dominant peak of Cl-Fe-NC SAC at 1.5 Å, akin to Fe-NC SAC, indicative of Fe-N coordination at the first shell. The disappearance of Fe-Fe interaction peak at 2.2 Å in both samples signifies the presence of Fe species in an isolated single-atom state rather than as Fe clusters or nanoparticles. These findings affirm that Fe atoms are atomically dispersed in the nitrogen-doped carbon (NC), in line with the HAADF-STEM and XRD results.

Furthermore, the wavelet transform (WT), known for its robust resolution in both *k* and *R* spaces, was applied to the Fe K-edge EXAFS oscillations to further underscore the atomic dispersion of Fe species.^{4,44} As presented in Figure 2c, the WT contour maximum at 3.6 Å⁻¹ for Cl-Fe-NC SAC might suggest the presence of Fe-N and Fe-O. The 0.2 Å⁻¹ difference between the maximum for Cl-Fe-NC SAC (3.6 Å⁻¹) and Fe-NC SAC (3.4 Å⁻¹) may stem from the longer value of the change in the coordination environment of the central Fe atoms due to the Fe-Cl coordination. Simultaneously, compared with the WT plots of Fe foil, no intensity maximum belonging to Fe-Fe contribution (7.9 Å⁻¹) can be observed in both Cl-Fe-NC SAC and Fe-NC SAC, ruling out the existence of metal-derived crystalline structures.

To further characterize the valence state of Fe by the XANES spectra at the Fe K-edge, a comparison of *E*₀ values (the first inflection point) has been presented, showing that Cl-Fe-NC and Fe-NC have *E*₀ of 7124.5 eV and 7124.1 eV, respectively, which fall between those of the FeO and Fe₂O₃ references (Table S1). It indicates the coexistence of Fe²⁺ and Fe³⁺ in Cl-Fe-NC and Fe-NC, which is in line with the XPS analysis. Fe K-edge XANES was further employed

to examine the valence of iron. Typically, the oxidation states of Fe, determined by the first inflection point of the derivative spectrum, exhibit a linear dependence on the position of the K-edge (Table S1). Therefore, a linear-fit curve was established using Fe foil, FeO, and Fe₂O₃, which represent iron oxidation states ranging from 0 to +3. The absorption threshold position for Cl-Fe-NC was located between FeO and Fe₂O₃ (Figure 2d),⁴⁵ indicating a valence state between +2 and +3 (calculated as +2.98). Similarly, the valence of Fe in Fe-NC was determined to be +2.84.

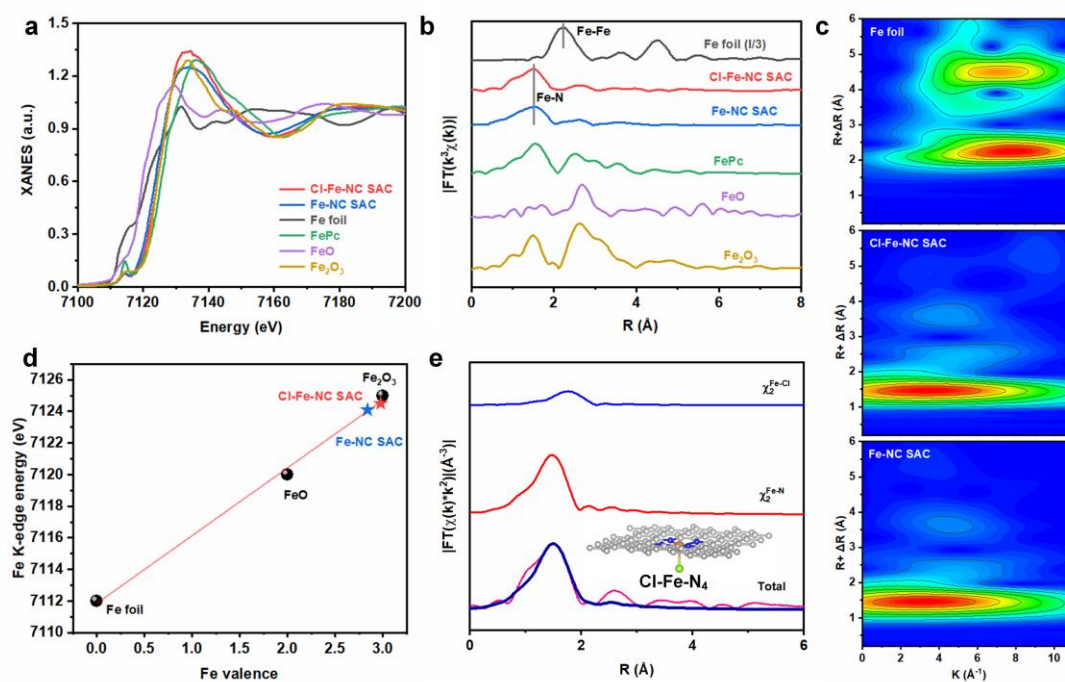


Figure 2 (a) XANES spectra at the Fe K-edge of the Cl-Fe-NC SAC and Fe-NC SAC. (b) FT K³-weighted $\chi(k)$ -function of the EXAFS spectra at the Fe K-edge of the Cl-Fe-NC SAC and Fe-NC SAC. (c) Wavelet transform EXAFS of the k³-weighted k space for Cl-Fe-NC SAC and Fe-NC SAC. (d) Linear fitting curve of Cl-Fe-NC SAC, Fe-NC SAC and reference materials from corresponding Fe K-edge XANES spectra. (e) EXAFS analysis of Cl-Fe-NC SAC at R space.

