

# Research progress of transition metals Cu, Fe and Ni as electrode materials for electrocatalytic nitrate reduction to ammonia

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**Abstract.** Nitrate is a common pollutant in surface water and groundwater. Electrocatalytic nitrate reduction method is an electrochemical reduction reaction of nitrate at the cathode by impressed current, and the reduced ammonia generated by the reaction is an important chemical raw material. The main step of this process is the selection of cathode electrocatalytic materials. In this paper, the mechanism of electrocatalytic nitrate reduction to ammonia production is briefly explained, then the research situation of transition metals Cu, Fe and Ni as electrode materials for electrocatalytic nitrate reduction to ammonia production at home and abroad is reviewed, and finally the future direction of electrocatalytic nitrate reduction to ammonia production is summarized.

**Keywords:** Cu, Fe and Ni, nitrate.

## 1. Introduction

At present, ammonia synthesis is mainly used in the Haber-Bosch process, that is, ammonia ( $\text{NH}_3$ ) can be produced by hydrogen and nitrogen to solve the energy crisis<sup>[1-2]</sup>. However, the Haber-Bosch method is highly dependent on fossil energy<sup>[3-4]</sup>, resulting in increased carbon dioxide ( $\text{CO}_2$ ) emissions and harming the environment. Therefore, it is necessary to find a new green ammonia synthesis process.

Human industrial and agricultural activities such as industrial wastewater lead to a large accumulation of nitrate ( $\text{NO}_3^-$ )<sup>[5-10]</sup>. These nitrogen-containing compounds can lead to eutrophication of water<sup>[11]</sup>. Excessive nitrate content in drinking water is also a major cause of high cancer incidence<sup>[12-13]</sup>. Therefore, it is urgent to solve the problem of high  $\text{NO}_3^-$  which is harmful to the environment and human health.

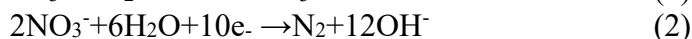
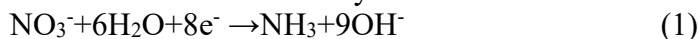
In recent years, some scholars have proposed a new technical route of electrocatalytic nitrate-to-ammonia reduction reaction (NARR)<sup>[14]</sup>. Materials with specific catalytic activity are loaded on the cathode by impressed current to achieve the purpose of degrading and converting nitrate<sup>[15-18]</sup>. NARR helps to :1) remove  $\text{NO}_3^-$  from various wastewater<sup>[19-21]</sup>; 2) Can "green" ammonia production [20-21]; 3) Reduce energy and carbon footprint<sup>[22]</sup>. Therefore, electrocatalysis of nitrate to ammonia is an effective way to solve  $\text{NO}_3^-$  pollution.

At present, the focus of electrocatalytic reduction is on the study of cathode catalyst materials to minimize by-products as well as competitive Hydrogen evolution reactions (HER) to achieve high  $\text{NH}_3$  Faraday efficiency (FE). Efficient cathode catalyst materials need to have excellent stability, conductivity and selectivity<sup>[23]</sup>. Previous studies have shown that transition metal electrode materials such as Copper (Cu), Ferrum (Fe), Nickel (Ni) and other catalytic materials have certain  $\text{NO}_3^-$  reduction activity<sup>[24-26]</sup>. However, there is a lack of relevant review reports on the influence factors of different transition metal electrode materials on NARR at home and abroad. This paper aims to summarize and further discuss the future development direction.

## 2. Electrocatalytic reduction nitrate reduction mechanism

The  $\text{NO}_3^-$  reduction reaction of ammonia synthesis is a process of 8-electron transfer of the N oxidation state from +5 valence to -3 valence (equation (1))<sup>[27]</sup>. The intermediates of the reaction

include  $\text{N}_2\text{H}_4$ ,  $\text{NH}_2\text{OH}$ ,  $\text{N}_2$ , etc. Among them,  $\text{N}_2$  has the most stable zero-valence state<sup>[28]</sup>. Therefore,  $\text{NH}_3$  and  $\text{N}_2$ (equation (2)) are often the end products of  $\text{NO}_3^-$  electrocatalytic reduction reactions<sup>[29]</sup>.

