Electrocatalytic Disproportionation of Nitric Oxide Toward Efficient Nitrogen Fixation

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Electrocatalytic conversion of waste nitric oxide into ammonia is a promising approach to achieve sustainable nitrogen fixation. Herein, a CoNi co-oxides catalyst is designed for NH₃ electrosynthesis with the merits of facilitating NO adsorption and reducing the reaction energy barrier. By synergistic coupling with anodic NO oxidation, electrocatalytic disproportionation of NO is first realized to simultaneously synthesize value-added double nitrogen products (NH₃ and nitrate) with increased total energy efficiency. Furthermore, decoupled acid–base asymmetric electrolyte design is proposed in a united assembled electrolyzer, enabling a high NH₃ production rate (26.27 mg h⁻¹ cm⁻²) with unit faradaic efficiency and a remarkable nitrate production rate of 68.41 mg h⁻¹ cm⁻² at the anode. A low cell voltage of 3.58 V is obtained by optimizing ion agglomeration within the membrane to promote the charge-ion exchange and electrode kinetics. Technoeconomic analysis demonstrates the economic feasibility of recycling waste NO by the electrocatalytic disproportionation strategy.

1. Introduction

Ammonia (NH₃), produced predominantly by the Haber– Bosch process (HBP), is a vital platform molecule for agriculture and industry.^[1,2] Relying heavily on harsh operating

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conditions (≈750 K, 150-350 atm) and fossil fuel-derived H₂, HBP consumes approximately 2% of the world's annual energy supply and releases superabundant CO_2 .^[3–6] As an appealing alternative, the electrochemical nitrogen reduction reaction (ENRR) driven by renewable energy in an aqueous environment can realize a carbon-neutral and onsite generation of NH₃ under mild conditions.^[7–9] Nevertheless, the commercial implementation of ENRR was impeded by low NH₃ production rate and faradaic efficiency (FE), due to the high stability of the N₂ bond (N \equiv N, 948 kJ mol⁻¹) and the competing hydrogen evolution reaction (HER).^[10,11]

Benefits from lower dissociation energy of N=O bond (204 kJ mol⁻¹) and better reaction kinetics, transforming reactive nitrogen oxide into NH₃ provide a promising technical route to address

the dilemma of ENRR.^[12–14] As nitric oxide (NO) is one of the major nitrogeneous pollutants abundant in fossil fuel combustion and other chemical industry,^[15,16] the rational utilization of waste NO via electrocatalysis can simultaneously alleviate the environmental load and reverse the anthropogenically



same reactant as the cathodic reaction.^[27]

