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Unlocking Sustainable Nitrate Reduction: Earth-Abundant Bimetallic Electrodes Under Galvanostatic Evaluation

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Abstract

The electrochemical reduction of nitrate (ERN) has emerged as a green alternative to alleviate the NH₃ production via the Haber-Bosch process. Harnessing earth-abundant materials for electrocatalysts is a logical strategy, minimizing dependence on the cost-prohibitive platinum group elements. While

previous research has delved into the preparation and evaluation of electrodes for NH_3 generation, much of it has been mainly focused on potentiostatic conditions and mechanisms elucidation, overlooking real-world scenarios precluding the advancement towards technology implementation. This study addresses this gap by screening the performance of earth-abundant bimetallic electrodes, leveraging Cu foam as a substrate and modifying it with Cu_2O , $\text{Ni}(\text{OH})_2$, SnO_2 , and $\text{Co}(\text{OH})_x$ through electrodeposition. A comprehensive characterization encompassing morphological, structural, and electrochemical analysis was performed on the novel bimetallic surfaces. Electrolysis experiments targeting $30 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ were conducted under galvanostatic conditions (2.5, 5, 10, 20, and 40 mA cm^{-2}), revealing the following trend in NH_3 yield ($\text{mmol NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$): $\text{Cu/Co}(\text{OH})_x > \text{Cu/Cu}_2\text{O} > \text{Cu foam} > \text{Cu/SnO}_2 > \text{Cu/Ni}(\text{OH})_2$. Engineering figures of merit required for techno-economic analysis, such as Faradic efficiency, electrical energy per order, kinetic constants, and NH_3 generation efficiency, were estimated for each configuration. This study not only sheds light on the operational conditions of ERN but also offers a roadmap toward sustainable and economically viable NH_3 production.

Keywords: Ammonia generation, copper oxide, nickel hydroxide, tin oxide, cobalt hydroxide, direct current

1. Introduction

The world's population is on track to reach 8.5 billion by 2030 [1]. Ammonia-based fertilizers have been vital in facilitating this growth by significantly enhancing food production over the past century, supporting approximately 50% of the global population [2]. As a result, ammonia (NH_3) has emerged as one of the pivotal chemicals in the food industry [3,4]. The Haber-Bosch process, responsible for producing over 450 million metric tons of NH_3 in 2022, combines nitrogen (N_2) and hydrogen (H_2) under high temperatures and pressures using an iron (Fe) catalyst [5]. However, despite its critical role in global NH_3 production, this process has a substantial carbon footprint, contributing to around 2% of global CO_2 emissions [6,7]. Given that Haber-Bosch dominates large-scale NH_3 output, producing approximately 1200 metric tons per day, there is a growing need to develop sustainable alternatives for NH_3 production, particularly tailored to medium- and small-scale operations [3,8,9].

Nitrate ion (NO_3^-) represents an untapped N-source small molecule with high solubility in water and a lower energy barrier (245 kJ mol^{-1}) compared to N_2 [10–12]. Nevertheless, the electrochemical reduction of nitrate (ERN) involves a complex multi-step 8-electron reaction to produce NH_3 [13–15], but other contaminant products are also formed such as nitrite (NO_2^-) in solution and different N-gas species (i.e., N_2 , NO , NO_2 , N_2O). Thus, modifying the electrode chemical composition [16], as well as its interface [17], impact on the ERN catalytic performance and selectivity. Hence, the strategic design of catalysts becomes essential in identifying materials with high selectivity towards NH_3 and fast kinetics.

Both experimental and theoretical studies have identified platinum group materials (PGMs) like iridium (Ir), ruthenium (Ru), and platinum (Pt) as promising candidates for achieving high NH_3 yield [18–25]. However, the prohibitive cost associated with these materials limits the feasibility of the process [26,27]. As a result, there is a pressing need to shift research efforts towards sustainable and environmentally compatible earth-abundant materials, including copper (Cu), cobalt (Co), nickel (Ni), tin (Sn), iron (Fe), and manganese (Mn). Exploring various electrode compositions such as alloys, oxides, hydroxides, bimetallic, and multimetallic configurations holds significant promise in ERN [28–34]. Among these, Cu-based electrodes appeared as potentially viable alternatives for NH_3 production from ERN. The negative energy adsorption of NO_3^- on Cu surfaces promotes efficient electron transfer at the electrode surface [35,36]. However, it is essential to note that Cu surfaces also exhibit high adsorption of NO_2^- , which may lead to NO_2^- accumulation because Cu-based electrodes exhibit much higher activity for NO_3^- than for NO_2^- reduction. In particular, introducing Ni sites may be an alternative to boost electron transfer for NO_2^- reduction and provide sites for binding atomic hydrogen adsorption $^*\text{H}$ necessary for NH_3 production [37,38]. Studies using Sn in conjunction with Pt and Pd demonstrate that Sn sites exhibit high NO_3^- conversion to NO_2^- [39–41]. Moreover, adding Co sites have shown experimental and theoretical capabilities in facilitating hydrogenation steps of NO_3^- reduction intermediates [42–44]. Therefore, the use of bimetallic or multimetallic Cu-based electrodes could transform the inherent disadvantage of pristine Cu into an advantage by enhancing NH_3 production. Furthermore, these elements are affordable, with prices ranging from 3.8 to 12.8 $\text{\$ lb}^{-1}$ compared with Pd, which costs more than 14 500 $\text{\$ lb}^{-1}$ according to market prices [45].

When evaluating electrodes for ERN and other small molecules, assessments typically occur under potentiostatic conditions [10,46,47]. However, translating these findings to real-world field applications can prove challenging due to the complexities introduced by the three-electrode configuration. Potentiostatic conditions in large-scale systems are not feasible. Three electrode systems require a reference electrode, which proves challenging to implement when using large electrodes due to different current distributions on larger electrode dimensions. These challenges are aggravated especially in complex water matrices as those detrimentally affect the reference electrodes. Overall, this translates in the need for close technician attendance and therefore intermittent operation [48]. In contrast, galvanostatic conditions employing a two-electrode configuration offer a more practical evaluation of materials for real-world field applications. For example, industries focused on electrocoagulation, electrodesalination, electrooxidation, electrolyzers, cooling tower systems, electrowinning, electrochlorination systems, among others, are well-advanced electrochemical technologies working under galvanostatic conditions. Despite this advantage, galvanostatic studies are scarcely reported in literature for ERN. Fundamental potentiostatic experiments often exhibit higher Faradaic efficiencies than galvanostatic ones due to the avoidance of parasitic reactions in ultrapure waters, but these values may not directly inform large scale designs, despite their significance in advancing fundamental science. Bridging the gap between fundamental electrochemical studies and real-world applications necessitates reporting electrode performance under more representative operational conditions for larger engineered systems.

This study addresses this need through the galvanostatic evaluation of bimetallic electrodes modified on tridimensional (3D) Cu foam with Cu, Co, Sn, and Ni composites via an electrodeposition method. The bimetallic surfaces were morphologically, structurally, and electrochemically characterized. Intrinsic catalytic activity for ERN was examined under potentiostatic conditions and normalized by the electrochemical surface area (ECSA). Time-course N-species mass balances were conducted at a fixed current density of 20 mA cm^{-2} , identifying electrode composition, which exhibit high NH_3 yield. Moreover, the electrochemical reduction of NO_2^- was studied here to identify Cu-modified electrodes with high kinetics, reducing NO_2^- generated by Cu foam. Additionally, engineering figures of merit at different current densities were calculated to provide NH_3 yield rate, Faradaic efficiency, and electrical energy per order, essential parameters for subsequent techno-economic analyses.

