

High-Performance Ammonia Electrosynthesis from Nitrate in a NaOH–KOH–H₂O Ternary Electrolyte

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Abstract: A glut of dinitrogen-derived ammonia (NH₃) over the past century has resulted in a heavily imbalanced nitrogen cycle and consequently, the large-scale accumulation of reactive nitrogen such as nitrates in our ecosystems has led to detrimental environmental issues. Electrocatalytic upcycling of waste nitrogen back into NH₃ holds promise in mitigating these environmental impacts and reducing reliance on the energy-intensive Haber–Bosch process. Herein, we report a high-performance electrolyzer using an ultrahigh alkalinity electrolyte, NaOH–KOH–H₂O, for low-cost NH₃ electrosynthesis. At 3,000 mA/cm², the device with a Fe–Cu–Ni ternary catalyst achieves an unprecedented faradaic efficiency (FE) of 92.5 ± 1.5 % under a low cell voltage of 3.83 V; whereas at 1,000 mA/cm², an FE of 96.5 ± 4.8 % under a cell voltage of only 2.40 V was achieved. Techno-economic analysis revealed that our device cuts the leveled cost of ammonia electrosynthesis by ~40% (\$30.68 for Fe–Cu–Ni vs. \$48.53 for Ni foam per kmol-NH₃). The NaOH–KOH–H₂O electrolyte together with the Fe–Cu–Ni ternary catalyst can enable the high-throughput nitrate-to-ammonia applications for affordable and scalable real-world wastewater treatments.

Introduction

Nitrogen (N₂), the most abundant naturally occurring gas on Earth (~78 % of the atmosphere), serves little purpose unless “fixed” in the form of reactive nitrogen (Nr).^[1] These ‘fixed’ Nr compounds play a fundamental role in sustaining

and propagating all forms of life on Earth; from the tiniest bacteria to the 8 billion human population.^[2] The extensive deployment of the Haber–Bosch process for Ammonia (NH₃) synthesis catapulted the anthropogenic Nr production tenfold to > 150 teragrams a year,^[3] which sustains about 50 % of the world population’s need for nitrogen nutrition. However, the fixed and then released Nr have made the nitrogen cycle the most altered biogeochemical cycle, compared to any other element such as carbon.^[1]

Natural denitrification processes that convert these Nr species back into N₂ remain, but they are not capable of matching the rate of Nr generation, causing continued accumulation of Nr in air, water, and soil. The rising Nr levels nevertheless have resulted in progressively detrimental impacts on our fragile ecosystems and health, including soil acidification, coastal eutrophication, air pollution, declining biodiversity, and groundwater contamination.^[1] Among anthropogenic Nr species, waste nitrate (NO₃[−]) is the most prevailing one, because of the highest oxidation state, at an estimated accumulation rate of 40 million metric tons of nitrogen per year. Some of the severe health hazards associated with NO₃[−] include neural tube defects during pregnancy, infant methemoglobinemia aka ‘blue baby syndrome’, thyroidal diseases, and colorectal cancer.^[4]

Recycling this massive waste NO₃-N back into NH₃, through the electrochemical reduction of nitrate (NO₃RR), can greatly reduce the reliance on direct N₂ conversion to NH₃ via the Haber–Bosch process, helping close the nitrogen cycle and alleviating environmental stress. Notwithstanding the significant progress in the development of selective and active electrocatalysts for NO₃RR,^[5,6,15–21,7–14] the high-productivity and low-cost NO₃RR with both high selectivity and high efficiency on a desired industrial scale of current density (> 1,000 mA/cm²) remains very limited.^[8,21,22]

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Of the promising catalysts developed so far, most include derivatives of expensive noble metals and are often obtained through very complex synthesis techniques. Although inexpensive earth-abundant metals^[7,10,18,20,21,23,24] have also emerged as promising candidates for NO₃RR, their performance has been marred by moderate ammonia selectivity and/or large energy consumption for operation at industrially desirable current densities. The development of high-performance NO₃RR catalysts with high ammonia selectivity, low energy consumption, and inexpensive materials cost is of paramount importance to achieve high ammonia productivity at industrially desirable current densities.

An unexpected yet promising avenue to attain high-productivity NO₃RR is through a NaOH-KOH-H₂O ternary electrolyte with ultrahigh alkalinity. Very recently, we demonstrated the surprising capability of the ternary alkaline electrolyte to sustain high-current density NO₃RR operations using a plain Ni wire mesh as cathode, leading to an ammonia productivity of 4,200 mA/cm² (ammonia-oriented partial current density) with a faradaic efficiency (FE) of 84.5 % under a cell voltage of 4.5 V. Clearly, lower cell voltage and higher ammonia selectivity are critically needed to promote the high-productivity NO₃RR, therefore calling for the development of high-performance NO₃RR catalysts tailored to take full advantage of the robust ternary alkaline electrolyte system.

Herein, we report a high-performance Cu-Fe-Ni ternary catalytic system for high-productivity NO₃RR operation in the NaOH-KOH-H₂O ternary electrolyte. The ternary catalyst with equimolar combination achieved FEs of 96.5 ± 4.8 % at 2.40 V and 92.5 ± 1.0 % at 3.83 V at 1,000 and 3,000 mA/cm², respectively at 100 °C. The Cu-Fe-Ni ternary catalyst significantly outperforms any pristine metals (Cu, Fe, and Ni) under the same testing conditions, due to synergistic enhancement. The presence of Fe in the catalyst, more specifically the α -Fe₂O₃ phase, was observed to play a crucial role in granting the high ammonia selectivity and low energy consumption.

Results & Discussion

Pursuit of a High-Performance and Low-Cost Catalyst: Fe-Cu-Ni Ternary System

Various inexpensive earth-abundant metals and their derivatives have emerged as the forerunners for NO₃RR albeit in simple aqueous systems, including Ni-based electrodes^[9,25] with operation durability, Cu-based catalysts^[6,20,26] with high ammonia efficiencies, and Fe-based ones^[7,18,27] with high ammonia productivity. However, the applicability of those pristine/pure metallic catalysts in NaOH-KOH-H₂O ternary electrolytes is compromised due to the ultrahigh alkalinity environments.

Known for its excellent corrosion resistance in alkaline solutions,^[28] pure Ni has been the intuitive choice of cathode in ultrahigh alkalinity systems. In addition, Ni has been reported to be increasingly selective for NH₃ at more negative overpotentials in highly alkaline systems.^[29] Cu is

also well-known for its remarkable propensity for reducing NO₃⁻ to NH₃ with high ammonia selectivity (> 90 %).^[9] More interestingly, Cu-Ni alloys with proper compositional tuning tend to outperform their pure counterparts, at least in ambient aqueous electrolytes.^[9] However, Ni, Cu, and Cu-Ni alloy (Monel 400) as electrocatalysts at high current densities (1,000 mA/cm²) showed moderate NO₃RR performance (65 %–82 % as the highest NH₃ FE) in NaOH-KOH-H₂O electrolyte (see Figure 1a–c).

Similarly, Fe has also been extensively reported for its modest ammonia faradaic efficiency (ca. 75 %) in alkaline systems.^[7,30] In addition, its chemical stability is of concern under ultrahigh alkalinity.^[28] Stainless steel (such as SS304) was considered a corrosion-resistant substitute for pure Fe, its performance was comparable with Cu Foil at 1,000 mA/cm², however, the ammonia efficiency plunged sharply (< 35 % NH₃ FE) at higher current densities (Figure 1a–c).