global nitrogen cycle imbalance.^[17-19] For efficient electrocata-

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2. Result and Discussion

lytic NO reduction reaction (NORR), the Cu-based catalyst has been validated theoretically and experimentally.^[20] Neverthe-The electrode for NORR was prepared by sputtering a 100-nmless, it still suffers from high overpotential and competitive thick Cu nanolayer on carbon cloth followed by electrode-HER, which could be optimized by further modification such positing CoNi oxide with various Co/Ni ratios (Figure S1, as transition metal (oxide) deposition.^[21-24] Moreover, the slug-Supporting Information). The Cu layer serves as the substrate gish oxygen evolution reaction (OER) was conventionally used for catalyst deposition with improved interfacial contact and uniformity. The morphology and homogeneous element disas the anodic reaction together with NORR, which cost most of the overall electricity input.^[25] Exploring a suitable anodic tribution of CoNiOx@Cu were observed by scanning electron microscopy (SEM) (Figure S2, Supporting Information) substitution reaction with lower overpotential was essential to improving the overall energy and economic efficiency of and energy-dispersive X-ray spectroscopy (EDS) mapping the NORR system. Distinct from the prevailing anodic oxi-(Figures S3-S6, Supporting Information). X-ray diffraction dation of valuable organic chemicals (e.g., glucose, glycerol, (XRD) pattern of the electrode reveals the poor crystallinity of and urea),^[26] low-overpotential NO oxidation was selected as the catalyst with weak diffraction peaks assigning to NiO and a more applicable alternative in our system which uses the Co₃O₄ (Figure S7, Supporting Information), which is in line with the high-resolution transmission electron microscopy Therein, we report electrocatalytic disproportionation of NO (HRTEM) image and selected area electron diffraction (SAED) pattern (Figure S8, Supporting Information).^[28,29] To reveal the for efficient nitrogen fixation via coupling cathodic NORR with electronic properties of CoNi(5:5)Ox@Cu, Ni 2p, Co 2p, and Cu anodic NO electrooxidation simultaneously. This strategy maximizes the utilization of waste NO by the production of dual 2p X-ray photoelectron spectroscopy (XPS) spectra were inveshigh-value products (NH₃ and nitrate) in a single assembled tigated. The Co 2p3/2 binding energy (BE) of CoNi(5:5)Ox@Cu shifted to a lower energy by 0.18 eV compared with that of electrolyzer. For the efficient NORR, CoNiO_x@Cu catalyst was Co₃O₄@Cu located at \approx 780.7 eV (Figure 1a). For the Ni $2p_{3/2}$ developed to improve NO adsorption and lower the reaction energy barrier, validated by theoretical calculations and in situ BE of $CoNi_{(5,5)}O_x@Cu$, the value shifted to higher energy by characterization. The microenvironment and reaction kinetics 0.31 eV compared with that of NiO@Cu located at ≈855.5 eV of each half-cell reaction were optimized independently using (Figure 1b). The shifts of BE indicate the modulated electronic decoupled acid-base asymmetric electrolytes via a bipolar structure due to the formation of CoNi co-oxide.^[30] Cu exists membrane (BPM) design. Relying on this technology portas metallic state in both the substate and CoNi(5:5)Ox@Cu, indifolio (Scheme 1), we achieved a record high NH₃ production cating no chemical change occurred over the substrate during rate of 26.27 mg h⁻¹ cm⁻² with a FE of \approx 100% and nitrate acid electrodeposition (Figure 1c). Furthermore, X-ray absorption production rate of 68.41 mg h^{-1} cm⁻² with a FE of 50.42% at a spectra were investigated to reveal the coordination structure low cell voltage of 3.58 V for continuous 36-h stable operating. at the atomic level (Tables S1-S3, Supporting Information). The technoeconomic analysis (TEA) demonstrated that electro-By comparison with the reference samples (Figures S9-S11, catalytic disproportionation of NO significantly reduced the lev-Supporting Information), it was concluded that the Co and elized cost of NH₃ to \$544 ton⁻¹ with economic feasibility for Ni in CoNi_(5:5)O_x@Cu were in the oxidized state while Cu was in the metallic state, which was consistent with the wavelet



Electrocatalytic Disproportionation

Scheme 1. Schematic of the electrocatalytic disproportionation system toward efficient nitrogen fixation. Industrial waste nitric oxide (NO) is reduced into ammonia (NH₃) at the cathode and oxidized to HNO₃ at the anode, with the assistance of an acid-base asymmetrical electrolytes.

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Figure 1. Structural and compositional characterization of the CoNi co-oxide/Cu catalyst for NO-to-NH₃ conversion. X-ray photoelectron spectroscopy (XPS) spectra of a) Co 2p, b) Ni 2p, and c) Cu 2p spectra of CoNi_(5:5)O_x@Cu. Wavelet transformation of d) Co, e) Ni, and f) Cu K-edge EXAFS for the CoNi_(5:5)O_x@Cu. EXAFS of g) Co, h) Ni, and i) Cu spectra of CoNi_(5:5)O_x@Cu.