2. Materials and methods

2.1 Chemicals and materials

All chemicals used were acquired from Sigma-Aldrich at analytical purity grade or higher and used without further purification. Earth-abundant nanocomposites were synthesized using anhydrous coppers sulfate ($\text{CuSO}_4 \geq 99.0\%$), nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \geq 99.0\%$), tin chloride ($\text{SnCl}_2 \geq 99.0\%$), and cobalt sulfate hexahydrate ($\text{CoSO}_4 \cdot 6\text{H}_2\text{O} \geq 99.0\%$) as metal precursors. Boric acid ($\text{H}_3\text{BO}_3 \geq 99.5\%$), sulfuric acid ($\text{H}_2\text{SO}_4 \geq 98\%$), and sodium sulfate ($\text{Na}_2\text{SO}_4 \geq 99.0\%$) served as additives and electrolyte supports in specific electrochemical bath compositions. Model solutions containing inorganic N-species

such as sodium nitrate (NaNO_3), sodium nitrite (NaNO_2), or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) were prepared with reagents of analytical grade ($\geq 99.0\%$). All solutions were prepared using ultrapure water with resistivity $>18.2 \text{ M}\Omega \text{ cm}$ (Elga Water) at $25 \text{ }^\circ\text{C}$. Copper foam acquired from Futt (99.99% purity, 110 pores per inch, 2 mm thick) was used as the substrate of three-dimensional nano-enabled electrodes with a geometrical area of $1.5 \times 1.5 \text{ cm}^2$. Acetone ($(\text{CH}_3)_2\text{CO}$, $\geq 99.5\%$) and hydrochloric acid (HCl , $\geq 37.0\%$) were employed for copper foam pretreatment.

2.2 Synthesis of the nano-enabled electrodes

The pretreatment of Cu foam before electrodeposition involved a series of steps: firstly, immersion in an ultrasonic bath containing acetone for 15 min to remove organic compounds, followed by a 5 min soak in 1.0 mol L^{-1} HCl solution to remove surface oxides. Finally, electrodes were rinsed thoroughly with ultrapure water and air-dried at room temperature. For the modification of Cu foam, chronoamperometric electrodeposition was used, with potential controlled by a potentiostat (Metrohm, PGSTAT302N, USA). This process took place in an open three-electrode configuration, using Ag/AgCl (3.2 mol L^{-1} KCl) as the reference electrode, platinum plate as counter-electrode, and Cu foam ($1.5 \text{ cm} \times 1.5 \text{ cm}$) as the working electrode. Optimal electrodeposition conditions for each bimetallic configuration are summarized in Figure 1. All experimental conditions for bimetallic electrode synthesis were defined based on the reduction potential for metal depositions according to their corresponding cyclic voltammetry, and the achieved NO_3^- conversion for electrode material prepared at different electrodeposition times (see Figure S1). Following deposition, electrodes were air-dried at room temperature, and their masses were recorded for further calculations.

2.3 Characterization of the three-dimensional electrodes

The morphological distribution of nanocomposites was explored using a field emission scanning electron microscope (FE-SEM, Zeiss Auriga) operating at 5.0 keV with a working distance of 5 mm . Structural and elemental characterization was performed using a scanning transmission electron microscope JEOL JEM-ARM-200F operated at 200 kV and an Oxford Instruments Aztec energy-dispersive X-ray spectrometer (STEM-EDS). Samples for STEM-EDS of earth-abundant composites were obtained by sonication of bulk electrodes on ethanol and drop casting the obtained solution on carbon film-supported gold grids. To study the oxidation state of elements, X-ray photoelectron spectroscopy (XPS, Kratos Axis Supra+) was employed. The XPS system contained a dual monochromatic Al/Ag source with high energy resolution (Al $\text{K}\alpha = 1486.6 \text{ eV}$ and Ag $\text{L}\alpha = 2984.2 \text{ eV}$), providing a line width 0.48 eV on Ag $3d_{5/2}$ and 0.408 eV on Si $2p_{3/2}$.

All electrochemical characterization by cyclic voltammetry and linear sweep voltammetry was performed using a potentiostat (Metrohm, PGSTAT302N, USA) in a typical three-electrode cell configuration. The setup comprised a Pt plate as the counter-electrode, Ag/AgCl (3.2 mol L^{-1} KCl) as the reference electrode, and Cu foam modified with earth-abundant nanocomposites as the working electrode. Before electrochemical measurements, solutions were purged with Ar.

2.4 Electrochemical reduction of nitrate and nitrite

The electrochemical reduction of nitrogen species was conducted in an open-air batch glass reactor under magnetic stirring at 500 rpm to ensure mass transfer at 25 °C. The non-deaerated solution to be treated (100 mL) contained either 30 mg NO₃⁻-N L⁻¹ or 30 mg NO₂⁻-N L⁻¹ in 12.5 mmol L⁻¹ Na₂SO₄. The initial pH and conductivity values were 6.35 ± 0.2 and 3.15 ± 0.05 mS cm⁻¹ for NO₃⁻ and 5.90 ± 0.2 and 3.20 ± 0.05 mS cm⁻¹ for NO₂⁻, respectively. Electrolysis were performed in a two-electrode system under galvanostatic conditions, using a TENMA 72-2720 DC power supply. Cu foam and nano-enabled electrodes served as cathodes, while a commercial Ti/IrO₂ (DeNora – USA) acted as the anode. The applied current intensity was determined based on the geometrical area of the electrodes (4.5 cm²) and areal density (0.32 g cm⁻²) provided by the manufacturer. The interelectrode distance between the anode and cathode was maintained at 1.0 cm. Samples were withdrawn periodically and analyzed for N-species concentration, pH, and conductivity. All experiments were performed in triplicate, with sample standard deviations consistently below 5% for all trials.

2.5 Analytical techniques, equipment, and system performance evaluation

The pH and conductivity values were measured using Thermo Scientific Orion Star A221 and Orion Star A322 meters, respectively. The concentration of nitrogen species, such as nitrate (mg L⁻¹ NO₃⁻-N), nitrite (mg L⁻¹ NO₂⁻-N), and ammonia (mg L⁻¹ NH₃-N), over time was quantified using colorimetric methods using TNT 835 (λ = 345 nm), TNT 839 (λ = 515 nm) and TNT 830 (λ = 694 nm) HACH kits with a HACH DR6000 UV-vis spectrophotometer. Concentrations of N-volatile species (N₂, NO, NO₂, or N₂O) were obtained by the difference between the initial N-content and the N-content at a given time of aqueous species. Nitrate conversion was determined using Eq. (1)

$$\text{Nitrate conversion (\%)} = \frac{C_{X,i} - C_{X,t}}{C_{X,i}} \times 100 \quad (1)$$

where $C_{X,i}$ and $C_{X,t}$ are the initial and final nitrate concentrations.

The ammonia yield was calculated using Eq. (2)

$$\text{NH}_3 \text{ yield} = \frac{C_{\text{NH}_3} V}{m_{\text{electrocat}} t} \quad (2)$$

where C_{NH_3} is NH₃ concentration in mmol L⁻¹, V is the volume of the solution to be treated in L, $m_{\text{electrocat}}$ is mass of the electrocatalyst in g, and t is time in h.

