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Efficient electrocatalytic nitrate reduction using 3D copper foam-supported Co hexagonal nanoparticles in a membrane electrode assembly



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ABSTRACT

Electrocatalytic nitrate reduction reaction (NO₃RR) provides a promising route for nitrate recycling and ammonia production. In this work, Co nanoparticle catalyst was developed on a copper foam substrate (CoNPs/CF) by electrodeposition. The CoNPs/CF catalysis exhibits a Faradaic efficiency (FE) of 92.0% at -0.2 V vs. RHE and an NH₃ yield rate of 14328.65 µg h⁻¹ cm⁻² at -0.5 V vs. RHE. In-suit Raman spectroscopy and theoretical calculations demonstrated that the 3D copper foam structure of the substrate enhances the electron exchange capacity, which promotes the adsorption of nitrate on the cobalt (Co) surface. Moreover, Membrane Electrode Assembly (MEA) is employed with CoNPs/CF, contributing to 98.43 mg h⁻¹ with FE over 80%. Coupled with an air stripping process, this configuration has enabled the successful production of high-purity gaseous NH₃ products. This work suggests a practical and viable approach for the conversion of wastewater nitrate into valuable ammonia products.

1. Introduction

Ammonia (NH₃) plays a pivotal role across diverse sectors such as agriculture and the chemical industry, with a global demand of over 150 million tons annually [1,2]. The Haber-Bosch process (HBP) stands as the prevailing technique for industrial NH₃ synthesis. Nevertheless, it required harsh reaction conditions, contributing to large energy consumption and substantial greenhouse gas emissions throughout the production process, which raised notable concerns regarding energy and environmental cost [3,4]. Recently, electrocatalytic ammonia production has attracted tremendous attention. In comparison to HBP, direct electrocatalytic nitrogen (N2) reduction reaction under moderate reaction conditions, is compatible with intermittent renewable electricity and has captured attention [1,5]. However, the high dissociation energy of the N \equiv N bond (941 kJ/mol) with ultralow N₂ solubility greatly affects the reaction activity, while competing hydrogen evolution reaction (HER) further deteriorates the product selectivity and NH₃ yield rate [6,7]. The Nitrate (NO₃) features a lower bond energy (204 kJ/mol) and higher solubility, rendering it a superior feedstock for NH₃ synthesis [8,9]. Furthermore, excessive nitrate in nature serves as a form of pollution and leads to groundwater contamination [10–12]. Therefore, electrocatalytic nitrate reduction reaction (NO₃RR) serves a dual role via concurrently enabling eco-friendly NH₃ production while effectively mitigating excessive nitrate pollutants in water.

NO₃RR is a complex reaction process involving eight electron transfers with various intermediates toward different products [13,14]. Noble metals are active for the NO₃RR [15,16], but their scarcity hamper their wide use. Transition metals such as Fe [17–19], Cu [20], Ni [21] and Co [22-27] were used as economic alternatives due to their catalytic power toward conversion of NO₃⁻ to NH₃. Previous research shows two most challenging steps (protonation of adsorbed NO₂ to form NO₂H and protonation of adsorbed NO to form NOH) were the keys to the high activity of the reaction in NO_3^- reduction to NH_3 [28], and metallic Co catalysts shown high intrinsic activity and were widely used in NO₃RR. Apart from the material properties, the electrode material's structure plays a crucial role in influencing electrochemical activity. Electrode materials featuring three-dimensional (3D) porous foam structures offer significant advantages for electrocatalytic reactions, characterized by abundant electroactive sites and efficient electron transport channels [29-31].

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Besides electrocatalyst design, the electrocatalytic device is also important for NO3RR. Current research is predominantly centered on the H-type electrolytic cell to assess the intrinsic activity of electrocatalysts [21-33]. However, this device introduces multiple internal resistances that diminish energy efficiency, which was not suitable for scale-up and practical industrial applications. In contrast, membrane electrode assembly (MEA) represent a structural design extensively applied in fuel cells, where the cathode, membrane, and anode are tightly compressed in unison [34-36]. This configuration exhibits attributes such as a negligible gap, minimal internal resistance, and greater adaptability for expansion into large-area reactors or stacks, rendering it more suitable for industrial-scale production. Besides, in the conventional flow electrosorption system, as an aqueous solution flows through an electrode, reactants are adsorbed onto the electrode, leading to an immediate reduction in the concentration of the reactants around the electrode, while the forced flow of liquid in the MEA reactor introduces ensures uniform concentration of nitrate around the electrode during electroadsorption. This uniformity facilitates contact adsorption of nitrate on the catalyst surface, enhancing the reaction rate and product selectivity [37].