transformation (Figure 1d–f, Figures S12,S13, Supporting Information). The ~0.5 eV energy shift in the Co K-edge near-edge spectrum of CoNi_(5:5)O_x@Cu compared to the Co₃O₄ sample, indicated a lower Co valence state due to the formation of a composite oxide (Figure 1g,h).^[31] Also, the intensity of both Co and Ni white line peaks in CoNi_(5:5)O_x@Cu increased compared to standard NiO and Co₃O₄, reflecting the increase of *p*-electrons in Co and Ni atoms.^[32] The first Fourier transform (FT) peak of Ni at 1.5 Å in EXAFS oscillation spectra represented a single scattering path of Ni-O, and the second peak at 2.5 Å revealed that the Ni atom binding to the nearest surrounding transition metal Co considering the offset from the typical Ni-Ni bond.^[33] As for the Cu nanolayer, the profile and peak position of CoNi_(5:5)O_x@Cu were similar to those of the Cu foil (Figure 1i, Figure S14, Supporting Information).

To investigate the electrocatalytic NORR activity and reaction kinetics, polarization curves of different catalysts were measured in 1 M KOH electrolyte. Compared to the sputtered Cu, Co₃O₄@Cu, and NiO@Cu, the current density of CoNiO_x@Cu with different Co/Ni ratios all increased prominently regardless of the cathodic potential (**Figure 2**a). Based on EIS measurements, we calculated the charge transfer resistance (R_{ct}),

electrolyte resistance (R_s) , Warburg impedance (W), and constant phase-angle element (CPE) by fitting the circuit model of Nyquist curve (Table S4, Supporting Information). Obviously, the value of R_{ct} is strongly correlated with the catalyst performance, and CoNiO_x@Cu delivers a decreased R_{ct} compared with single metal oxide^[34] (Figure 2b, Figure S15, Supporting Information). Therefore, it was speculated that the reaction activity might originate from the combination of Co₃O₄ and NiO in a form of CoNi co-oxide. In addition, electrochemically active surface areas determined by double-layer capacitance measurement^[35] of CoNi_(5:5)O_x@Cu electrocatalyst exhibited a superior value of 1.91 mF cm⁻² than other electrocatalysts (Figures S16,S17, Supporting Information). A multiphysical field coupling simulation was built to reconstruct the microscale current density distribution and NH3 concentration over the CoNiO_x@Cu electrocatalyst–electrolyte interface (Figure 2c, Figures S18,S19, Supporting Information). The calculated current density of $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu catalyst (~36.0 mA cm^2) was 2.3 times higher than that of sputtered Cu (≈ 15.8 mA cm⁻²). The "hot area" with high current density indicates an electron aggregation effect caused by the $CoNi_{(5:5)}O_x$ nanoparticles, enabling the fast transport of electrons and accelerating the

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Figure 2. Evaluation of ammonia (NH₃) synthesis activity and nitric oxide (NO) reduction reaction (NORR) reaction mechanism. a) Polarization curves measured by linear sweep voltammetry (LSV) with a scan rate of 10 mV s⁻¹ over Cu, $Co_3O_4@Cu$, NiO@Cu, $CoNi_{(3:7)}O_x@Cu$, $CoNi_{(5:5)}O_x@Cu$, and $CoNi_{(7:3)}O_x@Cu$. b) Nyquist curves of electrochemical impedance spectroscopy (EIS) with the frequency range from 0.01 Hz to 100 kHz at open circuit potential. c) Current density distribution of electrocatalyst–electrolyte interface obtained by multiphysical fields coupling simulation. The white arrows demonstrated the dissipation of NH₃ and OH⁻, respectively. d) Comparison of electrocatalytic NH₃ production rate and faradaic efficiency (FE) at –0.68 V versus reversible hydrogen electrode (RHE). e) Stability test and morphologies of $CoNi_{(5:5)}O_x@Cu$ electrocatalyst before and after long-term operating. f) In situ Raman spectra at various potentials from –0.08 V versus RHE to –1.08 V versus RHE. g) Reaction free-energy diagram for NORR over $CoNi_{(5:5)}O_x@Cu$ electrocatalyst.