The selectivity towards NH₃ (S_{NH_3}) was determined following Eq. (3), and the NH₃ generation efficiency can be estimated by Eq. (4). Selectivity represents the percentage of NH₃ electrogenerated from the reduced NO₃⁻, whereas NH₃ generation efficiency indicates the amount of electrogenerated NH₃ related to the theoretical maximum achievable if all the initial NO₃⁻ concentration in solution was reduced solely to NH₃. NH₃ generation efficiency serves as an engineering metric for efficiently recovering added-value resources, encompassing both selectivity and conversion attained during treatment time.

$$S_{NH_3}(\%) = \frac{C_{NH_3,exp}}{C_{nitrate,i} - C_{nitrate,t}} \times 100 \quad (3)$$

$$NH_3 \text{ generation efficiency } (\%) = \frac{C_{NH_3,exp}}{C_{NH_3,theo}} \times 100 \quad (4)$$

where $C_{NH_3,exp}$ is the NH_3 concentration experimentally obtained in $mg\ NH_3\text{-N}\ L^{-1}$ for S_{NH_3} and $mmol\ L^{-1}$ for NH_3 generation efficiency, $C_{nitrate,i}$ and $C_{nitrate,t}$ corresponds NO_3^- concentration in $mg\ NO_3^-\text{-N}\ L^{-1}$ before and after treatment, respectively. The $C_{NH_3,theo}$ is the theoretical NH_3 concentration in $mmol\ L^{-1}$ if the entire initial amount of NO_3^- is converted to NH_3 .

Regarding the engineering figures of merit, the Faradaic efficiency (FE) and the electrical energy per order (EE/O) were determined by Eq. (5) and Eq. (6), respectively. The FE evaluates system performance by comparing the actual number of electrons consumed in an electrochemical reaction to the theoretical expected conversion ruled by Faraday's law. At the same time, EE/O represents the electric energy required to reduce the concentration of NO_3^- concentration by one order of magnitude in a unit volume during batch operation mode.

$$FE(\%) = \frac{n F N_i}{3600 I t} \times 100 \quad (5)$$

$$EE/O (kWh\ m^{-3}\ order^{-1}) = \frac{E_{cell} I t}{V_s \log(C_0/C_t)} \quad (6)$$

where n is the number of electrons required per mol of ammonia in mol, F is the Faraday constant ($96\ 487\ C\ mol^{-1}$), N_i is the mol of NH_3 generated during the electrolysis, I is the applied current intensity in A, t is the electrolysis time in h, and 3600 is a unit conversion factor ($3600\ s\ h^{-1}$). E_{cell} represents the average of the cell potential in V, V_s is the volume of the solution in L, and C_0 and C_t are the initial and final NO_3^- concentrations.

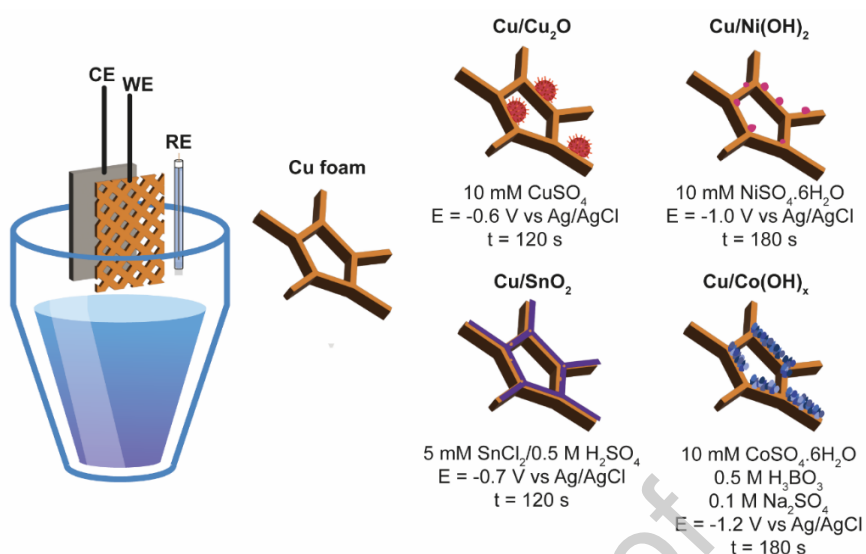


Figure 1. Summary schemes of experimental conditions containing electrochemical bath concentrations, applied potential, and optimal time to prepare different bimetallic electrodes in a three-electrode configuration cell.

3. Results and discussion

3.1. Electrodeposition generates electrocatalytic earth-abundant bimetallic surfaces

The electrochemical modification of Cu foam with various earth-abundant compounds was morphologically characterized using FE-SEM images. Figures 2a and 2b depict the configuration of Cu foam, featuring an average pore size of $167.8 \pm 28.6 \mu\text{m}$ and a pore pillar width of $55.7 \pm 4.7 \mu\text{m}$, resulting in a calculated pore per inch (PPI) of approximately 115.0 ± 14 . At higher magnification (Figure 2c), the smooth Cu foam surface resembles fish scales, with some craters but devoid of particles. Upon modification with Cu_2O nanocomposites (Figure 2d), the Cu foam surface exhibits nano-urchin particles with a wide size range around $138.2 \pm 39.6 \text{ nm}$. Electrodeposition of $\text{Ni}(\text{OH})_2$ yields nanosphere composites on the foam surface (Figure 2e), characterized by an average size of $119.7 \pm 21.2 \text{ nm}$. Following the electrodeposition of SnO_2 nanoparticles, the surface displays high area coverage, forming a thin film with particle sizes averaging $52.7 \pm 7.0 \text{ nm}$ (Figure 2f). Finally, the electrodeposition of $\text{Co}(\text{OH})_x$ nanoflakes results in an average particle size of $98.7 \pm 28.1 \text{ nm}$ (Figure 2g). These findings underscore the diverse shapes generated from the electrodeposition of different compounds and highlight the generation of bimetallic surfaces, exposing Cu foam and metal composite nanoparticles that alter the overall morphology of the system.