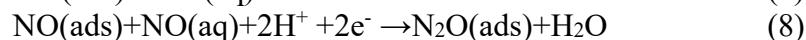
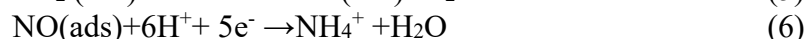
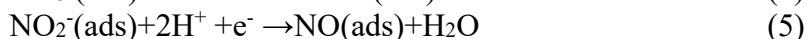


Therefore, the key to electrocatalytic nitrate reduction of ammonia production is to design a catalyst with high reaction selectivity and high FE.

The reaction path of electrocatalytic nitrate to ammonia is mainly divided into direct path and indirect path, and the concentration of  $\text{NO}_3^-$  and the pH of electrolyte are the key to determine the reaction<sup>[30]</sup>. Direct reaction needs to be carried out under low concentration conditions, while indirect reaction needs to be carried out under high concentration conditions<sup>[31]</sup>. The direct reaction mechanism of  $\text{NO}_3^-$  can be divided into two ways<sup>[32]</sup>:

(1) The electron direct reduction path of the cathode.

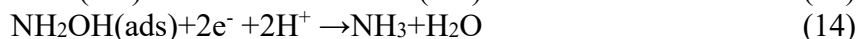
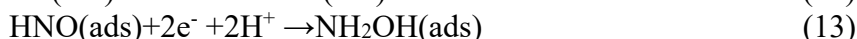
There are several main paths for generating  $\text{N}_2$ : One is that  $\text{NO}_3^-$  is first adsorbed on the cathode surface and then reduced to nitrite ( $\text{NO}_2^-$ ), which is the rate-determining step for  $\text{NO}_3^-$ <sup>[33-35]</sup>. The  $\text{NO}_2^-$  generated by the reaction quickly reacts on the electrode surface to produce adsorbed nitric oxide (NO), which is an important intermediate for the generation of  $\text{N}_2$  and  $\text{NH}_4^+$ <sup>[32]</sup>. Subsequently, the adsorbed NO is desorbed from the electrode surface into the solution, and the NO in the solution can form weakly adsorbed nitrous oxide ( $\text{N}_2\text{O}$ ) with the adsorbed NO, which is further reduced to nitrogen ( $\text{N}_2$ )<sup>[36]</sup>. Formula (3-9)<sup>[37]</sup>



The other is that the adsorption state NO is reduced and dissociated into the adsorption state nitrogen (N), and then the two adsorption states N combine to form  $\text{N}_2$ <sup>[38]</sup>. Formula (10-11).

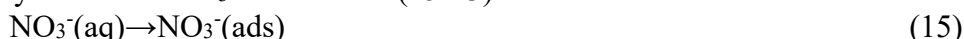


$\text{NH}_3$  can be produced by the adsorbed state NO through a continuous electron transfer process. First, an electron obtained from the intermediate NO adsorption state is reduced to the adsorption nitric acid (HNO) state<sup>[39]</sup>. The adsorbed state HNO is then reduced to the adsorbed state hydroxylamine ( $\text{NH}_2\text{OH}$ ). Finally, the adsorption state  $\text{NH}_2\text{OH}$  is reduced to  $\text{NH}_3$ <sup>[32]</sup>. Formula (12-14).



(2) Adsorption of atomic hydrogen mediated reduction pathways.

The reaction begins with the adsorption of water ( $\text{H}_2\text{O}$ ) and  $\text{NO}_3^-$  on the electrode and can quickly reach dynamic equilibrium. When a constant current is applied to the electrode surface, water is reduced to proton H, and proton H reduces and absorbs  $\text{NO}_3^-$ . This step is the rate-limiting step<sup>[34,40]</sup>. The intermediates  $\text{NO}_2^-$  and NO can also be reduced by proton H. Kinetically, proton H mediated N-H bond formation is more favorable than N-N bond formation. Therefore, the main product of this process is the economically beneficial  $\text{NH}_3$ <sup>[41]</sup>. Formula (15-23)<sup>[37]</sup>.





The remaining  $\text{NH}_3(\text{ads})$  will continue to reduce to form ammonium ions ( $\text{NH}_4^+$ ):



Kinetically, the reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  is an eight-electron transfer process, which is challenging. The reduction of  $\text{NO}_3^-$  to  $\text{N}_2$  is a five-electron transfer process<sup>[42]</sup>, which is more selective than the generation of  $\text{NH}_3$ . Therefore, the main challenge of electrocatalytic reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  is the selectivity of the reaction.