In this study, cobalt nanoparticles (CoNPs) were synthesized on a three-dimensional copper foam (CF) skeleton substrate through a facile electrodeposition process. The CoNPs/CF catalyst exhibited a remarkable Faradaic efficiency (FE) of 92.0% at -0.2 V vs. RHE with 0.1 M nitrate, and an impressive $\rm NH_3$ yield rate of 14328.65 $\mu g \ h^{-1} \ cm^{-2}$ at -0.5 V vs. RHE. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) reveals that the surface undergoes significant reconstruction during the NO3RR process. In-situ Raman spectroscopy and density functional theory (DFT) calculations indicate that, in comparison with CoNPs, the lower energy barrier observed on CoNPs/ CF reflects a more spontaneous thermodynamic tendency. Furthermore, the 3D copper foam structure of the substrate enhances electron exchange capacity, thereby facilitating the adsorption of nitrate on the cobalt (Co) surface. This allows nitrate radicals to occupy more active sites on the catalyst surface, thereby promoting the reaction. Additionally, a MEA reactor was specifically designed for continuous NO3RR and NH₃ synthesis using CoNPs/CF, achieving a high NH₃ yield rate of 100 mg h^{-1} , while maintaining Faradaic efficiencies of approximately 90%. The Techno-Economic Analysis (TEA) results indicate that the CoNPs/ CF catalyst, coupled with the developed electrocatalytic system, can substantially reduce production costs, thus offering a viable pathway for large-scale electrocatalytic synthesis of ammonia.

2. Materials and methods

2.1. Materials synthesis

The Cu foam was cut into rectangle of area $1 \times 2 \text{ cm}^2$, and then ultrasonicated in ethanol, 0.05 M H₂SO₄ and ultra-pure water for 20 min, respectively. A certain amount of CoSO₄·7H₂O (Aladdin Ltd.) was diluted in ultra-pure water to prepare 0.33 mol L⁻¹ CoSO₄ solution (100 ml). Next, the treated Cu foam, Ag/AgCl electrode, and platinum foil $(1.5 \times 1.5 \text{ cm}^2)$ were used as working electrode, reference electrode, and counter electrode, respectively. The CoNPs/CF was synthesized by electrodeposition method at -1.4 V vs. Ag/AgCl for 1800s in the electrolyte of 0.33 mol L⁻¹ CoSO₄. The loaded Cu foam was rinsed by ultrapure water for several times, and used for electrochemical experiment immediately. For MEA, the Cu foam was cut into appropriate area and was electrodeposited in 200 mL of 0.33 mol L⁻¹ CoSO₄ solution at 500 mA cm⁻².

2.2. Material characterization

Scanning electron microscopy (SEM) (ZEISS Sigma 300) and transmission electron microscopy (TEM) (FEI Tecnai F20) were employed to investigate the morphology of the samples before and after NO_3RR . The

crystal structures of the samples were characterized via X-ray diffraction (XRD) with the Bruker D8 Advance at room temperature. The surface compositions of the electrocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha) with Al K α source of 1486.6 eV. In-suit Raman was performed by Renishaw inVia Reflex with EmVision HT-PROB-END0-785 system.

2.3. Electrochemical measurements

The electrochemical investigations were carried out with the CHI760E electrochemical workstation. The H-type electrolytic cell was adopted for electrocatalytic nitrate reduction reaction (NO₃RR) and was partitioned by the Nafion membrane. The prepared CoNPs/CF was applied as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode.