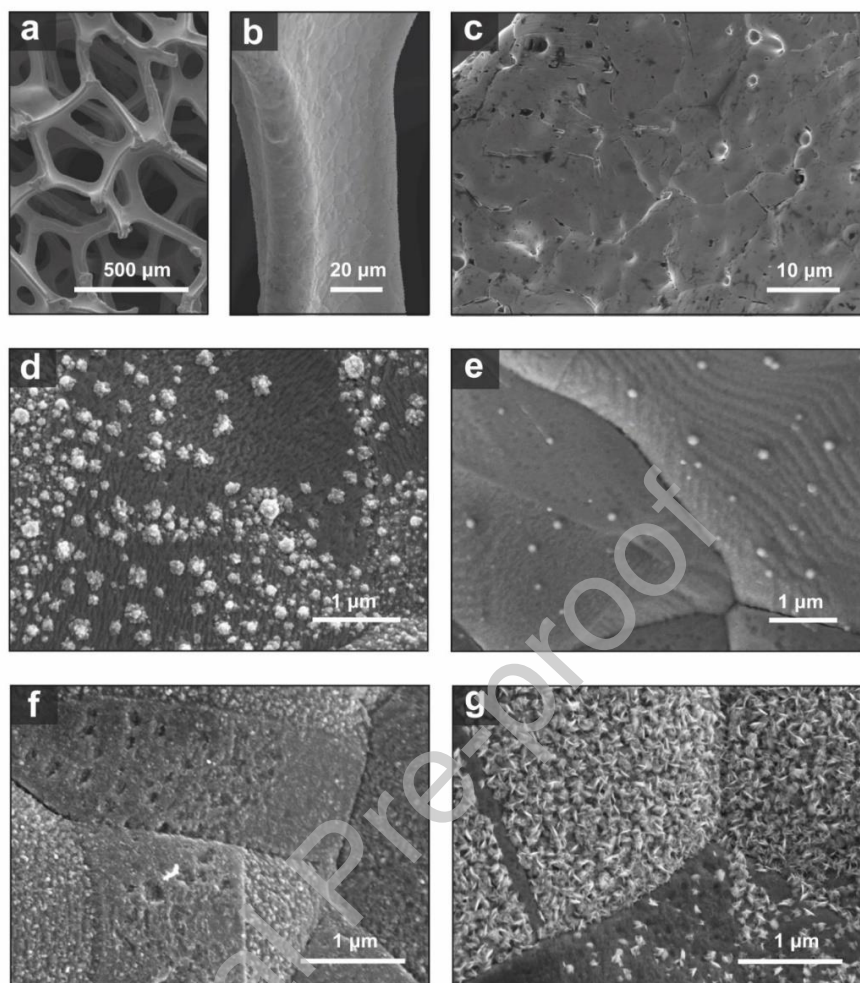


Figure 2. SEM images of Cu foam (a), (b), and (c) at different magnifications, (d) Cu/Cu₂O, (e) Cu/Ni(OH)₂, (f) Cu/SnO₂, and (g) Cu/Co(OH)_x.

The electrodeposition modification was through elemental mapping via energy dispersive spectroscopy (EDS-mapping), scanning transmission electron microscope (STEM) bright-field (BF) images, and chemical identification by X-ray photoelectron spectroscopy (XPS). Initially, characterization of the Cu foam provided a pristine substrate for comparison with various nano-enabled compounds generated during the electrodeposition process. Figure S2 displays the EDS mapping, predominantly revealing the presence of Cu and O on the surface, where the presence of oxygen can be attributed to inevitable oxide formation under atmospheric conditions after the cleaning treatment. Crystallographic structure, determined using interplanar distance obtained from BF-STEM images, identifies the plane (111) in CuO with an interplanar distance of 0.21 nm for bare Cu foam [49]. High-resolution Cu 2p XPS spectra demonstrate the presence of Cu²⁺ and Cu⁺¹/Cu⁰ at 934.6 and 932.2 eV, respectively, with a shake-up satellite confirming CuO in the pristine foam [50,51].

In Figure 3a, EDS mapping after modification with Cu_2O indicates the uniform distribution of Cu and O elements on the particles obtained after sonication treatment. Crystal structure identification by BF-STEM image reveals an interplanar distance of 0.30 nm corresponding to the plane (110) present in the Cu_2O structure [52,53]. Additionally, the high-resolution Cu 2p XPS spectra demonstrate a higher intensity for $\text{Cu}^{+1}/\text{Cu}^0$ than Cu^{2+} , supporting the plane obtained by BF-STEM. Figure 3b shows the EDS mapping of the bimetallic surface Cu foam and $\text{Ni}(\text{OH})_2$, evidencing the coexistence of Cu and Ni elements in the particle. BF-STEM images identify an interplanar distance of 0.27 nm corresponding to the plane (100) present in the $\text{Ni}(\text{OH})_2$ structure [54,55]. Moreover, the high-resolution XPS spectra for Ni 2p demonstrate the coexistence of Ni^{2+} and Ni^{3+} at 853.2 and 854.6 eV, respectively. Figure 3c presents the EDS mapping for Cu/ SnO_2 , evidencing the uniform distribution of Cu and Sn elements on the particle, confirming the successful generation of the bimetallic electrode. The interplanar distance determined by BF-STEM identifies an interplanar distance of 0.25 nm corresponding to the plane (101) in the SnO_2 structure [56,57]. Furthermore, XPS spectra for Sn 3d demonstrate the predominant Sn^{4+} compared to Sn^0 at 486.6 and 485.0 eV, respectively [58]. Finally, the Cu/ $\text{Co}(\text{OH})_x$ EDS mapping demonstrates the coexistence of Cu and Co elements on the electrode surface. The BF-STEM image determines an interplanar distance of 0.27 nm corresponding to the plane (010) in the $\text{Co}(\text{OH})_2$ structure [59]. Nevertheless, the Co 2p XPS spectra suggests the coexistence of Co^{2+} and Co^{3+} at 779.6 and 782.1 eV, respectively [60,61]. According to these results, the bimetallic electrodes obtained represent an intricate surface with different composites of the elements generating different sites for adsorption and electron transfer processes. Therefore, under practical conditions, the materials prepared are designated as Cu foam, Cu/ Cu_2O , Cu/ $\text{Ni}(\text{OH})_2$, Cu/ SnO_2 , and Cu/ $\text{Co}(\text{OH})_x$.

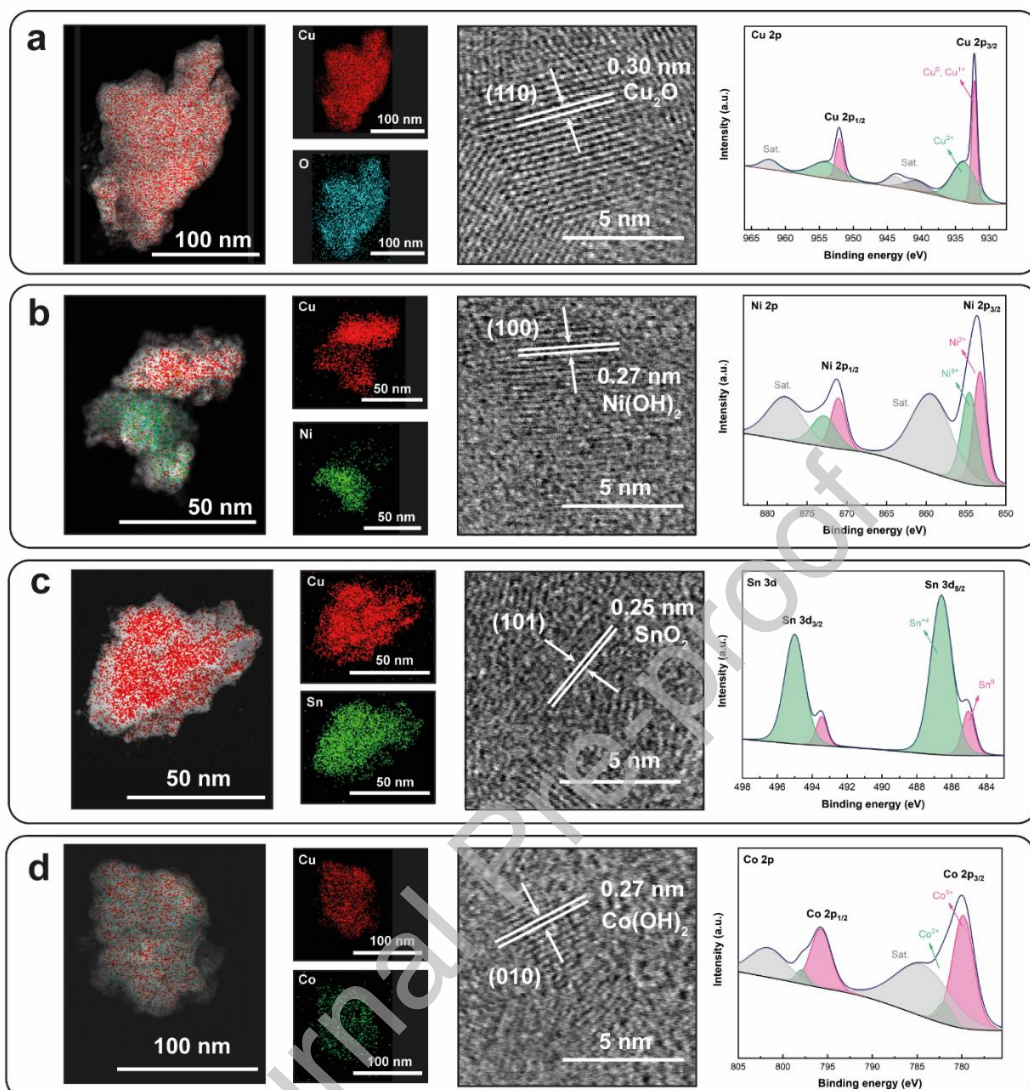


Figure 3. EDS mapping, BF-STEM images, and high-resolution XPS spectra for (a) Cu/ Cu_2O , (b) Cu/ Ni(OH)_2 , (c) Cu/ SnO_2 , and (d) Cu/ Co(OH)_x . Complete XPS analysis for each composition is available in the supplementary material as Figures S3-S6.