### 3. Transition metal electrode materials

#### 3.1 Copper series metals and their compounds

Among the catalytic materials for electrocatalytic  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ , transition metal Cu has good  $\text{NH}_3$  selectivity and  $\text{NO}_3^-$  conversion<sup>[43]</sup>. The excellent performance of metal Cu is due to its good electrical conductivity, weak hydrogen evolution ability and stable catalytic performance, which improves the first charge transfer reaction controlled by adsorption<sup>[44-45]</sup>.

Close control of catalytic particle size and shape is a necessary condition for achieving optimal activity of copper-based catalysts<sup>[46]</sup>. Fu et al.<sup>[47]</sup> found that for Cu nanosheets covered by Cu(111), at a potential of -0.15V, the reduction rate of  $\text{NO}_3^-$  to  $\text{NH}_3$  of Cu nanosheets was higher than that of ordinary Cu foils, Cu nanoblocks and Cu nanoparticles, and the Faraday efficiency was as high as 99.7%<sup>[37]</sup>. The order of NARR activity of Cu with four morphologies under alkaline conditions is Cu nanosheets > Cu nanoblocks > Cu nanoparticles (Table 1)<sup>[48]</sup>. The improvement of the performance of reducing nitrate to ammonia by Cu nanosheets comes from the coating of Cu(111)<sup>[43]</sup>. The excellent catalytic performance of Cu(111) nanosheets in electrocatalytic nitrate reduction of ammonia is due to the inhibition of hydrogen evolution reaction, the improvement of the current density of the speed determination step<sup>[48]</sup>, and the significant improvement of the selectivity of electrocatalytic nitrate  $\text{NH}_3$  production<sup>[37]</sup>.

Table 1 Summary of electrochemical performance of copper electrodes for nitrate reduction reaction

Cathode material	Cathode area (cm <sup>2</sup> )	Electrolyte	$\text{NO}_3^-$ conversion	Selectivity (%)	Time (h)	References
Cu nanoparticles	0.785	0.1 mol/L $\text{NO}_3^-$ + 1mol/L NaOH(75ml)	73~74	97( $\text{NH}_4^+$ )	8	(49)
Cu nanosheets	10	140 mg/L $\text{NO}_3^-$ + 0.1 mol/L $\text{Na}_2\text{SO}_4$	99.7	97.2( $\text{N}_2$ )	6	(50)
Cu nanoribbons	4	30mg/L $\text{NO}_3^-$ + 0.5mol/L $\text{Na}_2\text{SO}_4$ (50ml)	100	— <sup>a)</sup>	1	(51)
Cu nanoparticles	75	100 mg/L $\text{NO}_3^-$ (200ml)	60	— <sup>a)</sup>	1.5	(52)

a)“—”Indicates that relevant data is not provided in the original text

Wang et al.<sup>[53-54]</sup> obtained island-like Cu particles by electrodeposition of Cu particles with nickel foam. The active site in island-like Cu particles is electrochemically converted from CuO to Cu/Cu<sub>2</sub>O. As the active phase, electron transfer from Cu<sub>2</sub>O to Cu at the interface can promote the formation of \*NOH intermediates and inhibit hydrogen evolution reaction. Thus, high selectivity and Faraday efficiency are achieved. The formation energy barrier of H<sub>2</sub> on Cu/Cu<sub>2</sub>O nanowires is 0.33eV, while the formation energy barrier of H<sub>2</sub> on Cu nanowires is only 0.12eV, indicating that a higher energy barrier means that Cu<sub>2</sub>O can block competing HER reactions, thus significantly improving Faraday efficiency<sup>[55]</sup>.

Wang et al. synthesized a series of CuNi alloys, among which Cu<sub>50</sub>Ni<sub>50</sub> alloy has the highest

catalytic activity, and its electrocatalytic reduction activity is 6 times that of pure Cu, because Ni alloying can adjust the D-band center of Cu and increase the adsorption energy of intermediates such as  $^*\text{NO}_3^-$ ,  $^*\text{NO}_2$  and  $^*\text{NH}_2$ <sup>[48,55]</sup>. Compared with Cu (and Ni), Cu-rich alloys, especially  $\text{Cu}_{90}\text{Ni}_{10}$  and  $\text{Cu}_{80}\text{Ni}_{20}$ , show excellent properties in reducing nitrate, especially higher efficiency, better stability and higher selectivity at medium negative potentials, and Cu-rich alloys almost only produce  $\text{NH}_3$ <sup>[48]</sup>.