The concentration of NH₃ production was measured by the indophenol blue method. A certain of the electrolyte after NO₃RR was taken and diluted to 4 mL with 1 M KOH with 0.1 M KNO₃. A 2.4 mL solution containing 0.4 M sodium hydroxide (NaOH) and 0.32 M sodium salicylate (C₇H₅O₃Na) was added. Afterward, 800 µL of sodium hypochlorite (NaClO) solution (effective chlorine 0.35 wt%) and 320 µL of sodium nitrite ferricyanide (C₅FeN₆Na₂O) solution (33.6 mM) were added to the above solution. The absorbance was determined by UV–Vis spectrophotometry at 655 nm after 30 min. The alignment curve could be derived from various concentrations of NH₄⁴ solutions and the relevant absorbance. To calculate the NH₃ concentration, the concentrationabsorbance curve was calibrated using the standard ammonia chloride solution. NH₃ yield rate was calculated via the equation as follows:

$$Y_{NH_3} = c_{NH_3} \times V/t$$

where Y_{NH_3} was the NH₃ yield rate; c_{NH_3} was the measured NH₃ concentration; V was the volume of electrolyte; t was the reaction time during electrocatalysis.

The Faradaic efficiency (FE) was calculated according the following equation:

$$FE = \frac{n \times V_{catholyte} \times c_{NH_3} \times F}{i \times t}$$

where i is the total current; n represents the number of electron transfers toward the formation of 1 molecule of ammonia, which is 8 for nitrate reduction; $V_{catholyte}$ is the volume of catholyte (mL); c_{NH_3} represents the concentration of ammonia (M); F is the Faraday constant (96485 C mol⁻¹); t is the electrolysis time.

To exclude the influence of N-source from the environment, $a^{15}N$ isotope labeling experiment was performed combined with ¹H NMR (600 MHz, Agilent Technologies) test. KNO₃–¹⁵N (Macklin, >98.5%) was utilized as the nitrogen source, and ¹⁵NH⁴Cl was utilized to calibrate the standard curve. The NH₄⁺ product with KNO₃–¹⁵N nitrogen source was tested to confirm the source of nitrogen in ammonia by comparison with the ¹⁴NH₄⁺ peak.

2.4. DFT calculation

All the density functional theory calculations were employed by using Vienna Ab initio Simulation Package (VASP) [38]. The exchange-correlation interactions were described by the generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof functional (PBE) [39]. The projector augmented-wave pseudopotential (PAW) was used to describe electron–ion interactions and the cutoff energy of 450 eV for plain-wave basis sets was adopted [39]. The convergence threshold was 10^{-5} eV and 5 × 10^{-2} eV/Å for energy and force, respectively. The weak interaction was described by the DFT + D3 method using empirical correction in Grimme's scheme [40]. The vacuum space was set to be more than 15 Å, which was sufficient to avoid interactions between periodical structure.

Structural optimizations were performed on slab models with a grid of 3 x 3 x 1 k-point, and the band structures were calculated with the linear k-point setting. The reaction Gibbs free energy changes (ΔG) for each elementary step were based on the computational hydrogen electrode model, which can be calculated by the following equation:

$$\Delta G = \Delta E + \Delta Z P E T \Delta S$$

where ΔE represented the total energy, ΔZPE represented the change in zero-point energies (ZPE), T represented the temperature of 298.15 K, and ΔS represented the change in entropy of products and reactants. LOBSTER and VASPKIT were utilized to further analyzed the result from wavefunction [41,42].

2.5. MEA system for NO₃RR

The galvanostatic electrodeposition was performed in a MEA electrolyzer with a two-electrode system using a constant current power supply (Rigol PD832A). CoNPs/CF ($2 \times 2 \text{ cm}^2$) and Ni foam ($2 \times 2 \text{ cm}^2$) were used as the working and counter electrode, respectively. The catholyte (0.1 M KNO₃ + 1 M KOH) was singly passed through the cathode chamber at a constant rate of 100 r/min by a peristaltic pump. The anolyte (1 M KOH) was circulated through the anode chamber. An anion exchange membrane (AEM) (Fumasep FAA-3-50, 3*3 cm²) was used to separate the cathode and anode chambers. The AEM was soaked in 1 M KOH for 20 min at 60 °C.