NH₃ generation rate during NORR (see details in the Experimental Section). Accordingly, the highest NH₃ production rate of 20 mg h⁻¹ cm⁻² with nearly unit FE was achieved using CoNi_(5:5)O_x@Cu catalysts at -0.68 V versus reversible hydrogen electrode (RHE) (Figure 2d), which outperformed previously reported NH₃ synthesis over various state-of-art electrocatalysts (Table S5, Supporting Information). To evaluate the stability for long-term operation, we performed a NORR conversion at -0.88 V versus RHE. The total current density remained stable at \approx 165 mA cm⁻² and the FE fluctuated slightly within the acceptable range for continuous 36-h operation (Figure 2e). The morphology of the CoNi_(5:5)O_x@Cu electrocatalyst was unchanged. Besides, XPS characterization after electrocatalysis confirmed the almost unchanged oxidation state of Co and Ni, suggesting decent stability of the catalyst (Figure S20,

Supporting Information). In addition, the low decay rate of the current density (0.92% after 36 h) confirms the excellent stability compared with other reported catalysts.^[36]

In situ Raman spectroscopy was performed to reveal the active center and monitor the corresponding evolution on the active sites over $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu electrocatalyst during NORR (Figure 2f). The broad peak at ~200 cm⁻¹, which was assigned to Co-N,^[37] increased with the potential varying from -0.08 V versus RHE to -0.88 V versus RHE, indicating the elevated NO adsorption on the Co site. With further negatively shifting potential to -1.08 V versus RHE, the Co-N peak intensity kept almost unchanged, which implied that the adsorption of NO on the catalyst surface realized dynamic saturation. Similarly, the strong intensity of the broad N-O band (~1375 cm⁻¹) and NH band (1580 cm⁻¹) were located within -0.28 to -0.88 V versus

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RHE.^[38,39] The intensity of the Raman peak at \approx 998 cm⁻¹, assigned to NH₃,^[40] turned saturated when the potential was lower than -0.78 V versus RHE. As the NORR proceeded, the peak intensity of NH₃ strengthened from 1 to 60 min, implying the accumulation of NH₃ in the electrolyte (Figure S21, Supporting Information).

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Furthermore, a molecular-level investigation of the reaction mechanism was performed by DFT calculation. The NORR process (Figures S22,S23, Supporting Information) consisted of a series of deoxidation reactions followed by the hydrogenation reaction.^[41] Based on the energy barrier comparison of the ratedetermining step (RDS) between the Co site and Ni site on the CoNi_(5:5)O_x@Cu surface, we identified that the reaction tends to occur at the Co site (0.14 eV) rather than the Ni site (0.22 eV) (Figure S24, Supporting Information). Combined with the previous in situ Raman characterization, a Cu-supported CoNi cooxide model was established, in which NO was adsorbed on the Co site. The NO adsorption on CoNi(5:5)Ox@Cu displayed a better spontaneity of -2.82 eV (Co₃O₄@Cu: -2.05 eV, NiO@ Cu: -2.45 eV) (Figure 2g, Figure S25, Supporting Information), and the RDS with the lowest energy barrier of +0.14 eV for CoNi_(5:5)O_x@Cu demonstrated higher activity (Co₃O₄@Cu: +0.52 eV, NiO@Cu: +0.53 eV). Besides, the reaction routes toward other products (N2, N2H4, etc.) were also compared, which further validated the high FE of NH₃ synthesis derived from the intrinsic characteristics of $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu. The relatively high energy barrier of 0.43 eV for HER proved that CoNi_(5:5)O_x@Cu electrocatalyst possessed a weak HER competition (Figure S26, Supporting Information).^[42] Dependent on