Considering Wu et al.'s^[7] Fe single atom catalyst's high ammonia selectivity and productivity for NH₃ in simple aqueous electrolytes, we conjectured that the inclusion of Fe atoms into the Cu-Ni system may yield a synergistic effect—boosting the NO₃RR performance in the NaOH-KOH-H₂O ternary electrolyte while leveraging the material's resilience of Cu-Ni binary system in the ultrahigh alkalinity. The inclusion of multiple redox-active metal ions at the catalytically active sites also helps buffer the multi-electron transfer process essential for NO₃RR thus increasing overall performance.^[31] In short, the Fe-Cu-Ni ternary catalytic system may offer unprecedented performance at industrially desirable current densities for low-cost and high-productivity NO₃RR operation.

Synthesis and Characterization of Fe_xCu_y@Ni Ternary System

The traditional physical mixing approach can be used to synthesize the Fe-Cu-Ni ternary alloys, however, the synthesized ternary alloys obtained through such an approach often have large crystal sizes, and therefore a very limited electrochemically accessible surface area.^[32] Alternatively, electrodeposition can overcome the drawback of the physical mixing approach to achieve atomic synergy among the three metal elements, resulting in improved NO₃RR.^[33] Modifying Zhang et al.'s^[31] electrodeposition approach to synthesize the ternary alloys (core-shell structured Fe-Cu-Ni electrodes), we prepared a ternary alloy electrode intentionally free of the core-shell features. The electrochemical dealloying process used by Zhang et al.^[31] to obtain the core-shell features relied upon preferential discharge of the Cu metal due to its higher chemical activity relative to Ni and Fe which left behind a metal oxide layer on the surface. Such an oxidized surface structure is not desirable considering the poor electrical conductivity of most metal oxides, therefore, was intentionally avoided. Our Fe-Cu-Ni ternary electrode (denoted as Fe_xCu_y@Ni, hereinafter, Table 1) was fabricated via chronopotentiometric electrodeposition of the three elements from an equimolar electrolyte bath onto a Ni foil substrate (detailed method described in electronic Supporting Information (ESI†)). The

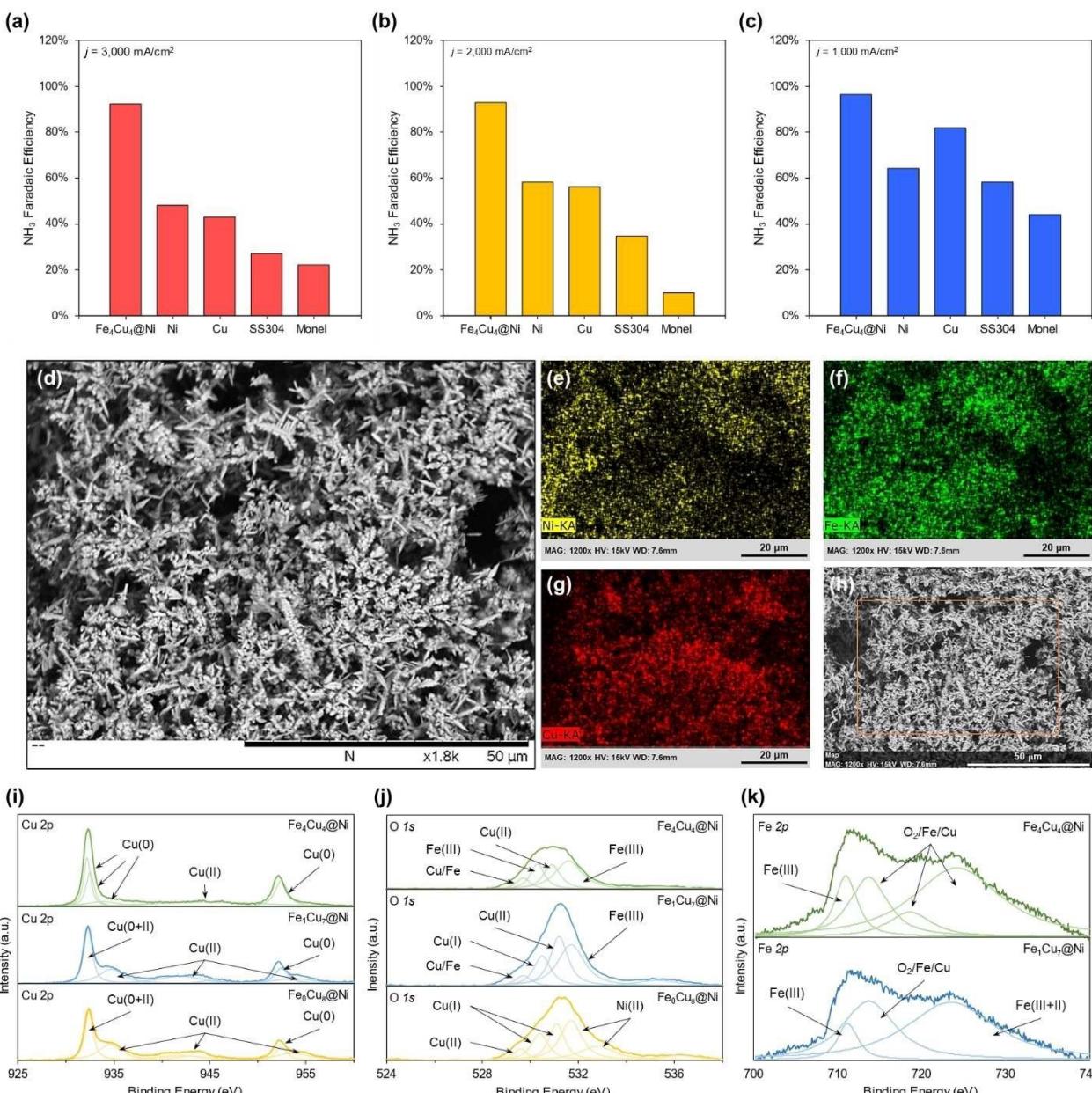


Figure 1. NO3RR performance and materials characterization of the Fe₄Cu₄@Ni catalyst. (a) NO3RR performance comparison at 3,000 mA/cm² of current density between the Fe₄Cu₄@Ni and four chosen common electrode materials. (b) and (c) NO3RR performance comparison at 2,000 mA/cm² and 1,000 mA/cm², respectively. (d) Scanning electron microscope (SEM) images of the as-prepared Fe₄Cu₄@Ni catalyst. Energy-dispersive X-ray spectroscopy (EDXS) elemental maps for (e) Ni, (f) Fe, and (g) Cu, (h) SEM of section probed for EDXS. A comparison of XPS profiles of (i) Cu 2p, (j) O 1s, and (k) Fe 2p for Fe₀Cu₈@Ni, Fe₁Cu₈@Ni, and Fe₄Cu₄@Ni electrocatalysts.

atomic compositions of Fe: Cu: Ni in the deposited alloy at each electrode were then quantified through ICP-MS (Table S6–S7, ESI†) and the results correlated well with the electrolyte bath concentrations used for electrodeposition.