The MEA based NH_3 Production and Purification system consists of two parts. The nitrate is reduced to ammonia in MEA, and exists together with K⁺, OH⁻ in the catholyte storage bottle. The catholyte with the generated NH_3 in it was air stripped for an efficient ammonia product collection due to the high ammonia vapor pressure in the alkaline environment. The air containing ammonia gas is then passed into a three-necked flask filled with pure water, and finally a high concentration of ammonia water is obtained. Heating the ammonia water and pure ammonia gas can be obtained.

Energy efficiency (EE) is the percentage of energy reserved in the targeted product divided by the total energy input to the electrolysis system. A high EE is indispensable in order to lower the electricity cost and improve the economic efficiency of the NO₃RR. In principle, the full-cell EE is highly associated with the cell voltage and Faradaic efficiency, as given by the equation:

$$EE = \frac{Energy required}{Energy input} = \frac{E_{OER} - E_{NO_3RR}}{E_{cell}}FE$$

where E_{OER} is the equilibrium potential of water oxidation (1.23 V vs. RHE); E_{NO_3RR} is the equilibrium potential (0.70 V vs. RHE) of nitrate electroreduction to ammonia in alkaline media; E_{cell} is the full-cell voltage; FE is the Faradaic efficiency for NH₃.

2.6. Techno-economic assessment

The energy consumption of electrolyzer was calculated by the full voltage and current density measured during electrochemical NRR reaction and the production rate of ammonia was obtained from experimental data. The capital cost and operational cost of extracting NO_3^- from waste water was taken from Ramesh et al. [43]. The electrochemical system cost was calculated to be 2770 \$/kW, which consists of the price of electrolyzer system and replacing the proton exchange membrane with the membranes used in our experiments at a cost of 901 \$/m². The designed output of ammonia was assumed to be 1000,000 kg/day (Table S1).

The following CAPEX and OPEX (Table S2) were used for the calculation of LCOA [44].

The fixed operating and maintaining cost for the electrochemical nitrate reduction reaction mainly contained the electricity, water and NO_3^- extraction cost. The main reactions for the entire electrochemical

production process were:

Cathode :
$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$$

Anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

The ratio of the ammonia to oxygen produced corresponds to the ratio of the respective stoichiometric number under the assumption of charge conservation. The water produced at the anode were considered recoverable. The variable operating and maintaining cost was assumed to be 1.5% of EPCC.

A sensitivity analysis was performed by varying different parameters (Table S3), including electricity and water prices, OPEX of NO₃⁻ extraction, discount rate, capacity factor, FE, full voltage and current density. In the base case, the capacity factor was set as 85 % assuming that the whole system requires 55 days of maintenance per year of production, which may be further reduced in the future considering that low-capacity renewable energy (e.g., solar, wind, etc.) may be used as a sole source of electricity. The FE under pessimistic case was set to be 75 % considering the catalyst performance degradation in the process.

3. Results and discussion

3.1. Characterization of CoNPs/CF

CoNPs/CF is obtained by facile electrodeposition at 0.33 M CoSO4 solution by manipulating pH to 7. Cu foam was employed as the 3D skeleton to ensure high conductivity. Electron microscopy is used to investigate the morphological and crystalline structure of the catalysts in Fig. 1(a), indicating homogeneous nano bundles structure was formed constituted by interweaved nanosheets with domain size below 300 nm. High-angle annular Dark Field (HADDF) images confirm the ultra-thin feature of the nanosheet (Fig. S5). According to STEM-EDS elemental maps, homogeneous distribution of Co was observed and no Cu was found (Fig. S3), which shows that Co is the main active site of the catalyst and the Cu foam plays the role of modifying the electronic structure. According to transmission electron microscopy (TEM) images, typical lattice spacings were observed with values of 0.216 nm corresponding to Co (100), 0.204 nm corresponding to Co (111), 0.191 nm corresponding to Co (101), and 0.125 nm corresponding to Co (110), respectively as depicted in Fig. 1(b)(c). The crystal structure is further investigated by X-ray diffraction (XRD). As presented in Fig. 1(h), the diffraction peaks at 41.7°, 44.2°, 47.6° and 75.9° exhibited a close alignment consistent to TEM images. Besides, the diffraction peak at 43.3° was corresponded to Cu(111) derived from the Cu foam skeleton.