the partial density of state calculation (Figure S27, Supporting Information), d-band centers of $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu exhibited closest to the Fermi level, which pushed up the antibonding state of $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu (compared to Co_3O_4 @Cu and NiO@Cu) and promoted the hybrid bonding of catalyst-NO.^[43] To further reveal the adsorption mechanism, the PDOS of the N atom and O atom in NO before and after the adsorption was investigated (Figure S28, Supporting Information). Hybridization occurred between the $2\pi^*$ orbital of NO and the 3d orbital of $\text{CoNi}_{(5:5)}\text{O}_x$ @Cu near the Fermi level by comparing the DOS peak positions. Meanwhile, the 1π and 5σ orbitals were pushed to the lower energy state, which decreased the energy level of the bonding state, thereby improving the stability of the adsorption structure.^[44]

Besides the optimization of cathodic electrocatalysts (CoNi_(5:5)O_x@Cu), electrochemical NO oxidation (NOOR) was proposed as an alternative anodic reaction to substitute OER, aiming at improving the energy efficiency of the full cell. Regarding the sensitivity of the NOOR reaction to the pH variation, different anodic electrolytes (0.5 \times H₂SO₄, 1 \times PBS, and 1 \times KOH) were comparatively evaluated (**Figure 3**a), while 1 \times KOH electrolyte was maintained for cathode NORR to suppress the competing HER. It was observed that acidic conditions favored NOOR with an extremely low onset potential of 0.83 V versus RHE at the current density of 10 mA cm⁻², which was much lower than that in neutral (1.42 V versus RHE) and alkaline (1.99 V versus RHE) electrolytes, respectively.

Different reaction modes dependent on the combination of anodic and cathodic electrolytes configurations (Figure 3b,c,



Figure 3. Electrocatalytic performance of the optimized reaction system. a) Linear sweep voltammetry (LSV) curves of nitric oxide (NO) reduction reaction (NORR) systems at different anodic reaction conditions. b) Different working modes of the electrocatalytic system. Mode 1: conventional NORR system with oxygen evolution reaction (OER) as the anodic reaction; Mode 2: the upgraded NORR system with NO oxidation reaction (NOOR as the anodic substitution reaction; Mode 3: the upgraded NORR/NOOR system using asymmetric acid–base decoupling electrolytes with bipolar membrane (BPM). c) Ammonia (NH₃) production rate and faradaic efficiency (FE) for different electrocatalytic systems using CoNi_(5:5)O_x@Cu.



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Tables S7,S8, Supporting Information) were comparatively evaluated in terms of NH₃ production rate and selectivity. For the conventional symmetrical alkaline electrolyte using a cationexchange membrane (CEM), NH₃ production rate and FE were similar for both Mode 1 (cathodic NORR and anodic OER) and Mode 2 (cathodic NORR and anodic NOOR) (see details in the Experimental Section). A slight increase in NORR yield was observed for both modes with the potential increase. Nevertheless, the anodic nitrate production rate increased prominently from 4.36 to 34.23 mg h^{-1} cm⁻² with the potential increase under Mode 2, achieving the maximum anodic FE of 64.01% (Figure S29, Supporting Information). As a result, the total FE for NO conversion approached "164%," which comprised the FEs from cathodic NORR and anodic NOOR, exceeding the 100% limit for each individual electrode reaction. An asymmetric electrolyte configuration (alkaline electrolyte for the cathode and acidic electrolyte for the anode) was designed within a united assembled electrolyzer as Mode 3 to facilitate pH-sensitive NO redox kinetics both in the optimal microenvironment and improve the full-cell performance. To realize this design, a BPM consisting of a CEM and an anion-exchange membrane (AEM) was employed to separate the anode and cathode compartments.^[45–49] Compared to the reverse bias BPM (cathode-CEM-AEM-anode) with voltage consumption in intermembrane H₂O electrolysis, we used the forward bias BPM (cathode-AEM-CEM-anode) to promote ion agglomeration and electron transfer during reactions. Inspiringly, relying on the forward bias BPM-based asymmetric electrolytes system, the cathodic NORR reaction exhibited a volcano-type trend of NH₃ production rate with increased potential, reaching the maximal NH₃ production rate of 26.27 mg h⁻¹ cm⁻² at –0.88 V versus RHE with nearly 100% FE, which was notably higher than those obtained most of the previous reports (Table S5, Supporting Information). Even for anodic NOOR, the production rate of nitrate also improved dramatically to a maximum of 68.41 mg h⁻¹ cm⁻² with an FE of 50.23%.