To further probe the coordination configuration of Cl-Fe-NC SAC and Fe-NC SAC, EXAFS fitting was conducted to obtain the structural parameters (Figure 2e, Figure S7 and Table S2). The EXAFS spectrum of Cl-Fe-NC SAC was initially analyzed by considering two backscattering pathways including Fe-N and Fe-Cl. The optimal results clearly show that the primary peak at 1.51 Å corresponds to the first-shell Fe - N coordination, while the shoulder peak at 1.75 Å arose from Fe-Cl contribution (Figure 2e).⁴⁵ The coordination numbers for N and Cl atoms were 4.1 and 0.6 at distances of 1.98 Å and 2.25 Å, respectively, confirming the

presence of axial Cl in the Cl-Fe-N₄ coordination complex. Nevertheless, only Fe-N coordination exists in Fe-NC SAC, with a coordination number of 4.3.

Electrocatalytic nitrate reduction performance of Cl-Fe-NC SAC

The NO₃⁻RR performance was systematically investigated by employing a customized three-electrode H-type electrolytic cell (Methods). Experiments were performed in 1 M KOH solution with 0.1 M KNO₃ electrolyte over different catalysts (NC, Fe-NC SAC, Cl-Fe-NC SAC). Each catalyst was held at a specific potential for 0.5 h, and the produced ammonia was measured by ultraviolet-visible (UV-Vis) spectrophotometry based on the indophenol blue spectrophotometric method (IBS) (Figure S8; see “Methods”). Other products, such as NO₂⁻ and H₂, were quantified by UV-Vis (Figure S9) and gas chromatography (GC).

As presented in the linear scanning voltammetry (LSV) curves in Figure 3a, the pure NC exhibits a current density of only <40 mA cm⁻² under the investigated potentials, notably lower than that of Cl-Fe-NC SAC and Fe-NC SAC, suggesting significant activity of the metal sites for NO₃⁻ reduction. Notably, Cl-Fe-NC SAC demonstrates a much higher current density compared to Fe-NC and NC, reaching up to approximately ~170 mA cm⁻² at -0.8 V vs. RHE (only ~35 mA cm⁻² for NC and ~105 mA cm⁻² for Fe-NC at the same potential). Consistently, Cl-Fe-NC SAC exhibits high selectivity and superior yield rate for NH₃, as shown in Figure 3b-3c. A maximal FE of up to ~99.4% for NH₃ can be reached at -0.28 V vs. RHE over Cl-Fe-NC SAC. Despite a decreasing trend from -0.28 V to -0.78 V vs. RHE, the FE for NH₃ of Cl-Fe-NC SAC can still be maintained at >95 % from -0.28 V to -0.48 V vs. RHE. In comparison, the FE for NH₃ is significantly lower for Fe-NC SAC, approximately 20% lower than that for Cl-Fe-NC SAC under the studied potentials (Figure 3b). The parasitic HER can be significantly inhibited over Cl-Fe-NC SAC, as evidenced by the substantially reduced FE for H₂ compared to Fe-NC SAC (e.g., 23.9% for Cl-Fe-NC and 44.9% for Fe-NC at -0.68 V vs. RHE, see Figure S10). This inhibition can be ascribed to the transfer of electrons from atomically Fe active sites to the axial Cl and a slightly elevated oxidation state of Fe, resulting in the inhibition of proton adsorption.³⁶

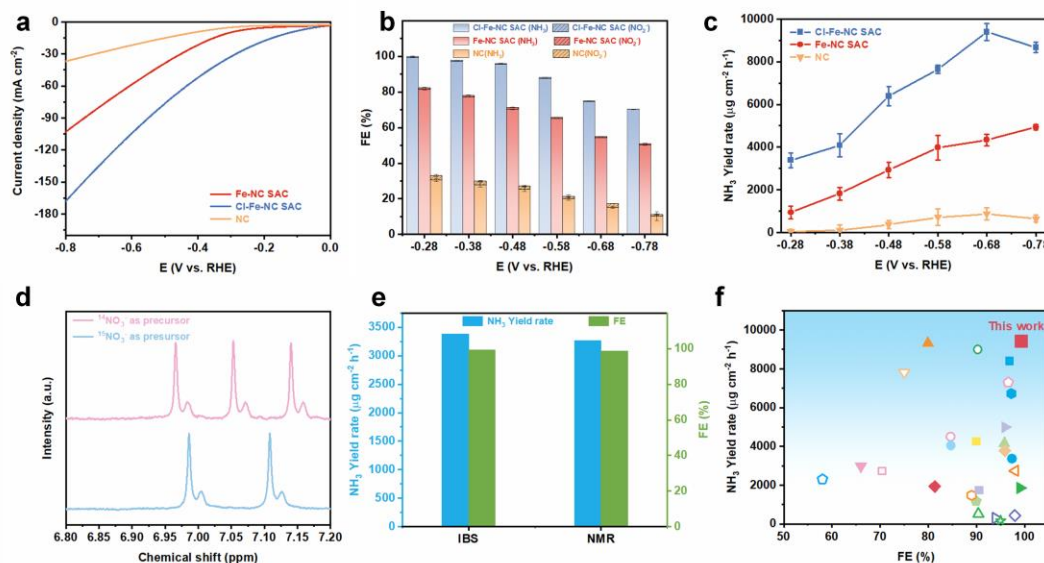


Figure 3 (a) LSV curves, (b) FE for NH₃ and NO₂⁻, and (c) NH₃ yield rates at different applied potentials for Cl-Fe-NC SAC, Fe-NC SAC, and NC in 1 M KOH electrolyte containing 0.1 M KNO₃. (d) ¹H NMR spectra of the post-reaction electrolyte after 1 h NO₃⁻RR at -0.38 V vs. RHE in 1 M KOH using 0.1 M K¹⁵NO₃⁻ or K¹⁴NO₃⁻ as the precursor. (e) ¹⁵NH₃ yield rate and FE for NH₃ of Cl-Fe-NC SAC at -0.28 V vs RHE in 1 M KOH and 0.1 M K¹⁵NO₃ determined by IBS and ¹H NMR. (f) Comparison of the NO₃⁻RR performance of Cl-Fe-NC SAC in this work with state-of-the-art literature results in terms of NH₃ yield rate and FE for NH₃.^{4,5,33,36,46–67} Hollow symbols represent single-atom catalysts, while solid symbols represent nano-particle catalysts.