To investigate the electronic structure of CuNi NPs/CF, X-ray photoelectron spectroscopy (XPS) was analyzed in Fig. 1(i), which shows the high-resolution Co 2p spectrum for the CoNPs/CF with two strong peaks at binding energies 781.05 eV and 797.24 eV, corresponding to $Co2p_{3/2}$ and $Co2p_{1/2}$, respectively. The binding energies at 781.05 eV should be attributed to the metallic state of $Co^0 2p_{3/2}$. The two satellite peaks located at 787.05 eV and 802.55 eV can be ascribed to the shakeup type peaks of Co. The atomic and chemical structure of the CoNPs/CF was comparatively investigated before and after NO3RR. The SEM and TEM images presented in Fig. 1(d)(g) and HADDF images (Fig. S25) illustrate the transformation of the initial Co nanobundles into hexagonal nanopieces, with crystal sizes at about 200 nm. The diffraction data of the catalyst after the reaction (Fig. S6) showed that the reconstructed catalyst crystal face was mainly Co(100) and Co(110), which was also confirmed in the HRTEM images (Fig. 1(e)(f)). Besides, two obvious peaks belonging to Co(OH)2 were found, indicating that parts of the metallic cobalt was converted into hydroxide during the reaction. The signals corresponding to other peaks attributed to hydroxides or oxides exhibit notably weak intensities, which are presumed to result from the minor oxidation of the sample during its storage and characterization processes. However, the XRD characterization shows that the crystal faces of the catalyst remain similar. After



Fig. 1. Characterization of CoNPs/CF electrocatalyst. (a–c) SEM and TEM image of initial CoNPs/CF. (d–g) SEM and TEM image of CoNPs/CF after NO₃RR. (h) Comparison of XRD spectra and (i) XPS peaks spectra of CoNPs/CF before and after NO₃RR.

electrocatalysis, the binding energy of Co $2p_{3/2}$ in CoNPs/CF shifted to a lower energy by 0.37 eV in comparison to the initial catalyst. Additionally, the satellite peak of Co $2p_{3/2}$ exhibited a shift to a lower energy by 1.37 eV. For Co $2p_{1/2}$, the binding energy shifted to a lower value by 0.56 eV. These alterations in binding energy are hypothesized to stem from shifts in the valence state of a portion of the cobalt during its transformation into hydroxide.

3.2. Electrocatalytic activity for NO₃RR

Electrocatalytic nitrate reduction reaction tests were performed using a typical three-electrode system in H-cell. Linear sweep voltammetry (LSV) was performed using the CoNPs/CF and CF with 1 M KOH electrolyte and a 1 M KOH + 0.1 M KNO₃ electrolyte, respectively, to assess its activity for nitrate reduction and the effect of substrate. As shown in in Fig. 2(a), the current density of CoNPs/CF reached 400 mA cm⁻² at ~ -0.26 V vs RHE, which is four times higher than that of Cu foam. The substantial increase of the current density suggests that the high catalytic activity of CoNPs/CF is not solely attributable to the copper foam substrate. Moreover, compared to pure KOH, the addition of 0.1 M KNO₃ electrolyte caused a great increase of the current density, which confirmed the occurrence of NO₃RR. Additionally, the onset potential shifted from around -0.3 V vs. RHE to approximately 0.05 V vs. RHE by adding nitrate, which displayed the excellent catalytic performance of CoNPs/CF in facilitating the nitrate reduction reaction.