A uniformly dense distribution of dendritic structures with distinct tip-splitting and hierarchical features characterized the surface of the as-prepared catalyst when observed under the SEM (Figure 1d). Further, an elemental map for the SEM images was generated using an energy-dispersive x-ray spectroscopy (EDXS) technique which revealed a uniform distribution of three key elements: Ni,

Fe, and Cu (Figure 1e–g). XPS analysis also confirmed the presence of the same three elements on the surface while deconvoluting the high-resolution spectrum for each, Cu 2p, Cu LMM, Fe 2p, and Ni 2p signals suggested a mixture of pure and their corresponding oxide phases (Figure S5, ESI†). Moreover, an XPS depth profile revealed similar Fe–Cu–Ni atomic ratios as that at the surface indicating the successful co-deposition throughout the deposited layer (Table S11, ESI†). Rietveld refinement of the XRD scan of the Fe–Cu–Ni catalyst also confirmed the presence of four

Table 1: List of catalysts synthesized in this study with their recipes of precursors.

Catalyst Name	Cu:Fe Ratio	The Concentration of Metal Precursors in Electrolyte (mM)	Fe(NO ₃) ₂ ·9H ₂ O	CuSO ₄ ·5H ₂ O	NiCl ₂ ·6H ₂ O
Cu ₁₀	10 : 0	0	60	0	
Fe ₀ Cu ₈ @Ni	8 : 0	0	40	20	
Fe ₁ Cu ₇ @Ni	7 : 1	5	35	20	
Fe ₂ Cu ₆ @Ni	6 : 2	10	30	20	
Fe ₃ Cu ₅ @Ni	5 : 3	15	25	20	
Fe ₄ Cu ₄ @Ni	4 : 4	20	20	20	
Fe ₅ Cu ₃ @Ni	3 : 5	25	15	20	
Fe ₆ Cu ₂ @Ni	2 : 6	30	10	20	
Fe ₇ Cu ₁ @Ni	1 : 7	35	5	20	

distinct crystalline phases: pure Cu, pure Ni, α -Fe₂O₃, and γ -Fe₂O₃ (Figure 3c).

High-Performance NO₃RR of Fe₄Cu₄@Ni Ternary Catalyst

Voltammetric studies of the Fe₄Cu₄@Ni alongside major control samples revealed the least negative onset potential for NO₃RR in the NaOH-KOH-H₂O ternary electrolyte with 40 wt% of H₂O at 100°C: 0.18 V on Fe₄Cu₄@Ni vs. -0.45 V on Cu foil and -4.02 V on Ni foil, against an Ag wire pseudo-reference electrode (Figure 2a). When compared with voltammetric curve without NO₃⁻, the change in the onset potential is also the largest on Fe₄Cu₄@Ni: 0.70 V cf. 0.38 V on Cu foil and 0.10 V on Ni foil. Both the least onset potential with NO₃⁻ and the largest change in onset potential (with vs. without NO₃⁻) imply a very high NO₃RR activity on Fe₄Cu₄@Ni.

The NO₃RR performance was evaluated by means of a chronopotentiometry study. At 250 mA/cm² of constant current operation, around 100 % of NH₃ FE (i.e., FE towards NH₃, hereinafter) was observed on the Fe₄Cu₄@Ni ternary catalyst. The NH₃ FE slightly decreased to 96.5 %, 92.8 %, and 92.5 % at a current density of 1,000, 2,000, and 3,000 mA/cm², respectively, demonstrating the robust catalytic performance (Figure 2b). Among the three current densities tested here, Fe₄Cu₄@Ni is much more selective than all catalytic materials we tested including Ni, Cu, SS304, and Monel (a Cu-Ni alloy). Specifically at 3,000 mA/cm², the NH₃ FE of Fe₄Cu₄@Ni roughly doubles that of Ni (47 %) or Cu (43 %), triples that of SS304 (28 %), and quadruples that of Monel (23 %) (Figure 1). To the best of our knowledge, all those NH₃ FE values are the highest at the corresponding current densities in the NO₃RR field.

The origin of produced NH₃ was confirmed to be from the catalytic reduction of NO₃⁻ in the electrolyte through a series of control experiments (Figure S7, ESI†). This catalytic reduction consisted of two components: a very minor spontaneous NO₃RR and the dominating electrocatalytic NO₃RR. The spontaneous NO₃RR is the generation of ammonia from the introduction of the electrode without applying any current. Pure Fe,^[34] pure Cu,^[34,35] and Fe oxides,^[36] all have been reported as chemically active for the

spontaneous reduction of NO₃⁻ to NH₃. Nevertheless, the observed spontaneous NO₃RR accounted for only 0.63 % of the total produced ammonia when operated at 1,000 mA/cm², and this component became increasingly insignificant when considering higher current densities. In all cases tested, the electrocatalytic NO₃RR dominates the NH₃ formation.

Probing the reaction kinetics behind the electrochemical NO₃RR, a reaction-order plot ($\log i_{NH_3}$ vs. $\log C_{NO_3}$, (Figure 2c) based on a variety of NO₃⁻ concentrations as the reactant feed showed that NO₃RR follows a reaction order close to unity for experiments conducted at 1,000 mA/cm². Similar observations were also made for experiments carried out at 2,000 mA/cm² (Figure S9, ESI†).

To demonstrate the industrial practicality of the Fe₄Cu₄@Ni electrode, we conducted a chronopotentiometric stability test in a membrane-free alkaline electrolyzer (MFAEL). The Fe₄Cu₄@Ni electrode was operated at 1,000 mA/cm² for 24 hours with an initial NO₃⁻ concentration of 300 mM, with the electrolyte being replenished with NO₃⁻ at regular intervals of 4 hours. The overall potential remained stable throughout the test, leading to a 24-hour average ammonia efficiency of 102 %[±]0.9 % (Figure 2e). To further demonstrate the advantage of the NaOH-KOH-H₂O electrolyte over ambient electrolytes we recorded the performance of the same electrocatalyst at different temperatures in a 1 M KOH electrolyte containing 0.5 M NaNO₃. We observed that the full cell voltages required to achieve similarly high current densities were almost double that required in the NaOH-KOH-H₂O electrolyte (Table S8, ESI†). A major reason for this is the much higher ohmic resistance (R_{ohm}) of the aqueous electrolyte, not to mention the competitive HER that compromises the overall NH₃ FE as well.

Unravelling the Synergistic Enhancement for NO₃RR in Fe_xCu_y@Ni Ternary System

A series of control experiments were conducted to understand the synergistic enhancement in catalytic activity and the crucial role of Fe in the Fe-Cu-Ni ternary system. The first of these instinctive controls is to examine the catalytic system without the introduction of the Fe component during the entire synthesis procedure, denoted as Fe₀Cu₈@Ni. To further test the impact of Ni presence, an electrode containing only Cu as the metal precursor (Cu₁₀) in the electrolyte bath was prepared. Additionally, the comparison between Cu₁₀ and Cu foil also helps inspect the effect of extended surface area for Cu. The ternary Fe₄Cu₄@Ni (chemically, Fe₄Cu₄Ni₄) significantly outperforms the binary Cu-Ni (named Cu₈Fe₀, or chemically, Cu₄Ni₄) and the singular Cu (Cu₁₀) (Figure S8, ESI†).