The NH₃ yield rates of NC, Fe-NC SAC, and Cl-Fe-NC SAC under different potentials are plotted in Figure 3c. Firstly, ammonia yield rates of Cl-Fe-NC catalysts synthesized at pyrolysis temperatures of 600°C, 700°C, and 800°C were all evaluated (Figure S11). The results demonstrate that the catalytic activity of Cl-Fe-NC (pyrolysis temperature of 800 °C) is markedly higher to those of the other catalysts synthesized at lower temperatures (600 °C and 700 °C). In figure 3c, a relatively low NH₃ yield rate of 869.4 μg_{NH₃} h⁻¹ cm⁻² was obtained on NC at -0.68 V vs. RHE, while Fe-NC largely enhanced the yield rate of NH₃ to a maximum of 4936.3 μg_{NH₃} h⁻¹ cm⁻² at -0.78 V vs. RHE (only 650.9 μg_{NH₃} h⁻¹ cm⁻² for NC at the same potential). Introducing axial Cl into Fe-NC SAC further significantly improved the NH₃ yield rate to a maximum of up to 9396.7 μg_{NH₃} h⁻¹ cm⁻² at -0.68 V vs. RHE, which is 2.2 times and 10.8 times higher than Fe-NC SAC and NC, respectively. These results confirm the superior NO₃⁻RR activity of Cl-Fe-NC SAC and the limited reactivity of the defective carbon. To further understand the results, electrochemical active surface areas (ECSAs) of Fe-NC SAC and Cl-Fe-NC SAC were determined using a cyclic voltammetry method⁴⁶ and presented in Figure

S12 (Methods). Consistently, the estimated ECSA for Cl-Fe-NC SAC is up to 78 cm², remarkably higher than that of Fe-NC SAC (42.5 cm²).

¹⁵N isotopic labeling measurements were conducted to verify the origin of NH₃ in NO₃⁻RR⁶⁸ and the ¹H nuclear magnetic resonance (NMR) spectra are shown in Figure 3d (Methods). Typical double peaks of ¹⁵NH₄⁺ were observed when adopting ¹⁵NO₃⁻ as the N source, while using ¹⁴NO₃⁻ led to a triplet peak corresponding to ¹⁴NH₄⁺. This clearly indicates that the nitrogen in the catalyst does not participate in the reaction, and the produced NH₃ is solely derived from the electroreduction of nitrate, ruling out contamination. Moreover, to ensure the accuracy of the employed quantification methods (calibration curve shown in Figure S13), both the FE and NH₃ yield rate at -0.28 V vs. RHE on Cl-Fe-NC SAC were verified by NMR using the ¹⁵N isotope labeled nitrate as the reactant, showing consistency with the results from the IBS method (Figure 3e). Moreover, post-reaction spectra of the catholyte from a 1 h reaction conducted over Cl-Fe-NC in 1 M KOH and 0.1 M KNO₃ without applied potentials closely resemble those of the blank 1 M KOH solution (Figure S14). Only a trace amount of NH₃ (0.006 mg_{NH3} h⁻¹ cm⁻²) was detected with IBS at -0.28 V vs RHE after 1 h reaction (Figure S14). These results demonstrated that NH₃ originates from NO₃RR and is not from contamination by the precursors or environment.

A comparison of the results with latest reports in Figure 3f exhibits that the NO₃⁻RR performances of Cl-Fe-NC SAC in this work outperforms most previous works in terms of both FE and NH₃ yield rate. A more detailed comparison is additionally tabulated in Table S3.

The stability of Cl-Fe-NC SAC was examined through a consecutive 50-cycle test at -0.28 V vs. RHE in an alkaline electrolyte. Figure 4a demonstrates that the NH₃ yield rate is stable at approximately 3657.3 μg_{NH3} h⁻¹ cm⁻² with a fluctuation of only 161.3 μg_{NH3} h⁻¹ cm⁻², and the FE remains centered at up to 94.7%, suggesting the reactivity stability of the developed catalyst. Post-stability test, XPS analysis was further performed to assess the chemical states of the metallic elements in Cl-Fe-NC SAC, as presented in Figure 4b and Figures S15-S16, respectively. High-resolution XPS spectra for Fe 2p of Cl-Fe-NC were obtained. High-resolution XPS spectra of the Fe 2p region revealed two broad peaks at 710 eV and 724 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively (Figure S16). Additionally, the Fe 2p region,

deconvoluted into contributions from various oxidation states of Fe, closely resembled the pretest state, indicating minimal changes in the chemical states of Fe. The Cl 2p and N 1s regions of the sample after the test also demonstrate a close resemblance to the pretest state, indicating that the chemical states of Cl and N elements remain similar. The element contents of Cl-Fe-NC SAC, such as Fe and Cl, analyzed by XPS characterization, are well-maintained after the stability test as well, as shown in Table S4. STEM imaging and EDS mapping results of Cl-Fe-NC SAC after the stability test revealed uniform dispersion of Fe and Cl elements on the NC with no evidence of metal nanoparticle or cluster formation (Figure 4c – 4d). Additionally, HAADF-STEM images of Cl-Fe-NC SAC after the stability test (Figure 4e and Figure S17) show single metal atoms well-dispersed across the catalyst. These results show that the element content (Fe, Cl, and N) is effectively preserved after the stability test.