To understand the mechanism of electrocatalytic disproportionation of NO with an asymmetric acid–base electrolytes system, the voltages across each component (cathodic reaction, anodic reaction, and membrane) were measured with different membranes (BPM, CEM, and AEM) (**Figure 4**a and Figure S30, Supporting Information, see details in the Experimental Section). By fixing the potential of the cathode to the reference electrode at –1.9 V versus RHE, the voltage loss of the anodic



Figure 4. Mechanism study of electrocatalytic disproportionation of nitric oxide (NO) using asymmetric acid-base decoupled electrolyte bipolar membrane (BPM) system. a) Voltages consumed by each component in different electrocatalytic systems (forward bias BPM, reverse bias BPM, cation-exchange membrane (CEM), and anion-exchange membrane (AEM)) at the current density of ~200 mA cm⁻² (meanwhile cathode potential = -1.9 V). The voltage for the cathode, anode, and electrolyte was labeled as red, orange, and blue, respectively. b) Mechanism diagram of BPM electrocatalytic system in forward bias and reverse bias. Comparison of multiphysical coupling simulation results of c) electrolyte potential and d) ion concentration between forward bias and reverse bias using BPM.



NO oxidation reaction was less than that of the OER regardless of membrane types. Prominently, the forward bias mode of the BPM consumed the lowest electrolyte-membrane voltage (0.51 V), compared to the monolayer CEM (1.23 V), AEM (1.37 V), and the reverse bias of BPM (1.51 V), featuring a superior energy efficiency. It was speculated that ion transportation and reaction microenvironment dominated the reaction activity during the electrocatalytic disproportionation of NO. Based on multiphysical coupling calculation, the water dissociation occurred at the CEM-AEM interface within a typical reverse bias BPM, resulting in the transportation of hydroxide and proton directionally to the anode and cathode, respectively. In contrast, counter ions (e.g., H⁺ and OH⁻) migrated into the AEM-CEM interface with high conductivity under forward bias. Moreover, the onset potential under forward bias increased significantly from -0.088 V versus RHE to 0.893 V versus RHE compared to reverse bias, which reflected better electrochemical activity and energy efficiency (Figure 4b, Figure S31, Supporting Information). According to the ion concentration gradient distribution, the agglomeration of H⁺ and OH⁻ in the forward-biased BPM promoted ion-charge exchange (Figure 4c,d).^[50,51] In contrast, the charge transport rate was suppressed in the reverse-biased BPM, which was based on the interlayer electrolytic water

decomposition rather than ion agglomeration, leading to a higher electrolyte potential consumption. Besides, almost no loss of electrolyte potential was observed in the forward bias, contributing to the prominent drop of full cell voltage with the lowest cell voltage of 3.58 V and a cathodic potential of -0.88 V versus RHE, respectively (Figure S32, Supporting Information).