The impact of Fe atoms on the synergistic enhancement of NO₃RR performance can clearly be seen in the comparative NO₃RR study on a series of electrodes with varying Fe: Cu ratios (from 0 : 8 to 7 : 1) under identical test conditions: at 3,000 mA/cm² at 100°C in the NaOH-KOH-H₂O with 40 wt% of H₂O (Figure 3a). The

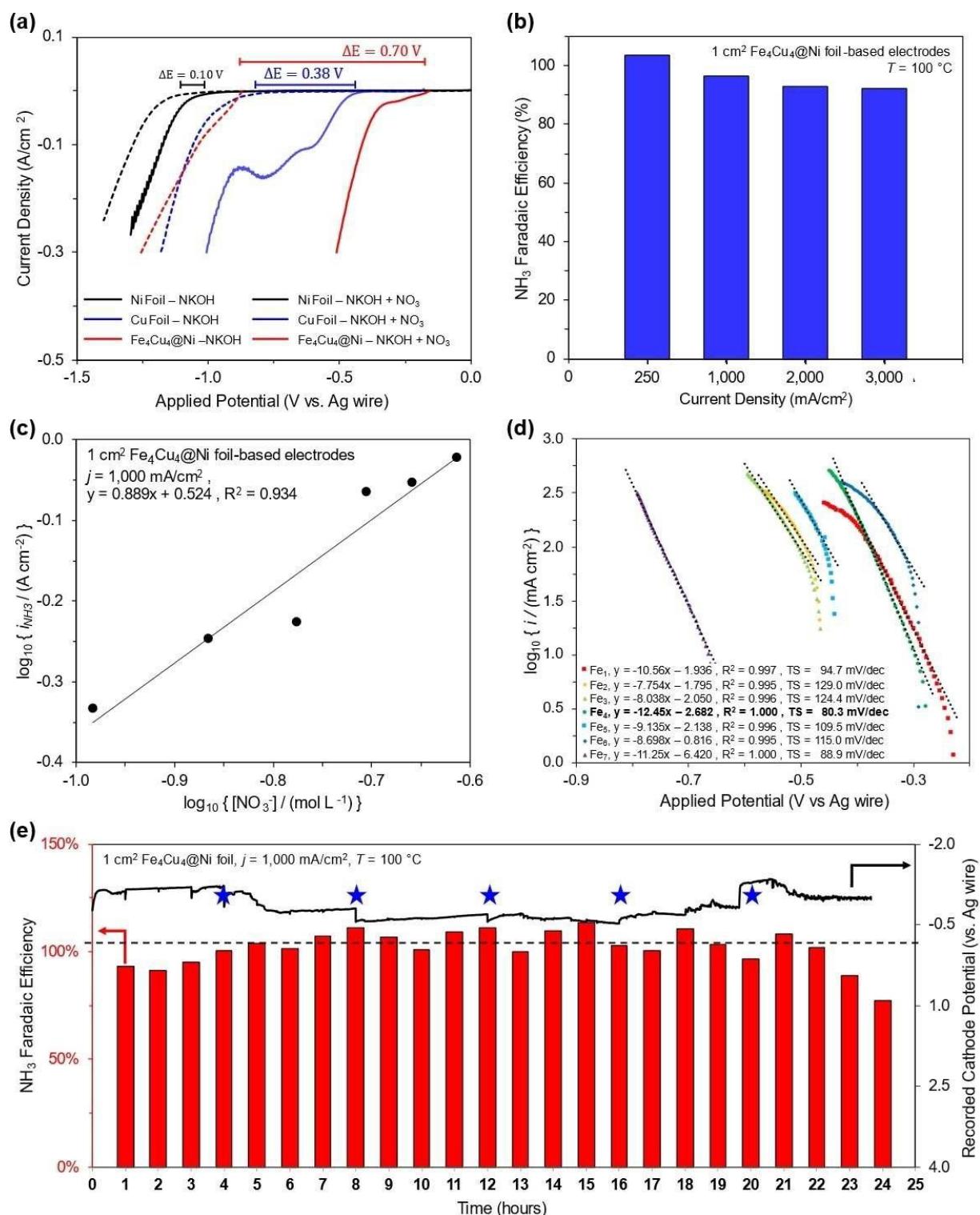


Figure 2. NO₃RR performance of $\text{Fe}_x\text{Cu}_y@\text{Ni}$ catalytic system. **(a)** Voltammetric curves for NO₃RR with different metals/catalysts as working electrodes with and without NO_3^- source in NaOH-KOH-H₂O (40 wt% water content). Test conditions: 50 mV/s of scan rate, 0.2 M of NO_3^- concentration, and 100 °C of cell temperature. **(b)** Coulombic efficiency of the $\text{Fe}_4\text{Cu}_4@\text{Ni}$ catalyst at four typical current densities (0.2 M NO_3^- and 100 °C). **(c)** Electrochemical reaction-order plot on the $\text{Fe}_4\text{Cu}_4@\text{Ni}$ catalyst operated at 1,000 mA/cm². **(d)** Tafel plot for $\text{Fe}_x\text{Cu}_y@\text{Ni}$ catalysts with different Fe:Cu ratios. **(e)** 24-hour stability test for NO₃RR on the $\text{Fe}_4\text{Cu}_4@\text{Ni}$ catalyst (1,000 mA/cm² and 100 °C), blue stars indicate times when the electrolyte was replenished with NO_3^- .