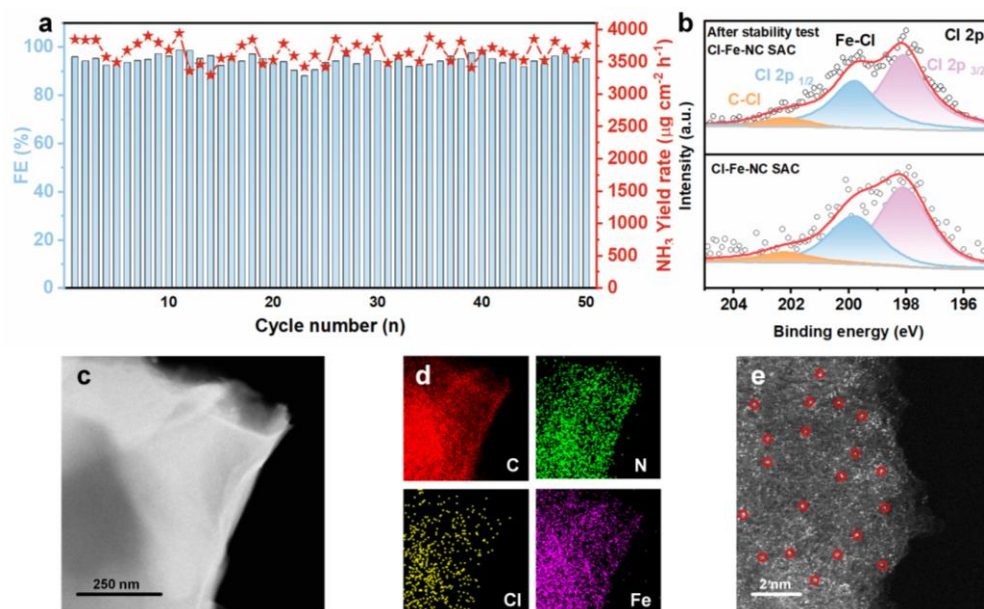
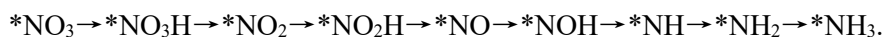


Figure 4 (a) Stability test of the Cl-Fe-NC over 50 consecutive cycles at -0.28 V vs. RHE. (b) The spectrum in the Cl 2p region fit to contributions of different oxidation states of Cl in fresh Cl-Fe-NC and Cl-Fe-NC after the stability test. (c) STEM image and element maps of (d) C, N, Cl, and Fe. (e) Atomic-resolution HAADF-STEM image of Cl-Fe-NC after the stability test.

Operando SR-FTIR measurements and electrocatalytic mechanism of NO_3^- RR

Operando synchronous radiation infrared spectroscopy (SR-FTIR) measurements over Fe-NC SAC and Cl-Fe-NC SAC were employed to delve deeper into the mechanisms of NO_3^- RR, via the *in-situ* detection of intermediates and reaction products (Methods). The operando cell and experimental setup are depicted in Figures S18-S19. Figure 5a shows the SR-FTIR spectra

collected during NO₃⁻RR in a 1 M KOH electrolyte containing 0.1 M KNO₃, spanning a potential range from -0.28 to -0.78 V vs. RHE on Cl-Fe-NC SAC. Intriguingly, the reduction of NO₃⁻ initiates readily at -0.28 V vs. RHE, evidenced by the emergence of distinctive negative peaks associated with various nitrogen intermediates. In particular, the band at 1250 cm⁻¹ signifies the *N-O stretching vibration, indicative of deoxygenation steps during NO₃⁻ electroreduction.⁶⁹ In addition, bands at 1355 cm⁻¹ and 1410 cm⁻¹ denote the stretching vibration mode of *NO-H_x, further corroborating the deoxygenation steps during NO₃⁻RR.⁶⁹ Furthermore, the appearance of the σ(N-H) bending mode of NH_x species at 1479 cm⁻¹ and 1683 cm⁻¹^{69,70} suggests substantial hydrogenation for NH₃ evolution after deoxygenation. Similar characteristic SR-FTIR fingerprints are observable for Fe-NC SAC, including *NO, *NOH, and NH_x species (Figure S20), indicating analogous reaction pathways between Fe-NC SAC and Cl-Fe-NC SAC. Based on the operando SR-FTIR results, it is postulated that *NO and *NOH serve as primary intermediates, with NH₃ as the final product during NO₃⁻RR. It can thus be inferred that the reaction pathway involves the stepwise formation of NH₃, initially via a series of deoxygenation and hydrogenation reactions:



Drawing from the active site structures of the catalysts and the discerned fingerprint of various intermediates through operando SR-FTIR, we embarked on DFT calculations to delve deeper into the electron-regulated effect of the axial Cl atom on the catalytic activity of Cl-Fe-NC SAC (Methods). Firstly, the free energy for each step of NO₃⁻RR on Cl-Fe-NC SAC and Fe-NC SAC was computed (Figure 5b-5c and Figure S21).³³ The *NO₃ by hydrogenation to form *NO₃H, progressing stepwise to form *NO₂, *HONO, *NO and *NOH species, subsequently chemically adsorbing on the single Fe site with a decrease in free energy (*NOH → *NH → *NH₂ → NH₃, every step ΔG ≤ 0 eV). For Fe-NC SAC, the hydrogenation of *NO to *NOH is the potential determination step (PDS), necessitating the surmounting of a certain ΔG (0.68 eV). In contrast, on Cl-Fe-NC SAC, the protonation of *NO₃ to *NO₃H serves as the PDS, requiring a remarkably lower free energy change value (ΔG) of only 0.15 eV. This finding furnishes compelling evidence for the markedly enhanced NO₃⁻RR activity of Cl-Fe-N₄, as discussed above.