Product selectivity was assessed through chronoamperometry at various applied potentials over 30 min of operation with 80% iR correction applied. The concentration of NH₃ generated was detected by the Indophenol blue colorimetric technique. In Fig. 2(b), FE and NH₃ yield rate were investigated at different applied potentials. The FE exhibited a linear increase as the potential increased from 0 V vs. RHE to -0.2 V vs. RHE, reaching a peak value of 92.0% at -0.2 V vs. RHE, while decreasing with the further negative shifting the potential. Besides, as the potential shifted from -0.2 V vs. RHE to -0.5 V vs. RHE, the NH₃ yield rate increased from 3475.97 μ g h⁻¹ cm⁻² to 14328.65 μ g h⁻¹ cm⁻². Maximum NH₃ yield rate of 15 mg h⁻¹ cm⁻² was achieved while maintaining a relatively high FE of approximately 83.1%. To confirm that nitrate was indeed the sole nitrogen source for NH_3 production, an isotope labeling experiment was conducted. As shown in Fig. 2(c), no triplet peaks corresponding to ¹⁴N were observed in the solution after electrocatalysis, indicating that nitrate served as the exclusive source of nitrogen, without contributions from other contaminants.

The effect of the nitrate concentration was also investigated regarding the nitrate source from different industrial applications. As shown in Fig. 2(d), a range of nitrate concentrations was selected, ranging from 2000 ppm to 10000 ppm at -0.2 V vs. RHE. The NH₃ yield rate exhibited a consistent increase with higher concentration from 1189.68 µg h⁻¹ cm⁻² at 2000 ppm to 6394.83 µg h⁻¹ cm⁻² at 10000 ppm. At relatively high nitrate concentrations exceeding 6000 ppm, the CoNPs/CF catalyst maintained FE over 90%. As the nitrate



Fig. 2. Electrochemical performance of NH_3 production from NO_3RR . (a) NO_3RR LSV curves of CoNPs/CF and Cu foam. (b) Effect of potential on the NH_3 yield rate and FE. (c) NMR spectra of ¹H for the electrolytes after NO_3RR test by using ¹⁵ NO_3^- and ¹⁴ NO_3^- . (d) Effect of nitrate concentration on the NH_3 yield rate and FE at -0.2 V vs RHE. (e) Stability test of CoNPs/CF. (f) *In-suit* Raman spectra of NO_3RR with CoNPs/CF.

concentration decreased from 6000 ppm to 2000 ppm, the FE of NH_3 exhibited a gradual decline to 80.7% attributed to the competitive hydrogen evolution reaction (HER). A long-term stability test of CoNPs/CF was conducted at a constant potential of -0.2V vs RHE. As shown in Fig. 2(f), the catalyst remained stable over 16 cycles with FE of NH_3 maintained at over 90%, further affirming its robustness and suitability for industrial applications.

To gain insight into the mechanism of NO_3RR , reaction intermediates at different potentials were probed using electrochemical in-situ Raman spectroscopy. As depicted in Fig. 2(f), two peaks were observed at 1050 cm⁻¹ and 1380 cm⁻¹, corresponding to the NO_3^- stretching vibrations as the spectral characteristics of free nitrate ion [45]. Three additional discernible peaks at 1019 cm⁻¹, 1184 cm⁻¹, and 1646 cm⁻¹ were attributed to the presence of bridging nitrate [45]. This suggests that nitrate was firmly adsorbed on the surface of the CoNPs/CF catalyst, even before an external potential was applied to the electrode. Additionally, a peak at 1069 cm⁻¹ appeared near the peak belonging to the free nitrate ion at 1050 cm⁻¹, and as the potential shifted negatively, the peaks intensity of the free nitrate ion decreased and the intensity of the peak at 1069 cm^{-1} became stronger, as shown in the red area in Fig. 2(f). Based on the observed phenomenon, it can be inferred that the peak at 1069 cm^{-1} can be considered as a shift from the peak at 1050 cm^{-1} . This shift may occur because the adsorption of cobalt (Co) induces a change in the vibrational state of nitrate radicals. Furthermore, as the potential decreases, more nitrate radicals likely transition from the free state to the adsorbed state, contributing to this shift in the Raman spectra. Besides, the peaks at 625 and 690 $\rm cm^{-1}$ can be assigned to $\rm CoO_x$ and CoOOH species [46]. Obviously, the bare Co converted into CoO_x and CoOOH species, which might contribute to the reconstruction of Co nanoparticles [46]. Simultaneously, this elucidates the origin of the robust signal attributed to Co(OH)2 in the diffraction data. These active materials undergo spontaneous conversion into hydroxides once the applied potential is discontinued. The observed presence of copper hydroxide in the reaction process might originate from a minimal amount of the exposed copper foam base or metallic copper within the 3D structure. In an alkaline environment during the reaction, it is feasible

that these components oxidize, leading to the formation of copper hydroxide.