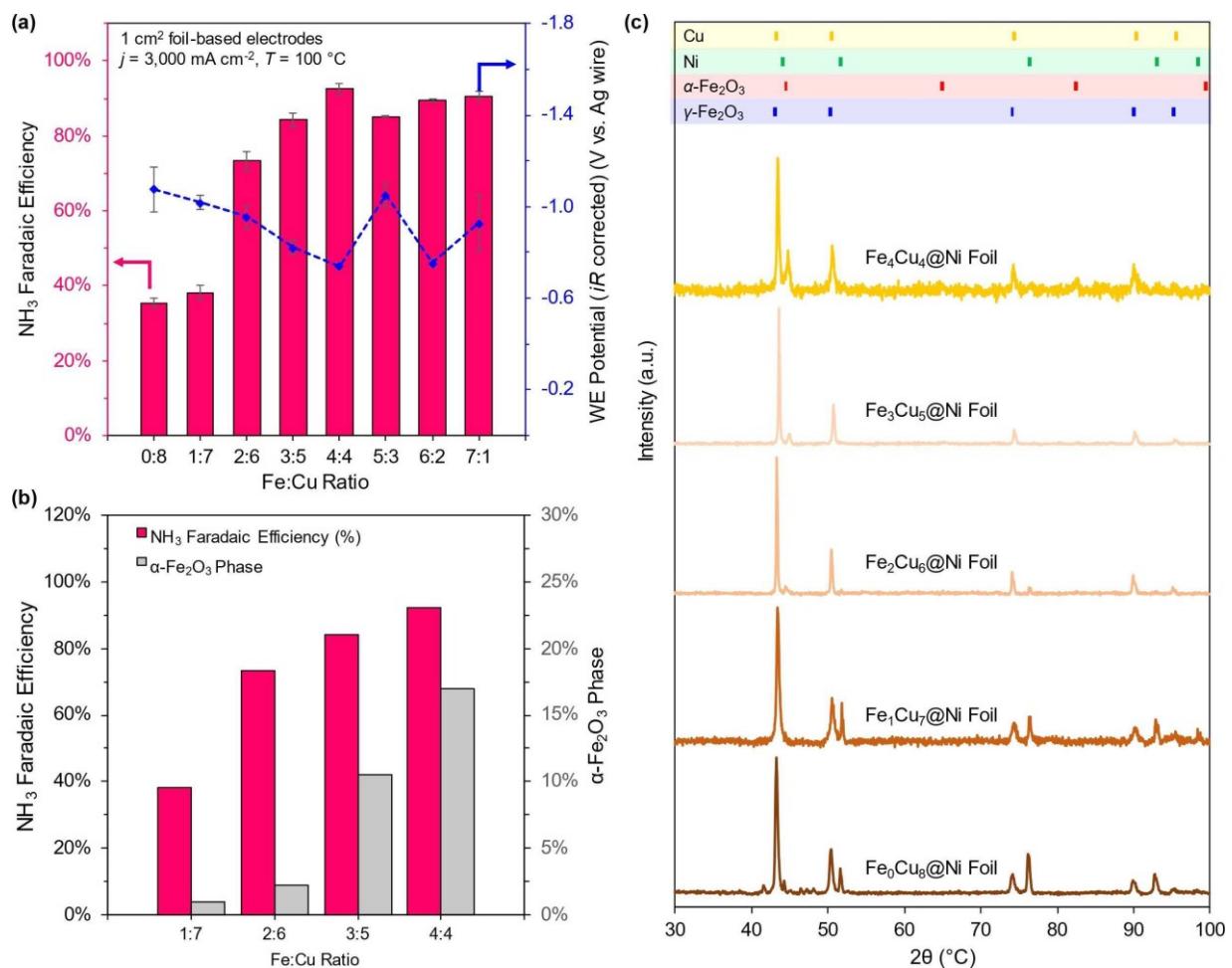


Figure 3. Coulombic efficiency and rationale of $\text{Fe}_x\text{Cu}_y@\text{Ni}$ catalytic system. (a) The impact of Fe: Cu ratio on the coulombic efficiency of $\text{Fe}_x\text{Cu}_y@\text{Ni}$ (3,000 mA/cm² and 100 °C) (b) The correlation between coulombic efficiency and the content of α -Fe₂O₃ phase in $\text{Fe}_x\text{Cu}_y@\text{Ni}$, and (c) α -Fe₂O₃ phase evolution with increasing Fe: Cu ratios.

NH₃ FE quickly increases with increasing Fe: Cu ratio until equimolar ratio (Fe₄Cu₄), beyond which it slightly slides down and plateaus. The observed cathode potential follows a fairly consistent trend: it shifts to less negative potential when raising the Fe: Cu ratio until reaching equimolar, and it goes slightly more negative afterward, albeit with a large fluctuation admittedly. Specifically, Fe₄Cu₄@Ni with the equimolar ratio showed the peak NH₃ FE 92.5 % as well as the least negative cathode potential of 0.75 V vs. Ag wire (iR corrected). Tafel slope analysis for the different Fe: Cu ratios also shows a trend similar to that observed for the ammonia FE and cathode potential: the Fe₄Cu₄@Ni exhibiting the lowest Tafel slope of just 80 mV dec⁻¹ (Figure 2d).

To further understand the outstanding performance, we explored the electronic and atomic structure of the Fe–Cu–Ni catalyst in more detail through a high-resolution XPS analysis.

The XPS results for Fe₀Cu₈@Ni, Fe₁Cu₇@Ni, and Fe₄Cu₄@Ni revealed a significant change in the Cu 2p and O 1s profiles, while Ni 2p profiles remained almost unfazed (see Figure 1i–k and Figure S6, ESI†). The Fe 2p profile showed a marginal increase in intensity for Fe₄Cu₄@Ni and

dominance of peaks attributed to the O₂/Fe/Cu 2p_{3/2} environment whereas for Fe₁Cu₇@Ni the peak with a binding energy of 723.5 eV was attributed to Fe₃O₄, i.e., a combination of Fe(III) and Fe(II) (Figure 1k and Figure S26, ESI†). For the O 1s profile, we observed an increase in the overall intensity of the signal upon a small loading of Fe (i.e., Fe₁Cu₇@Ni) compared to the sample with no Fe, however, upon further increase to the equimolar ratios we observed a relative decrease in overall intensity in the O 1s profile. For the Fe₀Cu₈@Ni O 1s profile, the peaks between 529.0–532.0 eV, are attributed to oxygen atoms bound to the Cu and Ni, and hydroxyl groups^[31,37] (Figure 1j). The same observation holds for samples Fe₁Cu₇@Ni and Fe₄Cu₄@Ni, however, we observe a significant plateauing and drop in intensity for Fe₄Cu₄@Ni between the 530.0–532.0 eV range (Figure 1j). These results suggest that the increased Fe loading results in the formation of an oxidation-resistant environment, especially for Cu, as observed in the Cu 2p profile (Figure 1i). The Cu 2p profile for both Fe₀Cu₈@Ni and Fe₁Cu₇@Ni contains peaks at 934.6, 941.9, and 943.0/944.8 eV (Fe₀Cu₈@Ni/Fe₁Cu₇@Ni) which are attributed to CuO 2p_{3/2}, and CuO 2p_{3/2,sat}. However, for

Fe₄Cu₄@Ni these aforementioned peaks are suppressed while the peaks for Cu 2p_{1/2} (952.5 eV) and Cu 2p_{3/2} (932.2 and 932.5 eV) become more intense. Moreover, the emergence of a peak at 933.8 eV attributed to the CuFe₂O₄ 2p_{3/2} and the absence of the CuO 2p_{3/2,sat} again suggests that the addition of Fe helps regulate the oxidation state of Cu species, primarily in the reduced metallic state. As also reported previously,^[8] Cu-based binary alloys with high performance commonly rely on the Cu in its reduced state, (i.e., Cu⁰) supporting the secondary metal to boost the overall performance.

Moreover, as previously established, the co-deposition of different metals does not guarantee the formation of a homogeneous solid solution. In fact, the deposit is more often a combination of different metallic phases.^[38,39] As expected, probing the as-prepared Fe₄Cu₄@Ni electrode through XRD characterization revealed the existence of four distinct phases: pure Cu, pure Ni, Austenite (γ -Fe₂O₃), and Ferrite (α -Fe₂O₃) in Fe_xCu_y@Ni ternary system with varying intensities subject to the Fe: Cu ratio (Figure 3c and Table S9, ESI†). The intensity of α -Fe₂O₃ increases with increasing Fe content (Figure 3c), which is correlated well with an increase in the overall performance for NO₃RR. Such correlation suggests that α -Fe₂O₃ may be the most active phase for NO₃RR, among other catalytic phases and sites. Thus, the XPS and XRD results strongly suggest that the presence of Fe in the form of α -Fe₂O₃ suppresses the oxidation of Cu, thereby promoting a synergistic boost in overall eNO₃RR performance in an ultrahigh alkalinity environment.

In addition, electrochemical impedance spectroscopic (EIS) analysis was conducted to examine the resistance of the Fe_xCu_y@Ni-based electrodes at different current densities. For these EIS experiments, a high concentration of NO₃⁻ was used to ensure that the change in electrolyte concentration was negligible and the electrolyte conductivity remained unchanged for each test. The same electrolyte was used for each electrode test. Consistently, EIS analysis revealed that the resistance of the cathode followed the same trend as that for the cathode potential and NH₃ FE for the NO₃RR in our system: Fe₄Cu₄@Ni has the lowest cathode resistance of 0.240 Ω cm², compared with that of other Fe: Cu ratios (0.243–0.327 Ω cm²) (Figure S24–25, Table S3, ESI†).

The highest NH₃ FE, the least negative cathode potential, the lowest Tafel slope, and the smallest electrode resistance clearly justify that the equimolar ratio is the optimum for Fe_xCu_y@Ni ternary catalyst for NO₃RR at very high current densities.