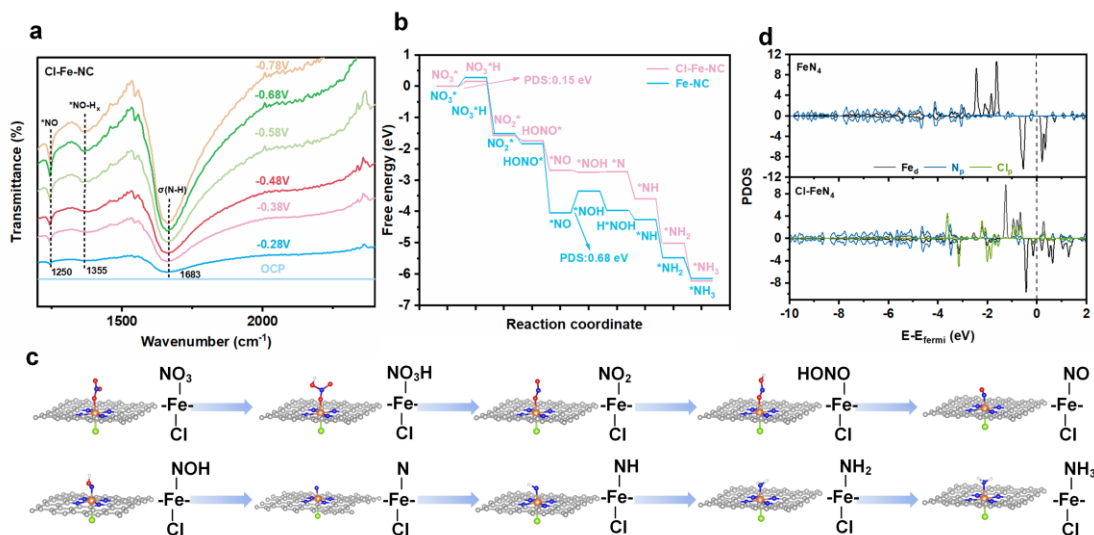


Figure 5 (a) Operando SR-FTIR spectra of the Cl-Fe-NC SAC at various applied potentials in 1 M KOH electrolyte containing 0.1 M KNO₃. (b) Gibbs free energy diagrams for NO₃⁻ conversion to NH₃ on Cl-Fe-NC SAC and Fe-NC SAC. (c) Optimized geometries of NO₃⁻RR intermediates for each elementary step of Cl-Fe-NC SAC. (d) Partial density of state (PDOS) of Cl-Fe-NC SAC and Fe-NC SAC.

Moreover, we also examined the adsorption free energy of H^{*} (ΔG_H) on the surface of the single-Fe-atom catalyst, a competitive step pivotal in limiting electrochemical nitrate reduction. Intriguingly, the ΔG_H value on the Cl-Fe-N₄ surface (0.82 eV) was significantly more positive than that on Fe-N₄ (0.35 eV), as shown in Figure S22. This observation underscores the inhibiting effect of Cl-Fe-NC SAC on H₂ production, therefore facilitating the attainment of high FE. Consistent with the XPS and XAS results, the axial Cl in Cl-Fe-NC SAC regulates a lower electron density at the single Fe site compared to Fe-NC SAC, leading to the mitigation of H^{*} adsorption. Additionally, analysis of the partial density of states (PDOS, Figure 5d and Figure S23) reveals that due to the regulation by axial Cl, the 3d_{Fe} orbit electron of Cl-Fe-N₄ aligns closer to the Fermi energy level ($E-E_{\text{fermi}}=0$ eV) relative to Fe-N₄, especially the d_{xz} of 3d_{Fe} orbital. This alignment is conducive to charge transfer between the Fe active site and the adsorption of NO₃⁻RR intermediates, thus resulting in a lower PDS value (Figure 5d). Remarkably, the substantial overlap of the peaks of 3d_{Fe} and 2p_{Cl} orbits underscores a robust interaction electronic state. Therefore, the axial Cl atom assumes a pivotal role in breaking symmetry in Cl-Fe-NC SAC, effectively modulating the electron distribution of Fe active center.

The inherent catalytic activity of electrocatalysts is closely associated with the electronic structure of Fe active sites. As shown in Figure S24, the charge density difference shows charge

distribution between $^*\text{NO}_3$, $^*\text{NO}_2$ of Cl-Fe-NC SAC, Fe-NC SAC. Upon the bare surface, during the adsorption of $^*\text{NO}_3$, the Cl-Fe-N₄ configuration exhibits a relatively weaker electron depletion on the Fe single site (Charge value of Bader charge, $\Delta Q = -1.212 - (-1.145) = -0.67$ e) compared to the Fe-N₄ configuration ($\Delta Q = -1.228 - (-1.141) = -0.87$ e), resulting in a steady charge fluctuation of the center Fe in the Cl-Fe-N₄ configuration (Figure S24). Furthermore, the axial coordinated Cl embodies a charge fluctuation, effectively serving as an electron reservoir that can supply and discharge electrons. Consequently, the introduction of axial Cl for synergistic coordination serves to stabilize the local charge variation of the active center Fe atom, thereby augmenting the catalytic activity for the NO_3^- RR process.

Conclusions

In conclusion, we introduced a symmetry-breaking iron single-atom catalyst coordinated with axial chlorine on nitrogen-doped carbon for boosting the electrochemical conversion of nitrate to ammonia. Rigorous characterization techniques such as HAADF-STEM, XPS, and XAS analysis confirmed the homogeneous dispersion of Fe and Cl species and elucidated the coordination environment. Benefiting from the rational design of atomic-level active sites and the symmetry-breaking effect induced by the axial chlorine coordination, Cl-Fe-NC achieved an outstanding NH_3 yield rate of $9396.7 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{cm}^{-2}$ and an excellent NH_3 FE of up to 99.4%. Additionally, operando SR-FTIR spectroscopy was performed, identifying key intermediates that are helpful in elucidating the reaction pathways of NO_3^- RR. Supported by DFT calculations, the outstanding activity of Cl-Fe-NC can be attributed to the facilitated adsorption of nitrate ions and the enrichment of crucial intermediates during NO_3^- RR, attributable to the symmetry-breaking effect resulting from the axial chlorine design. The proposed strategy of symmetry-breaking holds promise for advancing research in ammonia electrosynthesis and other electrochemical conversion processes, opening avenues for further exploration and development in this field.