3.3. DFT calculations

Furthermore, the role of CoNPs/CF in promoting electrocatalytic behavior of ammonia synthesis was explored by density functionalized theory (DFT) calculation. We initially compared the reaction pathway during NO₃RR on both CoNPs/CF and CoNPs surfaces, focusing on the potential-dependent step (PDS) of *NO₃ to *NO₃H (Fig. 3(a)). Notably, the lower energy barrier of 0.53 eV on CoNPs/CF reflected a more spontaneous thermodynamic tendency than CoNPs (0.57 eV).

In addition, the concerted hydrogen evolution processes for CoNPs/ CF and CoNPs were also calculated (Fig. S9), where the CoNPs/CF significantly accelerated the absorption and inhibited the releasing of Hads with a large energy barrier of 0.51 eV compared with that of CoNPs (0.11 eV), revealing that the CoNPs/CF acted as an excellent H supply center for the protonation of intermediates, effectively restraining the HER activity. With the incorporation of a Cu substrate, CoNPs@CF demonstrated enhanced hydrogen (*H) absorption capabilities, thereby facilitating the hydronation of nitrogen species on the catalyst surface. As shown in Fig. 3(b), by comparing the charge density difference between CoNPs/CF and CoNPs after the absorption of the NO₃⁻ molecule, we observed that NO₃⁻ forms covalent bonds with the surface Co active sites. Bader charge analysis demonstrated that the charge transfer on Co site from CoNPs and CoNPs/CF to absorbed NO_3^- were -0.17 e and -0.20 e, suggesting the stronger electron exchange capacity to promote adsorption strength on CoNPs/CF surface. The charge density difference on Cu/Co interface further revealed that the existence of Cu thus played a role of electron donation, resulting in favorable state for surface absorption. As shown in Fig. 3(c) and (d), The partial density of states (PDOS) of CoNPs/CF and CoNPs were depicted in an atomic level, where the d-band centers of CoNPs/CF and CoNPs were calculated to be -0.23eV and -0.48 eV, respectively. The introduction of Cu modulation resulted in a shift of the d-band center to higher energy closer to the Fermi level. Consequently, the higher energy of the anti-bonding orbitals led to the return of electrons towards the system, promoting the formation of a stable absorption structure. The enhanced absorption ability of CoNPs/CF of -2.28 than CoNPs (-2.22) in crystal orbital Hamilton populations (COHP) results in Fig. 3(e) further substantiated

the assumption.

3.4. MEA based NH₃ Production and Purification

Membrane electrode assemblies (MEAs) with their zero-gap structure are particularly well-suited for commercial electrocatalytic applications. To enhance NH3 production, a continuous flow reactor with an anion exchange membrane (AEM) was employed for NO₃RR evaluation, as illustrated in Fig. 4(a). As shown in Fig. 4(b), with an increase in current from 0.2 A to 0.8 A, FE increased from 46.05% to 85.42%, accompanied by a continuous increase of the NH₃ yield rate to 54.18 mg h^{-1} . As the current further increased, the FE fluctuated slightly but stabilized at approximately 80%. Simultaneously, the NH₃ yield rate continued to grow with the current, eventually reaching 98.43 mg h^{-1} at 1.6 A. Furthermore, as depicted in Fig. 4(c), the energy efficiency (EE) for MEA reached 32.94% at a current density of 50 mA cm⁻², surpassing the performance of the H-cell (22.49%). However, as the current density increased, the EE decreased due to the larger overpotential. At a current density of 200 mA cm⁻², the EE decreased to 24.30%, which was still 2.5 times higher than that of the H-cell (10.91%). Even at 400 mA cm $^{-2}$, it remained at 21.34% compared to 7.71% of H-cell. The remarkably high EE for MEA demonstrated its potential for greater industrial applications when compared to the H-cell.