The unique synergy between the Fe–Cu–Ni ternary system was thus demonstrated through the series of investigations reported above. However, intrigued by this unique performance, we are left with the lingering question: is this synergy unique to Fe–Cu–Ni in this ultrahigh alkalinity system, or whether elements other than Fe also have the potential to demonstrate such synergy? To explore this aspect, we shortlisted two additional candidates: Ruthenium (Ru) and Cobalt (Co), two elements that have exhibited extraordinary performance for eNO₃RR in aqueous

electrolytes^[8,10,19,21,40] (performance summary available in Table S12, ESI†). Deploying the same strategy as that for the Fe–Cu–Ni ternary catalyst, we prepared the Ru–Cu–Ni and Co–Cu–Ni ternary catalysts with equimolar Ru: Cu: Ni and Co: Cu: Ni ratios. Under similar testing conditions as that of the Fe–Cu–Ni ternary electrode, we observed that at 1000 mA/cm² all three elements exhibit almost similar performance, i.e., NH₃ FE of 96 %, 94 %, 92 % for Fe, Ru, and Co respectively. However, as we ramp up the current densities to 2000 and 3000 mA/cm² the NH₃ FE drops dramatically for both Ru and Co, but the drop is sharper for Co. The same trend follows for ammonia production rates as well. Moreover, the overpotential required for both, Ru and Co for 1000, 2000, and 3000 mA/cm² current densities were also more negative than that needed for Fe-based ternary catalyst (see Table S10, ESI†). Therefore, we conclude that the high performance of the Fe–Cu–Ni ternary catalyst is due to the unique synergy between the Fe–Cu–Ni system.

Techno-Economic Analysis (TEA)

To examine the economic impact of introducing the Fe₄Cu₄@Ni catalyst in the ultrahigh alkalinity systems on the nitrate-to-ammonia process, we extended the techno-economic analysis (TEA) model established in our previous work^[22] by including the additional costs associated with catalyst synthesis. As defined widely in TEA studies and adopted in this study, LTC = LCC + OPEX, where the LTC stands for the “Levelized total cost”, and the LCC does for the “levelized capital cost”.

The LCC is derived from normalizing the capital cost (CAPEX) with all produced products during the entire serving time, and also by considering the maintenance cost and financial cost over those service years. A major deviation in CAPEX lies in the catalyst synthesis: the customized Fe₄Cu₄@Ni in this work vs. a commercial Ni foam in our previous work, while keeping the same electrode area (3.36 m²) and the same reactor volume (100 L). Based on the typical chronopotentiometric electrodeposition for making the Fe₄Cu₄@Ni (250 mA/cm², 75 % of current efficiency, 50 μ m of resulting catalyst thickness), the amounts of chemicals and associated materials costs for the needed electrodepositing electrolyte were calculated. The cost of the Ni substrate and electricity for the electrodeposition process was also included. The CAPEX of the cathode was found to be \$239 per 100 L-reactor, resulting in the total CAPEX for the entire electrolyzer to be \$3,492 per system (a \$371 increase from the system modeled for the commercial Ni foam). Additionally, the ultrahigh alkalinity environment and elevated temperature make the NH₃ separation intrinsic in the MFAEL, thus bypassing the need for additional purification units and thus restraining capital cost.

Thanks to the very low cost and high durability of earth-abundant materials for Fe₄Cu₄@Ni catalysts and electrodes, the contribution of the LCC is essentially insignificant,

thereby rendering the OPEX to denote the LCC in the range of current densities ($250\text{--}3000\text{ mA/cm}^2$).

OPEX was obtained by accounting for the energy consumed for electrolysis (dependent upon the cell voltage, operating current density, and FE of NO₃RR), electrolyte mixing, and cell heating. The industrial electricity price, 0.07 US\$ per kWh, was used as the default energy cost for calculations. Driven largely by the significantly reduced cell voltage (1.68 V vs. 2.70 V), the adoption of Fe₄Cu₄@Ni catalyst (replacing the plain Ni wire mesh) lowered the OPEX by 38 % (\$29.59 vs. \$47.45 per kmol-NH₃) at the same current density of 250 mA/cm² (Table S4, ESI†). The LTC with Fe₄Cu₄@Ni catalyst is 63 % less than that with the commercial Ni foam (\$30.68 vs. \$48.53 per kmol-NH₃). Evidently, the significantly reduced cell voltage translates into the much-improved economic viability for the nitrate-to-ammonia electrochemical process.

In practice, a much larger current density is desirable. Taking the wastewater with a typical nitrate content of 100 ppm (NO₃⁻, NH₄⁺) as an example, 250 mA/cm² of current density could only process 5.8 ton-wastewater/hour from the 100-L reactor system with 3.36 m² of total electrode area; but 1,000 mA/cm² and 3,000 mA/cm² may handle 23.2 and 69.5 ton-wastewater/hour, respectively, assuming 95 % of coulombic efficiency and 90 % of nitrate removal.

Of particular interest are the high-throughput applications, the LTC was examined at those larger current densities. As expected, the LTC increases substantially with rising current density, largely because of increasing cell voltage, given that coulombic efficiency is dropping slightly, Figure 4a. Compared with \$30.68/kmol-NH₃ at 250 mA/cm², the LTC obtained was \$42.34, \$53.91, and \$67.17 per kmol-NH₃, at 1,000, 2,000, and 3,000 mA/cm² of current density, respectively. It should be noted that the LTC with

3,000 mA/cm² of current density is still around the market cost of wastewater treatment (\$65 per kmol-N^[22]). The Fe₄Cu₄@Ni-enabled system allows for ultrahigh economic operation at a low rating of current density (such as 250 mA/cm²) but also offers ultrahigh throughput operation (up to 3,000 mA/cm²) without losing economic viability, and that too while ignoring the cost-benefit of ammonia as a value-added product.

The industrial price (0.07 US\$/kWh) of electricity cost was used for all TEA results above, but we also recognize that cheaper electricity (0.03 US\$/kWh) could be available when excessive renewable energy was harvested from wind and/or solar. Taking advantage of cheaper electricity is beneficial to achieve higher throughput operation, subject to a given cost constraint. The interplay between the electricity cost and applied cell voltage examined in this study is presented in a contour map, Figure 4b. Subject to any given applied cell voltage, the experimentally observed current density as well as the detected coulombic efficiency was incorporated in the TEA model for energy consumption, which led to the LTC by combining a given electricity cost (from 0 to 0.12 US\$/kWh). In Figure 4b, one can clearly pair the operational cell voltage and the available electricity price to satisfy a given cost constraint (from 0–10 US\$/kmol-NH₃ in black to > 110 US\$/kmol-NH₃ in red).