Methods

Materials and Chemicals. Ultra-pure water (H_2O , $18.2 \text{ M}\Omega \cdot \text{cm}$), hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, 99.99 %, Aladdin), urea ($\text{CO}(\text{NH}_2)_2$, 98 %, Aladdin), iron acetate ($\text{Fe}(\text{Ac})_2$, 98 %, Aladdin), glucose (99.5 %, RHAWN), anhydrous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.7 %, Aladdin).

Shanghai Chemical Reagents), ferric chloride (FeCl_3 , 98 %, Shanghai Chemical Reagents), these reagents are used for the synthesis of Fe-N-C catalysts. The reagents used for electrochemical experiments include: KNO_3 (99 %, Shanghai Chemical Reagents), KOH (85 %, Shanghai Chemical Reagents), Nafion solution (5 wt%, Dupont), and carbon paper (SGL29bc). The reagents used for spectrophotometric NH_3 quantification include: NaOH (97%), sodium salicylate (99.5%), Sodium hypochlorite solution (6–14% active chlorine), sodium nitroferrocyanide dehydrate (99%), and NH_4Cl (99.8%), all purchased from Aladdin. The reagents used for nitrite quantification include: H_3PO_4 (99.99%, Macklin), sulfonamide (99%, Aladdin), and N-(1-naphthyl) ethyldiamine dihydrochloride (98%, Aladdin). The reagents used for the quantification of NH_3 by ^1H NMR include: $^{15}\text{N-NH}_4\text{Cl}$ (> 99 atom %, Macklin), $^{15}\text{N-nitrate}$ (99 atom %, Aladdin), maleic acid (99%, J&K), and D_2O (99.9%, Macklin).

Synthesis of Catalysts. 3 g of urea and 1.44 g of glucose were dissolved in 200 mL of H_2O and 200 mL of ethanol solution, respectively. After sonication, the resulting urea-containing aqueous solution was added to the glucose solution, followed by a rotary evaporation at 70°C for 10 hours to produce a solid powder. Subsequently, a direct pyrolysis was conducted at 900°C with 2 h at a ramping rate of $5^\circ\text{C}/\text{min}$ under an Ar inert atmosphere to obtain nitrogen-doped carbon (denoted as N-C). Fe-NC SAC was synthesized using a similar procedure, with 3 g urea, 1.44 g glucose, and 20 mg iron acetate as the precursors. Cl-Fe-NC SAC was prepared similarly as well, using 1.44 g glucose, 20 mg ferric chloride, and 3.45 g hydroxylamine hydrochloride as precursors.

Characterization. Cu K_α radiation was employed to collect XRD patterns on a PANalytical X'pert diffractometer. An EM-ARM300F STEM/TEM instrument was employed to image the atomic metal species. The atomic Fe and Mo species were imaged via TEM using a FEI Talos F200S instrument. STEM and HAADF-STEM imaging were performed on a JEOL JEM-ARM200F instrument. EDS mapping was conducted using a JEOL JEM 2100F instrument. Electron microscopy samples were fabricated by drop casting the diluted catalyst ink onto a carbon film microgrid. The IRIS Intrepid II XSP instrument (Agilent 5110) was utilized to measure the Fe content via inductively coupled plasma–optical emission spectroscopy (ICP–OES). Nitrogen adsorption–desorption isotherms were measured at -196°C using a Micromeritics ASAP 2460 apparatus (Quadrastorb SI Automate Surface Area & Pore Size

Analyzer), and the specific surface areas were calculated via the Brunauer-Emmett-Teller (BET) method. The binding energy was calibrated based on the 284.8 eV peak of carbon (C 1s), and surface element compositions were quantified by XPS using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. The BL11B beamlines at the Shanghai Synchrotron Radiation Facility (SSRF) in Shanghai, China, were utilized to acquire XAS spectra, which encompass XANES and EXAFS spectra at the Fe K-edge. Samples were compressed into 1-cm-diameter thin sheets and sealed with Kapton tape film prior to the analysis at the beamline. A Bruker 5040 4-channel silicon drift detector (SDD) was employed to record the XAFS spectra at room temperature. The Fe K-edge EXAFS spectra, as well as the XAFS spectra of the standard samples (FePC, FeO, and Fe₂O₃), were recorded in transmission mode. In the line shape and peak position of the Fe K-edge XANES spectra, slight variations were observed between two scans of a specific sample. The Athena and Artemis software packages were employed to process and analyze the spectra.

Electrochemical Test. All these electrocatalytic performances were tested in 1 M KOH and 0.1 M KNO₃ solution in an H-type cell at a CHI electrochemical workstation (CHI1140E). This H cell was separated using a proton exchange membrane (Nafion-117). The reference and counter electrodes were Pt foil with a size of 2 cm* 2 cm and Ag/AgCl with saturated KCl solution. Cyclic voltammograms (CVs) measurements within the range of -0.28 to -0.78 V vs. RHE were firstly conducted at a scan rate of 50 mV s⁻¹ for 20 cycles. Polarization LSV curves were performed from 0 to -0.8 V vs. RHE with a 10 mV s⁻¹ scan rate. I-t curves were obtained at different applied potentials with 0.1 V intervals and 1 h operating time (-0.28, -0.38, -0.48, -0.58, -0.68, -0.78 V vs. RHE). These potentials were calibrated to RHE: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \cdot \text{pH} + 0.197 \text{ V}$. The corresponding current density was analyzed by normalizing the current to the geometric area (1 cm²). The catalyst durability of Cl-Fe-NC SAC was evaluated by performing 50 electrolyses at the selected potential of -0.28 V vs. RHE.