3.2. Bimetallic electrodes present different electrocatalytic intrinsic activity compared to Cu foam

After generating bimetallic electrodes, the electrochemical surface area experienced changes in comparison to the pristine Cu foam. Therefore, evaluating the electrochemical surface area (ECSA) becomes crucial for evaluating the ERN response across different configurations. The ECSA is estimated through the electrical double-layer approach using a specific capacitance (e.g., $40 \mu\text{F cm}^{-2}$), determined via cyclic voltammetry (CV) within a non-Faradaic current potential range e [62]. As illustrated in Figures

S7-S11 and summarized in Table S1, the calculated ECSA values for Cu foam, Cu/Cu₂O, Cu/Ni(OH)₂, Cu/SnO₂, and Cu/Co(OH)_x are 5.58, 3.73, 5.75, 22.05, and 23.40 cm², respectively. These results demonstrate both minor and substantial deviations from the initial ECSA of pristine Cu foam. Such disparities could lead to either over or underestimation of the electrochemical responses since the non-Faradaic current of the real ECSA is not accounted for. Consequently, the experimental ECSA values were used to normalize the electrocatalytic responses in terms of current density (mA cm_{ECSA}⁻²).

The electrocatalytic intrinsic activity was assessed by linear sweep voltammetry (LSV) in 12.5 mmol L⁻¹ Na₂SO₄ as support electrolyte, both in the absence and presence of 2 mmol L⁻¹ NaNO₃. Figure 4a illustrates the LSV of bare Cu foam, demonstrating a pronounced increase in current density in the presence of NaNO₃ in a range of -0.9 to -1.4 V vs Ag/AgCl. The highest current density difference, reaching -0.44 mA cm_{ECSA}⁻² occurs at -1.2 V vs Ag/AgCl, representing the specific potential for the ERN. Similarly, significant differences were observed for bimetallic electrodes (Figure S12), with values of -0.083, -0.15, -0.59, -0.74 mA cm_{ECSA}⁻² for Cu/Ni(OH)₂, Cu/SnO₂, Cu/Cu₂O, Cu/Co(OH)_x, respectively. Figure 4b presents the highest current density difference for each configuration at specific potentials (-1.3 and -1.2 V vs Ag/AgCl).

This evaluation indicates that modifying Cu with Ni(OH)₂ and SnO₂ nanocomposites decreases the intrinsic activity, resulting in a lower current density difference. On the other hand, modification with Cu₂O and Co(OH)_x enhances intrinsic activity, presenting a higher current density difference than Cu foam. Furthermore, this trend in intrinsic activity may reflect the performance of NO₃⁻ conversion using the bimetallic electrodes.

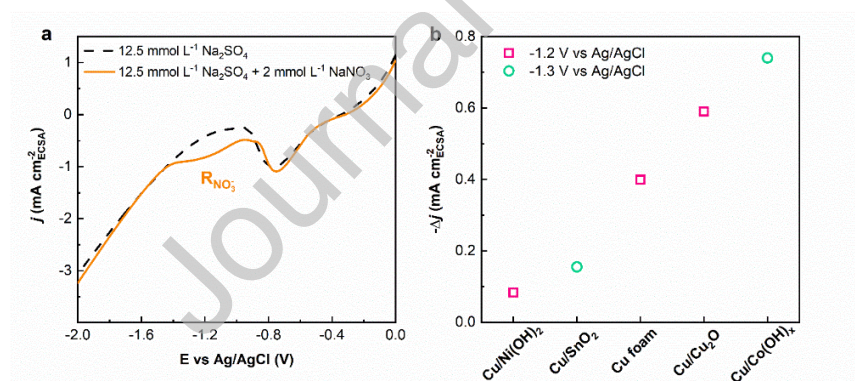


Figure 4. (a) LSV of Cu foam in the absence and presence of 2 mmol NaNO₃ with current density normalized by ECSA calculated. (b) Current density difference recorded in the absence and presence of NaNO₃ for bimetallic electrodes at the determined potential.

3.3. Bimetallic electrodes dominates the performance of ammonia production

The bimetallic electrodes were tested under galvanostatic conditions maintaining a current density of 20 mA cm^{-2} with an initial concentration of $30 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$. The time-course mass balance of N-species for bare Cu foam (Figure S13) reveals a NO_3^- conversion of 62.5 % after 240 min of treatment, resulting in a final concentration of $11.24 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$. Notably, the maximum NO_2^- peak production occurs at 90 min reaching $5.12 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$, while NH_3 reaches $14.7 \text{ mg L}^{-1} \text{ NH}_3 \text{-N}$ by the end of the 240 min period.

The NO_3^- conversion for $\text{Cu/Cu}_2\text{O}$ and Cu/Ni(OH)_2 (Figure 5a and 5b) after 240 min of electrolysis was 72.3 % and 29.3 %, respectively. In the case of Cu/SnO_2 (Figure 5c), the conversion reaches around 31.6% at 60 min without significant increase until 120 min. Conversely, Cu/Co(OH)_x (Figure 5d) achieves 98.3 % conversion in the first 120 min. These results indicate that $\text{Cu/Cu}_2\text{O}$ and Cu/Ni(OH)_2 demonstrate continuous NO_3^- conversion over time. In contrast, Cu/SnO_2 and Cu/Co(OH)_x represents cases with sluggish and outstanding conversion, respectively.

Regarding NO_2^- yield, $\text{Cu/Cu}_2\text{O}$ leads to the highest accumulation of undesired NO_2^- ($8.57 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$) in 30 min of electrolysis, followed by 3.62, 1.71, and $1.15 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ from Cu/SnO_2 , Cu/Ni(OH)_2 , and Cu/Co(OH)_x , respectively. Note that NO_2^- is a more harmful contaminant than NO_3^- with a maximum contaminant concentration limit of $1 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ [63]. Therefore, electrodes with higher concentrations of NO_2^- require further modification to completely reduce this N-species. For instance, the use of Cu/Co(OH)_x achieves almost 99% conversion of NO_3^- with negligible NO_2^- concentration after 120 min of electrolysis.