Conclusion

Advancing the field of NO₃RR-to-NH₃ towards commercialization, we present herein an inexpensive, earth-abundant metal-based ternary catalyst that enables low-cost and high-productivity NH₃ electrosynthesis from nitrates in an ultrahigh alkalinity NaOH–KOH–H₂O electrolyte. The equimolar combination of Fe–Cu–Ni ternary catalyst enabled us to

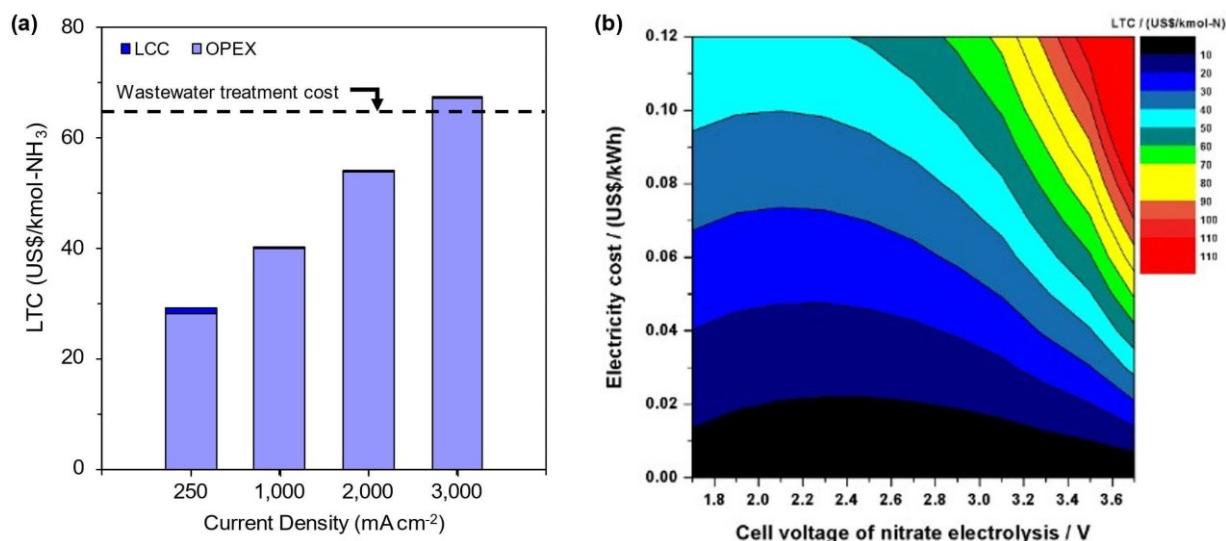


Figure 4. TEA results of NO₃RR with Fe₄Cu₄@Ni electrode. (a) LTC at four typical current densities (0.07 US\$/kWh). (b) Contour plot of LTC subject to the given electricity cost and the applied cell voltages. The TEA conducted in this study is based on a 100 L reactor and 3.36 m² of total electrode area with the ternary Fe₄Cu₄@Ni electrode (100 °C of cell temperature) and the ternary NaOH–KOH–H₂O electrolyte (40 wt % of water content).

achieve an unprecedented FE of 92.5 % at current density as high as 3,000 mA/cm² and a cell voltage of 3.83 V, while operation at milder current densities, e.g., 1,000 mA/cm², was realized at FE of 96.5% and a cell voltage of only 2.40 V. In comparison with a plain Ni wire mesh cathode (our earlier work), the Fe–Cu–Ni system helps reduce the overall cell voltage by 30 % and the leveled cost of ammonia electrosynthesis by ~40 %.

As demonstrated in our earlier work, such a system can be integrated into existing wastewater treatment processes to upcycle waste nitrates into a value-added commodity like ammonia (or its' derivatives). A detailed techno-economic analysis revealed that catalyst enhanced system can further reduce the current cost of N-removal (~65\$ per kmol-N) to as low as \$42.34 per kmol-N while operating at a current density of 1,000 mA/cm², and that too not accounting for the cost-benefit of the value-added ammonia as a product. Even integrating a pretreatment step for nitrate concentration by a low-energy cost-effective electrodialysis process (costing \$5.75 per kmol-NO₃⁻)^[22] does not blemish its commercialization prospects, and the combined system maintains its competitive edge over existing technologies. Furthermore, such a system can potentially increase the handling capacity of existing wastewater treatment plants by expediting the handling time by an order of magnitude.

This discovery presents a commercially viable pathway for ammonia electrosynthesis from nitrates, helping reduce the dependence upon the energy-intensive Haber–Bosch process while tackling the global sustainability challenge. At the same time, it presents an incentive to explore a sustainable route for direct fixation of N₂ into NO_x and eventually drive a shift away from the heavy reliance on the current Haber–Bosch process.

Author Contributions

The research article was planned, designed, and executed by **U.B. Shahid** and played a central role in the conceptualization of the study, data collection, analysis, and interpretation of the results. Additionally, **U.B. Shahid** wrote the first draft of the manuscript which was subsequently revised based on the valuable feedback from **S. Gu** and **M. Shao**. **Y. Kwon** provided valuable support by assisting with the preparation of electrocatalysts and determining the nitrate concentration of samples. **Y. Yuan** also supported the research by running several control tests for NO₃RR, helping determine nitrate and NH₃ concentrations, and helping prepare Figures. Their diligent work and attention to detail ensured accurate and reliable data for the study. **S. Gu** made substantial contributions during the review process, providing valuable insights and feedback that enhanced the quality of the manuscript. Additionally, **S. Gu** contributed to the techno-economic analysis section, bringing their expertise to bear on the economic aspects of the research. **M. Shao** supervised the entire research project, providing guidance and oversight throughout the process. His extensive knowledge and experience in the field were instrumental in shaping the study and ensuring its successful completion. All authors

reviewed and approved the final version of the manuscript, acknowledging their respective contributions to the research.

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Conflict of Interest

The authors declare no competing interests.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

- [1] S. Fields, *Environ. Health Perspect.* **2004**, *112*, A557–A563.
- [2] N. Lehnert, H. T. Dong, J. B. Harland, A. P. Hunt, C. J. White, *Nat. Chem. Rev.* **2018**, *2*, 278–289.
- [3] P. Heffer, M. Prud'homme, *Int. Nitrogen Initiat. Conf.* **2016**, 1–11.
- [4] M. Ward, R. Jones, J. Brender, T. de Kok, P. Weyer, B. Nolan, C. Villanueva, S. van Breda, *Int. J. Environ. Res. Public Health* **2018**, *15*, 1557.
- [5] Q. Gao, H. S. Pillai, Y. Huang, S. Liu, Q. Mu, X. Han, Z. Yan, H. Zhou, Q. He, H. Xin, H. Zhu, *Nat. Commun.* **2022**, *13*, 2338.
- [6] W. He, J. Zhang, S. Dieckhöfer, S. Varhade, A. C. Brix, A. Lieipetere, S. Seisel, J. R. C. Junqueira, W. Schuhmann, *Nat. Commun.* **2022**, *13*, 1129.
- [7] Z.-Y. Wu, M. Karamad, X. Yong, Q. Huang, D. A. Cullen, P. Zhu, C. Xia, Q. Xiao, M. Shakouri, F.-Y. Chen, J. Y. Kim, Y. Xia, K. Heck, Y. Hu, M. S. Wong, Q. Li, I. Gates, S. Siahrostami, H. Wang, *Nat. Commun.* **2021**, *12*, 2870.
- [8] F.-Y. Chen, Z.-Y. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Y. T. Kim, P. Zhu, Y. Z. Finfrock, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich, H. Wang, *Nat. Nanotechnol.* **2022**, *17*, 759–767.
- [9] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D.-H. Nam, C.-S. Tan, Y. Ding, J. Wu, Y. Lum, C.-T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.* **2020**, *142*, 5702–5708.
- [10] J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A. W. M. Chan, L. Xu, Y. Shi, Y. Du, W. Hao, P. K. Wong, J. Wang, S.-X. Dou, L. Zhang, J. C. Yu, *J. Am. Chem. Soc.* **2020**, *142*, 7036–7046.

[11] X. Zhao, G. Hu, F. Tan, S. Zhang, X. Wang, X. Hu, A. V. Kuklin, G. V. Baryshnikov, H. Ågren, X. Zhou, H. Zhang, *J. Mater. Chem. A* **2021**, *9*, 23675–23686.