Electrochemically Active Surface Area Measurements. The electrochemically active surface area (ECSA) of Cl-Fe-NC SAC and Fe-NC SAC evolved at -1.00 V vs. RHE for 30 min were measured by using electrochemical capacitance methods. The cyclic voltammograms during 0.05 ~ 0.15 V vs. RHE were firstly conducted with scan rate of 20, 40, 60, 80, 100, 120 mV s⁻¹. The linear slope of the scan rate as a function of current density was used to calculate the

electrochemical double-layer capacitance. The ECSA could be determined using the equation of $ECSA = C_{dl}/C_s$, in which both C_s of Cl-Fe-NC SAC and Fe-NC SAC is $88 \mu F \text{ cm}^{-2}$.⁴⁶

Quantification of Products and Calculation of FE. The current density, I_c , was calculated as follows:

$$I_c = I_m/S \quad (S1)$$

where I_m is the measured current of the cathode. Since the cathode was prepared by coating the catalyst ink onto 1 cm x 1 cm carbon paper, the area, S , was 1 cm^2 .

The FEs (%) for NH_3 and NO_2^- products were determined using the following equations:

$$FE_{\text{NH}_3} (\%) = 100 * (8 * F * C_{\text{NH}_3} * V) / (17 * Q)$$

$$FE_{\text{NO}_2^-} (\%) = 100 * (2 * F * C_{\text{NO}_2^-} * V) / (46 * Q)$$

where F is Faraday's constant (96485 C/mol), C_{NH_3} and $C_{\text{NO}_2^-}$ are the concentrations of NH_3 NO_2^- respectively, V is the catholyte volume, and Q is the total charge passing through the electrode.

NH_3 concentration was quantified using IBS method. To achieve this, three solutions (A, B, and C) were prepared. Solution A was prepared by dispersing 1.312 g NaOH and 6.404 g sodium salicylate in 100 mL H_2O . Solution B was prepared by dispersing 3.1 g NaOH and 7.5 mL of sodium hypochlorite solution in 100 mL H_2O . Solution C was prepared by dispersing 1 g sodium nitroferricyanide dehydrate in 100 mL H_2O . 50 μL of the post-reaction electrolyte was extracted and diluted with 1 M KOH to a 4 mL. Subsequently, 320 μL , 2.4 mL, and 800 μL of solution C, A, and B were added sequentially. The mixture was allowed to stand for 2 hours under ambient conditions, and its ultraviolet-visible (UV-vis) absorption spectrum was measured by a spectrophotometer (Mapada UV-3100). The calibration curve (absorbance vs. NH_3 concentration) was constructed by measuring extinction spectra of a series of standard NH_4Cl solutions to determine the NH_3 concentration in the analyte.

The Griess method was used for the detection and quantification of NO_2^- in the post-reaction electrolyte. The Griess reagent was prepared by dissolving 0.1 g of N-(1-naphthyl) ethylenediamine dihydrochloride, 1 g of sulfonamide, and 2.94 mL of H_3PO_4 in 50 mL of deionized water. The electrolyte was diluted to guarantee the nitrite concentration fell within the detection range. Subsequently, 1 mL of the Griess reagent solution was added to a mixture of 1 mL of the post-reaction electrolyte and 2 mL H_2O . After 10 minute, the absorbance of the

solution within the 500–600 nm range was measured using spectrophotometer (Mapada UV-3100). A calibration curve (absorbance vs. NO_2^- concentration) was constructed by plotting the absorbance at 540 nm as a function of NO_2^- concentration for a series of standard KNO_2 solutions to determine NO_2^- concentration in the analyte. The concentration of nitrite was determined using the established calibration curve.

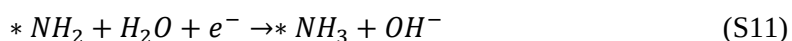
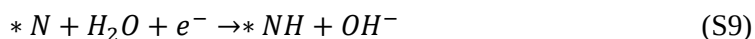
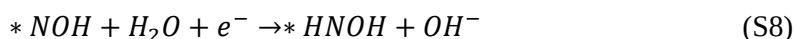
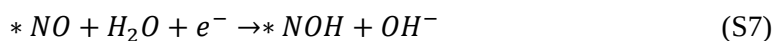
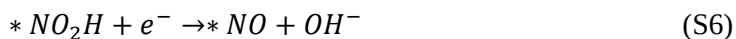
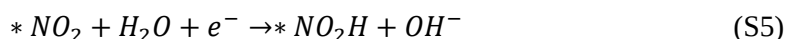
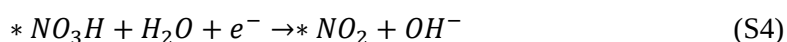
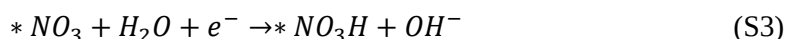
NMR and Isotopic Labeling Experiment. NH_3 generated was additionally measured by ^1H NMR spectroscopy using a 600 MHz spectrometer with D_2O as the solvent and maleic acid ($\text{C}_4\text{H}_4\text{O}_4$) as the internal standard. Initially, a specific amount of $^{15}\text{NH}_4\text{Cl}$ was dissolved in 40 mL of 1 M KOH to prepare standard solutions of $^{15}\text{NH}_4^+$ at concentrations of 50 ppm, 100 ppm, 150 ppm, 200 ppm, and 250 ppm (by mass).. To each solution, an appropriate volume of 4 M HCl was added to adjust the pH to 2–3. Subsequently, a 100 ppm standard solution of maleic acid was prepared. Each $^{15}\text{NH}_4^+$ solutions was mixed with 5 mL 100 ppm standard maleic acid. Finally, 0.5 mL of the solution was combined with 50 μL of D_2O , for ^1H NMR spectrum measurement in the NMR tube. A calibration curve (NH_3 concentration vs. NH_4^+ /maleic acid signal ratio) was developed by analyzing the ratio of the $^{15}\text{NH}_4^+$ and maleic acid peaks signals in the spectra . The ^{15}N isotope-labeling experiment was performed using a 1 M KOH and 0.1 M K^{15}NO_3 (99 atom %) electrolyte solution. For ^1H NMR analysis of the $^{15}\text{NH}_4^+$ produced by $^{15}\text{NO}_3^-$ reduction for 1 h at -0.28 V vs. RHE, a procedure similar to that used for standard spectrum measurements was employed.