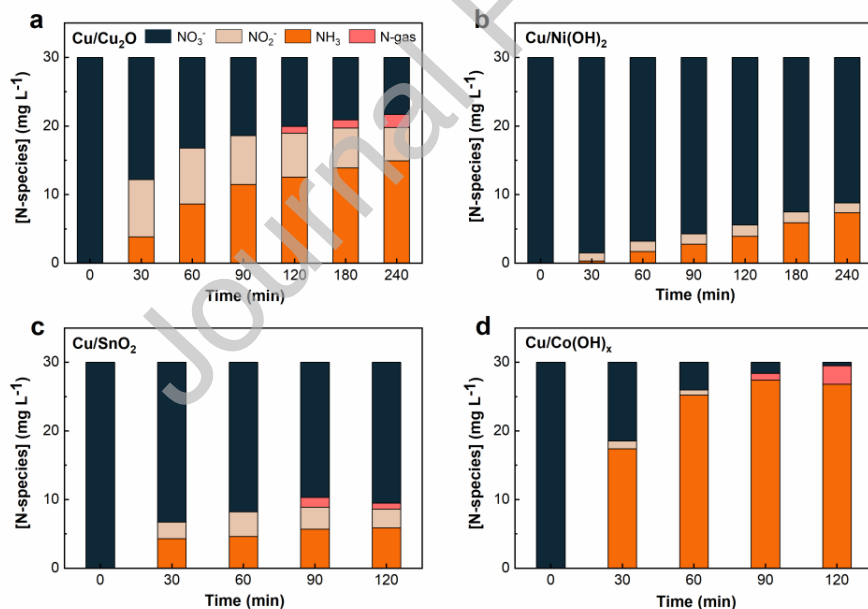


Figure 5. Time-course N-species mass balance during ERN at 20 mA cm^{-2} using different bimetallic electrodes in $30 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ (a) $\text{Cu/Cu}_2\text{O}$, (b) Cu/Ni(OH)_2 , (c) Cu/SnO_2 , and (d) Cu/Co(OH)_x .

To identify significant differences in conversion and time-course behavior of N-species after Cu foam modification, electrolysis experiments were conducted using an initial concentration of 30 mg L^{-1}

NO_2^- -N under identical conditions. Figure 6a illustrates the NO_2^- concentration profiles over a 240 min electrolysis at 20 mA cm^{-2} for different configurations. Employing a pseudo-first kinetic order as shown in Figure 6b, kinetic constants were calculated obtaining values of 1.4×10^{-2} , 1.8×10^{-2} , 25×10^{-2} , 2.8×10^{-2} , and $10.9 \times 10^{-2} \text{ min}^{-1}$ for Cu/SnO₂, Cu/Cu₂O, Cu/Ni(OH)₂, Cu foam, and Cu/Co(OH)_x, respectively. The minimal values corresponding to Cu/SnO₂ and Cu/Cu₂O materials demonstrate their low activity in converting NO_2^- , which explains the observed accumulation of NO_2^- . The sluggish activity of SnO₂ modification is related to the high solution pH (≥ 8) which promotes the formation of Sn(OH)⁺ and Sn(OH)₂ inhibiting the adsorption of NO_3^- at the electrode surface [39]. Meanwhile, the outstanding kinetics of Cu/Co(OH)_x can account for the significant difference on NO_2^- conversion kinetics observed among bimetallic configurations. Therefore, the mechanism can be explained by a two-step process, considering the rate-limiting step occurring over Cu sites (Equation (7)) and the subsequent reduction of NO_2^- on Co sites (Equation (8)). These results underscore Cu/Co(OH)_x as competitive bimetallic composition.

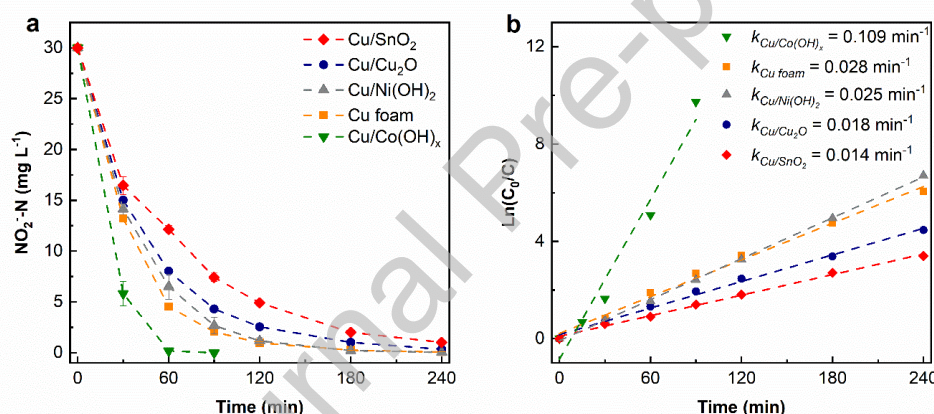
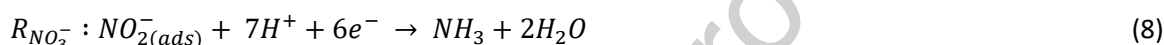
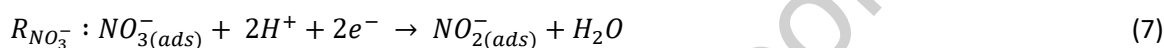


Figure 6. (a) Time-course concentration of initial 30 mg L^{-1} NO_2^- -N at 20 mA cm^{-2} using different electrode configurations. (b) Linear fit model for pseudo-first order reaction with calculated kinetic constants for the conversion of NO_2^- .

3.4. Figures of merit for bimetallic electrodes assess ammonia production

Advancing towards higher technology readiness levels (TRL) involves transitioning from laboratory-scale research to the development stages, requiring validation under relevant conditions. Considering that existing electrochemical systems in the market operate under galvanostatic conditions (e.g., electrochlorination, electrocoating systems), assessing nitrate reduction under such conditions becomes a crucial step before further refining designs of electrochemical NH_3 generators. Therefore, determining the NH_3 yield obtained under different current densities to establish the EE/O and Faradaic efficiency under realistic operational settings is essential. These parameters are required for conducting techno-economic analysis and discussing the process feasibility across various boundary scenarios.

Figure 7 illustrates the NH₃ yield (mmol NH₃ g_{cat}⁻¹ h⁻¹) at different current densities for each bimetallic configuration. Starting from an initial 30 mg L⁻¹ NO₃⁻-N, and assuming complete conversion with 100% selectivity towards ammonia within 2h of treatment using a standardized catalyst mass of 0.145 g, the maximum yield attainable is 0.74 mmol NH₃ g_{cat}⁻¹ h⁻¹. While selectivity performance can be overestimated due to dependency on the conversion levels reached, NH₃ generation efficiency offers a more comprehensive benchmarking tool, encompassing both the concepts of selectivity and conversion. For instance, Cu/Cu₂O generates 12.4 mg L⁻¹ NH₃-N after 2 h, representing a selectivity to NH₃ of 62.8 % at 20 mA cm⁻². With an NH₃ yield of 0.28 mmol NH₃ g_{cat}⁻¹ h⁻¹, it represents a NH₃ generation efficiency of 35 %. This comparison highlights the NH₃ generation efficiency as a more reliable measure concerning NH₃ generation.