[12] Q. Hu, Y. Qin, X. Wang, Z. Wang, X. Huang, H. Zheng, K. Gao, H. Yang, P. Zhang, M. Shao, C. He, *Energy Environ. Sci.* **2021**, *14*, 4989–4997.

[13] S. Ye, Z. Chen, G. Zhang, W. Chen, C. Peng, X. Yang, L. Zheng, Y. Li, X. Ren, H. Cao, D. Xue, J. Qiu, Q. Zhang, J. Liu, *Energy Environ. Sci.* **2022**, *15*, 760–770.

[14] R. Daiyan, T. Tran-Phu, P. Kumar, K. Iputera, Z. Tong, J. Leverett, M. H. A. Khan, A. Asghar Esmailpour, A. Jalili, M. Lim, A. Tricoli, R.-S. Liu, X. Lu, E. Lovell, R. Amal, *Energy Environ. Sci.* **2021**, *14*, 3588–3598.

[15] F. Du, J. Li, C. Wang, J. Yao, Z. Tan, Z. Yao, C. Li, C. Guo, *Chem. Eng. J.* **2022**, *434*, 134641.

[16] Z. Fang, Z. Jin, S. Tang, P. Li, P. Wu, G. Yu, *ACS Nano* **2022**, *16*, 1072–1081.

[17] N. Zhang, J. Shang, X. Deng, L. Cai, R. Long, Y. Xiong, Y. Chai, *ACS Nano* **2022**, *16*, 4795–4804.

[18] X. Fan, L. Xie, J. Liang, Y. Ren, L. Zhang, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. A. Alshehri, Q. Liu, Q. Kong, X. Sun, *Nano Res.* **2022**, *15*, 3050–3055.

[19] Z. Li, J. Liang, Q. Liu, L. Xie, L. Zhang, Y. Ren, L. Yue, N. Li, B. Tang, A. A. Alshehri, M. S. Hamdy, Y. Luo, Q. Kong, X. Sun, *Mater. Today Phys.* **2022**, *23*, 100619.

[20] H. Liu, X. Lang, C. Zhu, J. Timoshenko, M. Rüscher, L. Bai, N. Guijarro, H. Yin, Y. Peng, J. Li, Z. Liu, W. Wang, B. R. Cuenya, J. Luo, *Angew. Chem.* **2022**, *134*, DOI 10.1002/ange.202202556.

[21] X. Deng, Y. Yang, L. Wang, X. Fu, J. Luo, *Adv. Sci.* **2021**, *8*, DOI 10.1002/advs.202004523.

[22] Y. Chen, P. Ammari-Azar, H. Liu, J. Lee, Y. Xi, M. J. Castellano, S. Gu, W. Li, *EES Catal.* **2023**, *1*, 504–515.

[23] M. Xu, Q. Xie, D. Duan, Y. Zhang, Y. Zhou, H. Zhou, X. Li, Y. Wang, P. Gao, W. Ye, *ChemSusChem* **2022**, *15*, DOI 10.1002/cssc.202200231.

[24] Y. Xu, Z. Peng, Y. Han, H. Zhong, J. Yang, Y. Cao, *ChemSusChem* **2022**, *15*, DOI 10.1002/cssc.202102450.

[25] Q. Liu, L. Xie, J. Liang, Y. Ren, Y. Wang, L. Zhang, L. Yue, T. Li, Y. Luo, N. Li, B. Tang, Y. Liu, S. Gao, A. A. Alshehri, I. Shakir, P. O. Agboola, Q. Kong, Q. Wang, D. Ma, X. Sun, *Small* **2022**, *18*, DOI 10.1002/smll.202106961.

[26] J. Yuan, Z. Xing, Y. Tang, C. Liu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 52469–52478.

[27] Y. Wang, L. Zhang, Y. Niu, D. Fang, J. Wang, Q. Su, C. Wang, *Green Chem.* **2021**, *23*, 7594–7608.

[28] N. Guillet, P. Millet, in *Hydrog. Prod.*, Weinheim, Germany **2015**, pp. 117–166.

[29] H. Li, D. H. Robertson, J. Q. Chambers, D. T. Hobbs, *J. Electrochem. Soc.* **1988**, *135*, 1154–1158.

[30] B. P. Dash, S. Chaudhari, *Water Res.* **2005**, *39*, 4065–4072.

[31] P. Zhang, L. Li, D. Nordlund, H. Chen, L. Fan, B. Zhang, X. Sheng, Q. Daniel, L. Sun, *Nat. Commun.* **2018**, *9*, 381.

[32] M. Gong, H. Dai, *Nano Res.* **2015**, *8*, 23–39.

[33] K. H. Kim, J. Y. Zheng, W. Shin, Y. S. Kang, *RSC Adv.* **2012**, *2*, 4759.

[34] A. M. E. Khalil, O. Eljamal, S. Jribi, N. Matsunaga, *Chem. Eng. J.* **2016**, *287*, 367–380.

[35] S. Kerkeni, E. Lamy-Pitara, J. Barbier, *Catal. Today* **2002**, *75*, 35–42.

[36] D.-W. Cho, H. Song, F. W. Schwartz, B. Kim, B.-H. Jeon, *Chemosphere* **2015**, *125*, 41–49.

[37] L. Zhuang, L. Ge, Y. Yang, M. Li, Y. Jia, X. Yao, Z. Zhu, *Adv. Mater.* **2017**, *29*, DOI 10.1002/adma.201606793.

[38] S. Vesztergom, A. Dutta, M. Rahaman, K. Kiran, I. Zelocual-tecal Montiel, P. Broekmann, *ChemCatChem* **2021**, *13*, 1039–1058.

[39] I. Najdovski, P. Selvakannan, A. P. O'Mullane, *RSC Adv.* **2014**, *4*, 7207.

[40] J. Wang, C. Cai, Y. Wang, X. Yang, D. Wu, Y. Zhu, M. Li, M. Gu, M. Shao, *ACS Catal.* **2021**, *11*, 15135–15140.

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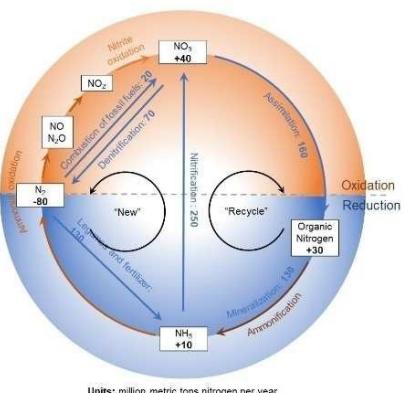
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Forschungsartikel

Ammonia Production

U. B. Shahid, Y. Kwon, Y. Yuan, S. Gu,
M. Shao* **e202403633**

High-Performance Ammonia Electrosynthesis from Nitrate in a $\text{NaOH}-\text{KOH}-\text{H}_2\text{O}$ Ternary Electrolyte



The glut in NH_3 production has resulted in a heavily imbalanced N-cycle causing massive accumulation of reactive nitrogen (Nr) in our ecosystems, destroying the environment. Upcycling these Nr via electrochemical conversion into NH_3 can partially close the N-cycle and reduce reliance on the carbon-intensive Haber-Bosh process. Here we report the remarkable performance of a $\text{Fe} \text{ Ga} \text{ Ni}$ catalyst at industrially relevant current densities.