The NORR performance of our system exceeded most reported state-of-art studies using conventional symmetric electrolyte and CEM systems (Figure 5a). A TEA model was developed to evaluate the industrial benefits of electrocatalytic NO disproportionation toward NH3 and nitrate synthesis (Figure 5b), by calculating the levelized cost of NH₃ (LCOA)^[52] at a medium-scale application (1000 tonnes per day) under basecase assumptions shown in Table S9 (Supporting Information). For an asymmetric acid-base decoupled system, it can be concluded that the LCOA is highly sensitive to the electrochemical system cost, the feedstock NO cost, and the product nitric acid price (Figure S33, Supporting Information). Recycling industrial waste gas as a low-cost NO source, while converting it and simultaneously producing of high-value-added nitric acid will reduce the LCOA to a great extent. The LCOA decreases from \$1533 to \$544 ton⁻¹ when the price of nitric acid from the anodic NOOR changes from zero to a base-case price of \$0.38 kg⁻¹.



Figure 5. Technoeconomic analysis (TEA) of the electrocatalytic nitric oxide (NO) disproportionation system. a) Performance comparison with previously reported work of NO reduction reaction (NORR), the yellow star represented the conventional cation-exchange membrane (CEM) system, and the red star represented the forward bias bipolar membrane (BPM) based asymmetric electrolyte system. b) Sensitivity of the levelized cost of ammonia to seven different parameters including electricity price, water price, electrochemical system cost, capacity factor, ammonia output, NO price, and nitric acid price.



Considering the scenario of renewable-powered industrial waste gas NO conversion (parameters shown in Table S9, Supporting Information), the LCOA was estimated to be \$1063 ton⁻¹ at the scale of 1000 tonnes-NH₃ per day, which might rival the HBP at a distributed production scale.

3. Conclusions

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In summary, we proposed an advanced electrolysis system to simultaneously synthesize green NH3 and nitrate based on the electrocatalytic disproportionation of NO. The synergistic effect of the CoNi oxide was derived from the strong active center of Co-N and the adsorption optimization from the electronic structure improvement. Furthermore, the acid-base decoupled electrolytic environment based on the forward bias BPM enhanced charge-ion transfer and inhibited competitive HER, leading to a recorded high NH₃ production rate of 26.27 mg h⁻¹ cm⁻² with an FE of 100% at a low cell voltage of 3.58 V. And the NO utilization efficiency was greatly improved regarding the combination of anodic nitrate production via NO electrooxidation. Based on an in-depth understanding of anodic substitution and decoupled acid-base reaction systems, electrocatalytic NO conversion using intermittent renewable electricity exhibited great potential to harvest green NH₃ while guiding the synthesis of other important base chemicals from inert molecules.

4. Experimental Section

Catalyst Preparation: The carbon paper (Sinero) was prepared as the catalyst substrate. The Cu nanolayer was deposited to the surface of the carbon paper with a thickness of 100 nm by magnetron sputtering in the Ar atmosphere. A solution of 20 mmol $Co(NO_3)_2 + Ni(NO_3)_2$ (Macklin) dissolved in 50 mL 0.05 M H₂SO₄ (Sinopharm) was used as the electrolyte for the electrodeposition process, while the Co:Ni ratio was controlled by the molar ratio of $Co(NO_3)_2$ and $Ni(NO_3)_2$. A single-cell three-electrode system was used as the electrodeposition cell. Pt foil (1 cm²) and Ag/AgCl electrodes (filled with 3 m KCl) were used as the counter electrode and the reference electrode, respectively. Electrodeposition was carried out for 300 s at the cathode with a current of 0.2 A. Rinsed with deionized water to remove surface impurities, the prepared catalyst was dried in a vacuum oven at 80° for 3 h to remove the surface moisture.