Similarly, Cu/Ni(OH)₂ reaches a maximum NH₃ yield of 0.21 mmol NH₃ g_{cat}⁻¹ h⁻¹ at 10 mA cm⁻², corresponding to 26.3 % NH₃ generation efficiency. Cu/SnO₂ configuration achieves a maximum NH₃ yield of 0.14 mmol NH₃ g_{cat}⁻¹ h⁻¹, with an NH₃ generation efficiency of 17.5 % at 20 mA cm⁻². While NH₃ generation efficiency remains low for the bimetallic Cu/Cu₂O, Cu/Ni(OH)₂ and Cu/SnO₂ due to low kinetics and NO₂⁻ accumulation, Cu/Co(OH)_x outperforms them. With a maximum NH₃ yield of 0.66 mmol NH₃ g_{cat}⁻¹ h⁻¹, Cu/Co(OH)_x demonstrates an NH₃ generation efficiency of 89.1 % at 20 mA cm⁻². This outstanding performance can be attributed to the higher kinetics constant of Co(OH)_x observed in the NO₂⁻ reduction experiment. The NH₃ generation efficiency provides a better comparison between materials under identical experimental conditions, revealing the trend of Cu/Co(OH)_x ≥ Cu/Cu₂O ≥ Cu foam ≥ Cu/SnO₂ ≥ Cu/Ni(OH)₂. While selectivity serves as a benchmarking parameter, indicating over 60% of selectivity for all configurations (see Table 1), NH₃ generation offers a more competitive assessment of each configuration.

The applied current density sets a related electrical potential on the electrodes. Measurements recorded using a multimeter and Ag/AgCl reference electrode indicate that at current densities 2.5 and 5 mA cm⁻², the electrical potential reached by the cathode across all configurations is lower than -1.6 V vs Ag/AgCl, confirming the low NH₃ yield due to low overpotential relative to NO₃⁻ and NO₂⁻ reduction potentials determined by LSV. However, at current densities exceeding 10 mA cm⁻², the cathode potential surpasses -2.2 V vs Ag/AgCl. Consequently, overpotential boosts the NH₃ yield at 10 mA cm⁻² and higher current densities until the hydrogen evolution reaction (HER) takes the primary role. Notably, Cu/Co(OH)_x exhibits a unique behavior with current density increase, where NH₃ production increases, contrary to the other configurations tested. This can be attributed to the ability of Co(OH)_x sites to adsorb atomic hydrogen which poses a high reductive potential demonstrated experimentally by electrochemical (e.g., Cyclic voltammetry), spectroscopy (e.g., electron spin resonance), and scavengers (e.g., tert-butyl alcohol) approaches [64–67]. Thus, the Cu/Co(OH)_x configuration performs both direct and indirect reduction (Equations (9) – (15)), boosted by the atomic hydrogen adsorbed [28,42,68].





The Faradaic efficiency (*FE*) for NH₃ generation represents the ratio between electrons supplied to the system and those used for NH₃ production. Generally, at a fixed potential, FE is high when a specific reaction occurs without any parallel reaction. However, under galvanostatic conditions the experimental potential changes depending on the applied current densities. Figure 7 presents the *FE* of each electrode at specific current densities. The HER for the bare Cu foam is around -1.1 V vs Ag/AgCl, with variations depending on the bimetallic surface (see Figure 4a and Figure S12). The maximum FE reached values of 14, 18, 8, and 41 % for Cu/Cu₂O, Cu/Ni(OH)₂, Cu/SnO₂, and Cu/Co(OH)_x, respectively.

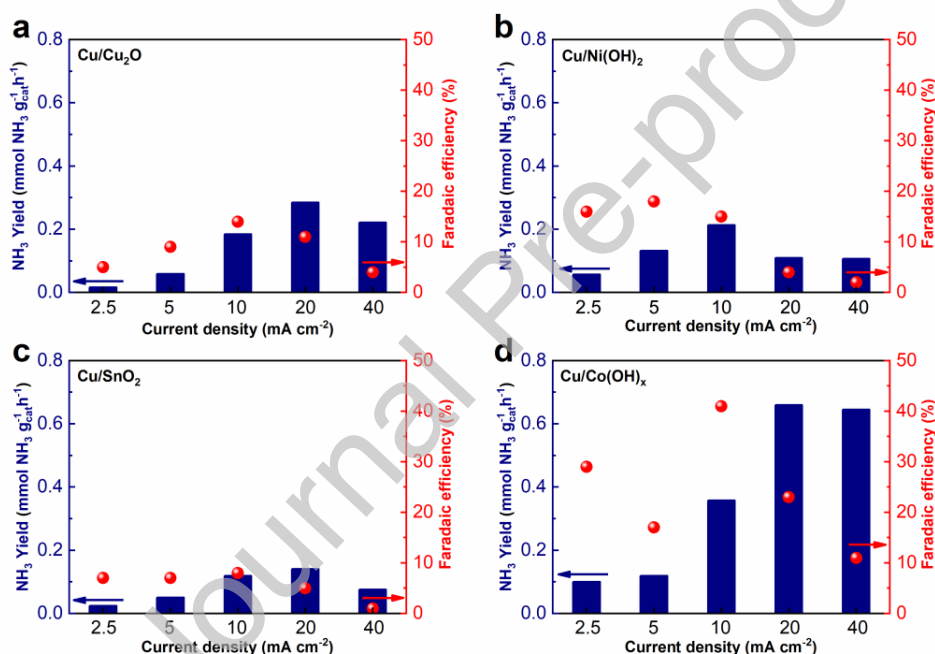


Figure 7. Ammonia yield ($\text{mmol NH}_3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and Faradic efficiency (%) after 2 h of electrolysis at different current densities (2.5, 5, 10, 20, and 40 mA cm^{-2}) using (a) Cu/Cu₂O, (b) Cu/Ni(OH)₂, (c) Cu/SnO₂, and (d) Cu/Co(OH)_x electrodes for ERN in a 30 mg L^{-1} NO₃⁻-N solution.

The electrical energy per order (*EE/O*) represents the energy required to decrease the concentration of NO₃⁻ by one order of magnitude, making kinetics for NO₃⁻ conversion play an important role in energy consumption. Figure 8 depicts the kinetic constants calculated considering a pseudo-first order reaction and the corresponding *EE/O* values for specific configurations, including bare Cu foam. Compared to Cu foam, which has a kinetic constant of $6.3 \times 10^{-3} \text{ min}^{-1}$ and *EE/O* of 44.5 $\text{kWh m}^{-3} \text{ order}^{-1}$, Cu/Ni(OH)₂ and Cu/SnO₂ present a kinetic constants of $1.79 \times 10^{-3} \text{ min}^{-1}$ and $4.25 \times 10^{-3} \text{ min}^{-1}$ resulting in *EE/O* values of 192 and 127 $\text{kWh m}^{-3} \text{ order}^{-1}$, respectively. Meanwhile, Cu/Cu₂O and Cu/Co(OH)_x display

kinetic constants of $8.21 \times 10^{-3} \text{ min}^{-1}$ and $33.8 \times 10^{-3} \text{ min}^{-1}$, yielding EE/O values of 39.0 and $11.0 \text{ kWh m}^{-3} \text{ order}^{-1}$, respectively. One of the key findings is the high activity of Cu/Co(OH)_x with superior NH_3 generation efficiency at lower energy consumption compared to other configurations. Table 1 summarizes the significant revelations for all configurations, including NO_3^- conversion, NH_3 selectivity, generation efficiency, NH_3 yield, Faradaic efficiency, kinetics constant, and electrical energy per order. These results suggest that bimetallic materials harnessing the synergies of indirect reduction through hydrogenation (i.e., Cu/Co(OH)_x) hold promise for boosting performance under galvanostatic operation while enhancing selectivity of ammonia production with reduce energy demands.