To further exemplify its commercial viability, we devised an NH₃ purification apparatus to be employed in conjunction with an electrocatalytic device for the continuous production of NH₃. As indicated in Fig. 4(d), the effluent containing the generated NH₃ was subjected to air stripping to efficiently collect the NH₃, leveraging the high NH₃ vapor pressure within the alkaline environment [15]. As a result, we successfully removed the NH₃ from the electrolyte and absorbed the NH₃ gas using deionized (DI) water, resulting in the generation of a high-concentration aqueous NH₃ solution. Furthermore, the aqueous NH₃ solution is heated to obtain pure NH₃ gas. By purging the NH₃ into pH detection reagent, the color changed from yellow to blue, indicated the solution changes from neutral/acidic to alkaline. Besides, the obtained ammonia was also verified in a combustion experiment, which could spontaneously combust in the presence of oxygen with a distinguished yellow flame. The Techno-economic assessment was performed to reveal the potential economic feasibility. The calculated average cost of ammonia production is 2526 \$/t, which exceeds the current market



Fig. 3. (a) Free energy diagram of Co and CoNPs/CF during NO₃RR. (b) Charge density difference between Co and CoNPs/CF with NO₃⁻ absorbate. (c)–(d) Partial density of states calculation on Co and CoNPs/CF. (e) Crystal orbital Hamilton populations of Co and CoNPs/CF with NO₃⁻ absorbate.



Fig. 4. (a) Scheme of NH_3 synthesis based on MEA. (b) The corresponding Faradaic efficiency and NH_3 production rate of CoNPs/CF in MEA. (c) Comparison of energy efficiency of H-cell and MEA under different current densities. (d) Schematic of the synthesis process of $NH_3(s)$ and concentrated ammonia from nitrate by MEA. (e) Techno-economic assessment results of the nitrate reduction plant.

price of ammonia [47]. Among all influencing factors, the capacity factor and discount rate exert the greatest impact on the cost of ammonia synthesis. Optimization of related processes has the potential to reduce the cost of ammonia synthesis by up to 352 \$/t and 420 \$/t, respectively. Inadequate technical control could lead to an increase in cost by up to 529 \$/t and 445 \$/t, respectively. Within the considered experimental factors, current density and Faradaic efficiency are identified as key influences on the economics of ammonia synthesis. Improvements in current density and product selectivity could result in a reduction of up to 487 \$/t in the cost of ammonia synthesis. Conversely, a decrease in catalyst performance would lead to an increase in cost, up to a total of 680 \$/t. In conclusion, to optimize the economy of the ammonia synthesis process, improving consumables utilization and reducing maintenance costs are crucial to developing efficient electrocatalytic systems. Additionally, the improvement of current density and Faradaic efficiency necessitates the development of efficient catalysts.

4. Conclusions

In summary, we successfully synthesized a high-performance catalyst for the Nitrate Reduction Reaction (NO₃RR) on a copper foam substrate. SEM and TEM analyses revealed that the surface structure underwent reconstruction from a Co nanosheet array into hexahedral nanoparticles during NO₃RR. The surface Co nanoparticles exhibited high Faradaic Efficiency (FE) and stability during the NO₃RR reaction. In-situ Raman and Density Functional Theory (DFT) calculations revealed that the introduction of the copper foam substrate enhanced the catalyst's electron exchange capability, promoting nitrate adsorption on the active sites of the Co surface. This enhancement facilitated the reaction while inhibiting side reactions. The application of the CoNPs/CF catalyst in MEA yielded higher ammonia yield and energy efficiency. The integration of MEA-based NO₃RR with a gas stripping process allowed the production of pure ammonia solution or ammonia gas. Techno-Economic Analysis (TEA) highlighted that, for the electrocatalytic ammonia synthesis system to achieve industrial production, production costs must be further reduced. The development of efficient electrocatalytic systems and stable catalysts emerges as the key

approach to achieving cost reduction in electrocatalytic ammonia synthesis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2024.03.119.

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Y. Qian et al.

International Journal of Hydrogen Energy 64 (2024) 178-185

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