Operando SR-FTIR Measurements. Operando SR-FTIR measurements were conducted at the infrared spectroscopy and microspectroscopy beamline (BL01B) of the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China, utilizing a custom-made cell reflection infrared setup.³⁶ A Bruker Vertex 70 V/s FTIR spectrometer, equipped with a LN_2 - MCT detector, was used to acquire the infrared spectra. With the support of a Bruker Hyperion 2000 microscope fitted with a $\times 15$ objective lens, the synchrotron radiation infrared beam was precisely concentrated on the reflection cell. Each spectrum was obtained by averaging 128 scans to ensure high accuracy. For the application of voltage to the custom infrared reflection cell, a Bio-Logic SP-150 workstation (Bio-Logic, France) was employed. All infrared absorption spectra were acquired using single-potential alteration FTIR spectroscopy, with the background spectrum measured under open-circuit voltage conditions prior to each systemic

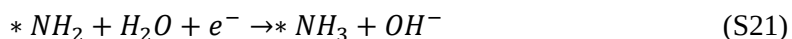
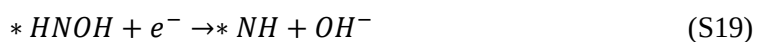
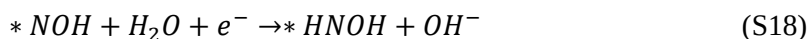
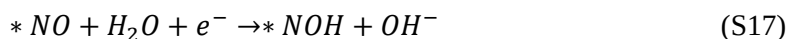
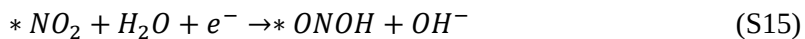
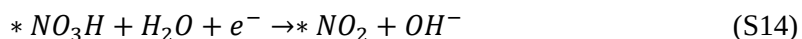
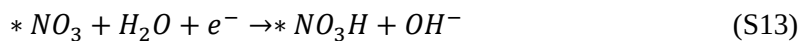
nitrate reduction reaction (NO_3^- RR). The measurements were conducted within a voltage range of 0.28 V to -0.78 V vs. the RHE, with a 0.1 V interval. A uniform settling time of 1 minute was allowed before applying each voltage step. The in-situ electrochemical setup and cell configuration are illustrated in Supporting Figures S17 and S18.

Computational Details. In this study, all DFT calculations were conducted with a periodic slab model using the Vienna ab initio simulation program (VASP), and the thermodynamic corrections due to solvent effect by using VASP.⁷¹ Vacuum layers were set with a distance of approximately 15 Å in the z-direction to prevent interactions between periodic images. The generalized gradient approximation (GGA) was employed with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Electron-ion interactions were described using the projector-augmented wave (PAW) method, and a plane-wave basis set with a cutoff energy of 450 eV was utilized. To account for the localized 3d electron correlation of iron (Fe) atoms, the DFT + U method was applied, incorporating on-site Coulomb (U) and exchange (J) interactions.⁷² Structural optimizations were conducted using a $1 \times 1 \times 2$ k-point grid. Relaxation was performed until the Hellmann–Feynman forces on all atoms were below 0.02 eV/Å, and the total energy converged to within 10^{-5} eV.

NO_3^- reduction was simulated in terms of the following elementary reaction steps on FeN_4 :



NO_3^- reduction was simulated in terms of the following elementary reaction steps on Cl-FeN_4 :



where the * represents an adsorption site. The Gibbs free energy changes (ΔG) for each of these reactions are associated with the adsorption free energies of the intermediate species. For a given electrode potential U and pH value, the changes of adsorption free energy for these intermediates are calculated by $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}}$, where ΔE is the adsorption energy, ΔZPE and $T\Delta S$ are respectively the zero-point energy difference and entropy change between the absorbed state and the gas phase form. $\Delta G_{\text{pH}} = -k_B T \ln[H^+]$, where k_B is the Boltzmann constant and T is the temperature (set to 298.15 K). $\Delta G_U = -eU$ is the free energy contribution due to the electrode potential U , where e is the elementary charge transferred.

Supporting Information

Additional TEM, BET, XRD, XPS, EDS, HAADF-STEM, EXAFS, Operando SR-FTIR, calibration curves of NH_3 and NO_2^- , ammonia yield rates over Cl-Fe-NC catalysts at different pyrolysis temperatures, ECSA normalized LSV, NMR detection for isotopic analysis, UV-Vis quantification for excluding NH_3 pollution, PDOS, differential charge density distribution, and comparison of the NO_3^- RR literature.

Corresponding Authors

Hao Zhang – State Key Laboratory of Clean Energy Utilization, Zhejiang University,

Hangzhou 310027, China; **Email:** zhang_hao@zju.edu.cn

Ji Yang – College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China; **Email:** chem.yang@xmu.edu.cn

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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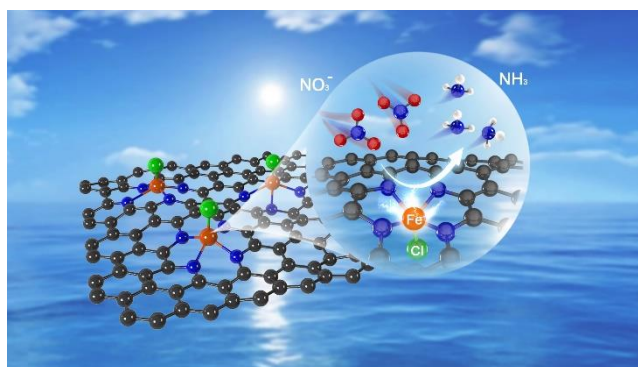
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We implement an iron single-atom catalyst where the axial chlorine induces symmetry-breaking to achieve full electrochemical conversion of nitrate to ammonia with excellent activity and stability, an ammonia yield rate of up to $9396.7 \mu\text{g}_{\text{NH}_3} \text{ h}^{-1} \text{ cm}^{-2}$ and a Faradaic efficiency up to 99.4%.