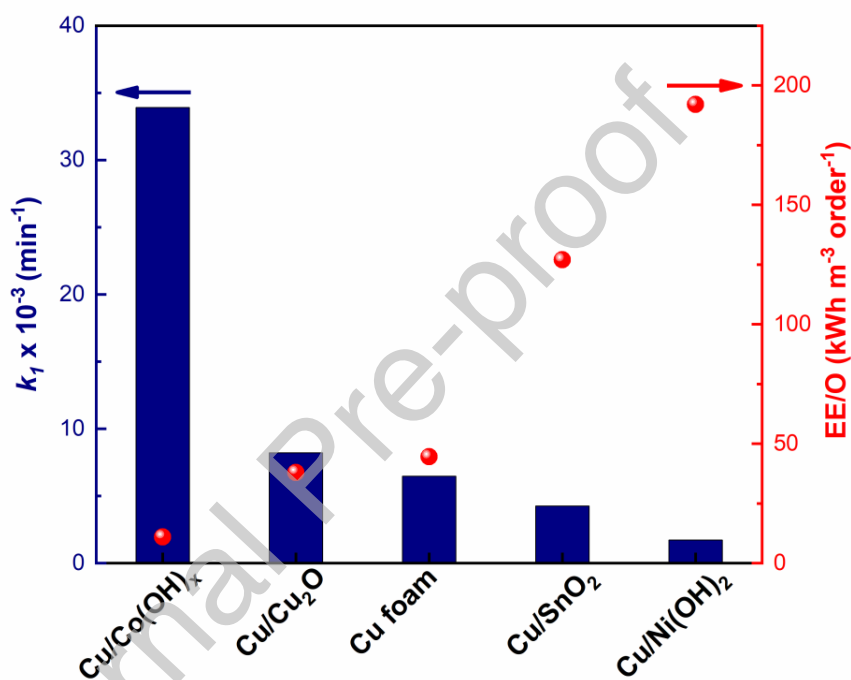


Figure 8. Pseudo-first order kinetic constant for NO_3^- conversion (min^{-1}) and the electric energy per order ($EE/O - \text{kWh m}^{-3} \text{ order}^{-1}$) for bare Cu foam, $\text{Cu/Cu}_2\text{O}$, Cu/SnO_2 , Cu/Ni(OH)_2 , and Cu/Co(OH)_x .

Table 1. Performance parameters of bimetallic electrodes for the electrochemical NH_3 generation from initial $30 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ under 20 mA cm^{-2} for 2 h including nitrate conversion (NC), ammonia selectivity (S_{NH_3}), ammonia generation efficiency (GE), ammonia maximum yield ($Yield_{max}$), Faradaic efficiency (FE), pseudo-first order kinetic rate constant (k_1), and electrical energy per order (EE/O).

Electrode	NC (%)	S_{NH_3} (%)	GE (%)	$\text{NH}_3 \text{ Yield}_{max}$ (mmol NH_3 $\text{g}_{cat}^{-1} \text{ h}^{-1}$)	FE (%)	k_1 (min^{-1})	EE/O (kWh m^{-3} order^{-1})
Cu foam	54	70.1	37.8	0.28	10	6.3×10^{-3}	44.5

Cu/Cu₂O	66.5	62.8	40.5	0.30	11	8.2 x 10 ⁻³	38
Cu/Ni(OH)₂	18.6	69.8	13.5	0.10	4	1.7 x 10 ⁻³	192
Cu/SnO₂	31.6	62.1	18.9	0.14	5	4.2 x 10 ⁻³	127
Cu/Co(OH)_x	98.3	91	89.1	0.66	23	33 x 10 ⁻³	11

4. Conclusions

This study evaluates bimetallic earth-abundant electrodes for electrochemical reduction of nitrate, employing environmentally relevant concentrations of 30 mg L⁻¹ NO₃⁻-N and 12.5 mmol L⁻¹ Na₂SO₄ under galvanostatic conditions. The electrodes Cu/Cu₂O, Cu/Ni(OH)₂, Cu/SnO₂, and Co(OH)_x were synthesized over 110 PPI Cu foam by a simple electrodeposition method and then thoroughly characterized. Evaluation of intrinsic activity via linear sweep voltammetry reveals the following trend for NO₃⁻ reduction: Cu/Co(OH)_x > Cu/Cu₂O > Cu foam > Cu/SnO₂ > Cu/Ni(OH)₂. Electrolysis at 20 mA cm⁻² validates this trend, with Cu foam, Cu/Cu₂O, and Cu/Ni(OH)₂ exhibiting continuous conversion over time accompanied by NO₂⁻ accumulation in solution, while Cu/SnO₂ faces challenges in conversion after 1 h of electrolysis. Conversely, Cu/Co(OH)_x demonstrates superior conversion and NH₃ generation efficiency compared to other configurations. Electrolysis of 30 mg L⁻¹ NO₂⁻-N at 20 mA cm⁻² for 2 h evaluates the capability to reduce the NO₂⁻, revealing a kinetic constant trend of Cu/Co(OH)_x > Cu foam > Cu/Ni(OH)₂ > Cu/Cu₂O > Cu/SnO₂. Evaluation of current densities determines optimal conditions for NH₃ yield, considering the Faradaic efficiency, NH₃ generation efficiency, and electrical energy per order. These findings shed light on electrocatalysis performed under galvanostatic conditions and inform the logical design of electrocatalysts using earth-abundant materials. The identification of electrocatalytic materials capable of exploiting parasitic HER reaction to stabilize strong reductant Hads appears as essential for enhancing the performance of galvanostatic systems. Enabling indirect electrochemical reduction processes holds promise for synergistically leveraging a once-considered parasitic reaction to facilitate a low energy, high-selectivity transformation of nitrate into ammonia through simultaneous electrocatalytic hydrogenation mechanisms.

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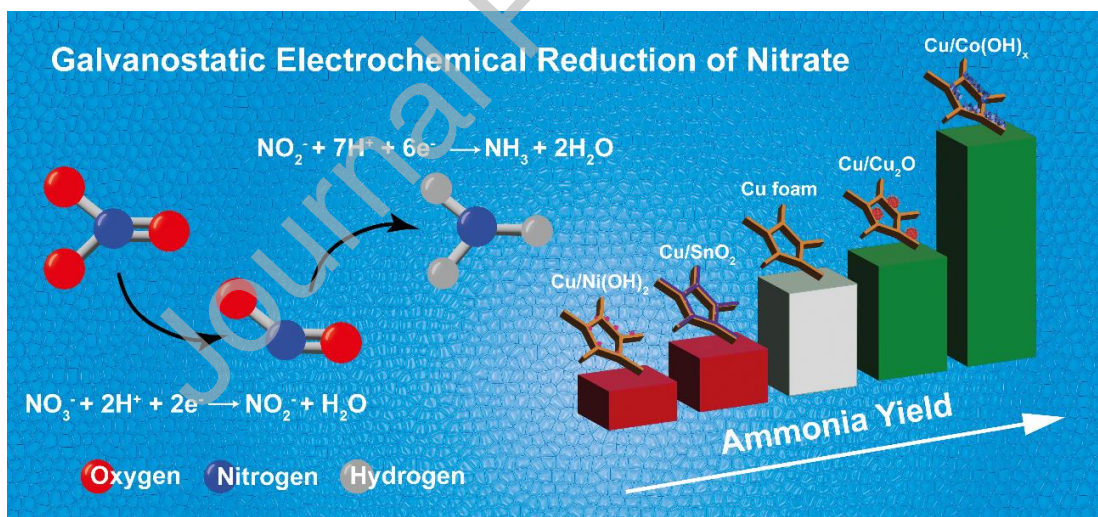
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Graphical Abstract



Conflict of interest

Authors declare no conflict of interest.