Materials Characterizations: The morphology and structure of the prepared electrocatalysts were characterized by the scanning electron microscope (SEM, ZEISS Sigma 300, SmartEDX) and the high-resolution transmission electron microscope (HRTEM, I Talos F200S). The crystal structure of the electrocatalyst was identified by XRD (Rigaku Ultima IV 3 kW, Cu K α I). The chemical components and states of the electrocatalysts were verified by XPS (Thermo Scientific K-Alpha). The X-ray absorption fine structure spectra (XAFS) V K-edge were collected at the 1W1B station in Beijing Synchrotron Radiation Facility (BSRF), China. The data were collected in fluorescence mode using a Lytle detector while the corresponding reference sample was collected in transmission mode. The electrode sheet was encapsulated on the Kapton adhesive tape. The reference sample was ground and uniformly daubed on the special adhesive tape. In situ Raman measurements were performed on a Renishaw inVia Raman microscope (Figure S34, Supporting Information). The wavelength of the Raman excitation laser was 633 nm. A three-electrode system was used during the in situ Raman characterization. A Pt wire and an Ag/AgCl electrode (filled with 3 м KCl) were used as the counter electrodes and reference electrode, respectively, and a $CoNi_{(5:5)}O_x@Cu$ was used as the working electrode. NO was kept saturated in 1 \mbox{M} KOH electrolyte during operation. The electrolysis was carried out with a potential range from -0.08 to -1.08 V versus RHE, and the potentiostatic electrolysis was carried out with a time range from 0 to 1 h at -0.88 V versus RHE.

Electrochemical Measurements: Electrochemical measurements were performed in a modified gas-tight H-type electrolytic cell (GaossUnion. 50 mL) using an electrochemical workstation (CHI 760E) (Figure S35, Supporting Information). A Platinum foil (1 cm²) and an Ag/AgCl electrode (filled with 3 M KCl) were used as the counter electrodes and reference electrode, respectively, and a glassy carbon electrode (GCE, GaossUnion) clipped with the electrocatalyst (0.5 cm²) as the working electrode. In the subsequent upgrade of the electrocatalytic system (Mode 2 and Mode 3), a commercial graphite electrode (GaossUnion) was employed as the anode electrode instead of Pt foil to decrease the cost. The modified H-type electrolytic cell consisted of a cathodic chamber and an anodic chamber, which are separated by a bipolar membrane (Fumatech). The cathode gas outlet was connected to the inlet of the anodic chamber to realize the continuous NO disproportionation reaction in both the cathode and anode. The two chambers maintained different pH values, with 50 mL 1 M KOH (Sinopharm) for the cathode and 50 mL 0.5 м H₂SO₄ (Sinopharm) for the anode.

For a typical reaction process, the mass flow meter (Sevenstar) was used to control the gas flow rate of 30 sccm (standard cubic centimeter per minute) to purge Ar for 15 min to eliminate the interference of N₂, O₂, or other gases. Then, NO was passed with the flow rate of 30 sccm for 10 min to saturate the solution. Linear sweep voltammetry (LSV) was performed at a rate of 5 mV s⁻¹ with a sweep voltage range of 1 to -2 V versus RHE. The electrochemical impedance was measured with the frequency range from 0.01 Hz to 100 kHz. The electrochemical active surface area was measured by cyclic voltammetry (CV) scanning in the nonredox region at a scan rate of 20, 40, 60, 80, and 100 mV s⁻¹. Potentiostatic experiments were performed at each set potential accompanied by stirring at a rate of 500 rpm for 1 h. In the experiment, potentials versus Ag/AgCl electrode was converted into RHE reference scale voltage as follows:

E(V vs. RHE) = E(V vs. Ag/AgCl)+0.0591×pH+0.210 ((1))
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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

A.W., J.L., and X.X. contributed equally to this work. A.W. conceived the project. A.W. and J.L. wrote the manuscript. J.L. carried out the experiments, conducted the synthesis of catalysts, and performed characterizations. X.X., L.L., and A.C. calculated the DFT results.

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X.X., M.W., and Y. Z. applied the Comsol simulations. X.-Y.W. and J.Z. conducted the technoeconomic analysis. H.B.W., Q.L., Q.H., S.Z., and Z.Q. analyzed the experimental results and revised the manuscript. All authors discussed the results and commented on the manuscript.

Data Availability Statement

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

Keywords

acid-base decoupling, ammonia, bipolar membranes, disproportionation, electrocatalysis, nitrogen fixation

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