Monatomic copper is a new type of catalyst that loads isolated dispersed metal copper atoms onto the surface of the carrier and shows high activity, selectivity and stability in the catalytic reaction<sup>[37]</sup>. Zhu et al.<sup>[52]</sup> reported for the first time that monatomic Cu was loaded onto carbon nitride nanosheets (Cu-N-C) as a catalyst for electrocatalytic nitrate reduction to ammonia production. A metal-nitrogen-carbon electrocatalyst (Cu-N-C-800) composed of monatomic Cu and carbon nanosheets was synthesized by pyrolysis of dispersed monatomic Cu with N in carbon nanosheets at 800°C (Fig. 1(a)). After the reaction for a period of time, Cu-N-C-800 electrocatalyzed the reduction rates of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to the highest extent, and the results showed that Cu-N-C-800 had a higher activity than Cu nanoparticles electrocatalyzed nitrate, and greatly inhibited the release of nitrite intermediates into the solution (Figure 1(b),c). After 20 cycle tests, The reduction rate of  $\text{NO}_3^-$  remains at a high level, and the selectivity of  $\text{NH}_3$  is 80.5%, which proves that Cu-N-C-800 has good stability. The advantages of monatomic Cu are as follows: (1) sufficient active atoms and low coordination metal centers promote the adsorption and conversion of active substances; (2) Uniform active site and geometric structure enhance the selectivity of the product; (3) Due to the strong interaction between a single atom and the surrounding coordination atom, its stability is significantly increased. The single atom Cu catalyst has the highest atomic utilization efficiency and good catalytic performance.

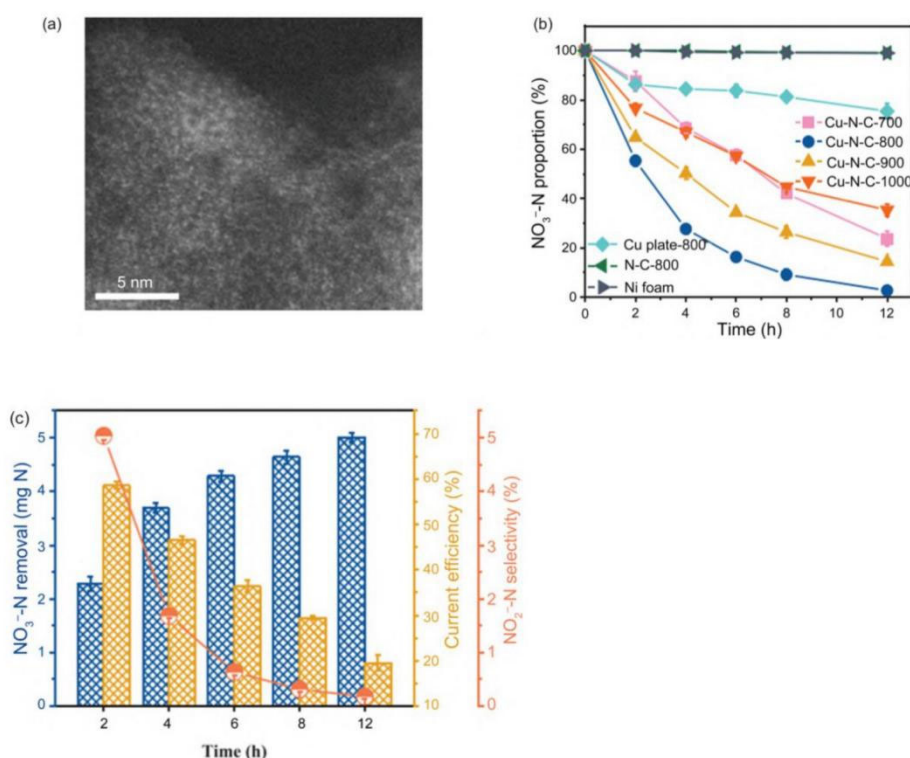


Figure 1(Color online) The characterization of structure and catalytic performance for Cu single-atom catalyst<sup>[52]</sup>. (a) TEM image of Cu-N-C-800 catalyst; (b) nitrate reduction of  $\text{NO}_3^-$  residual amount in different electrolysis time; (c) the  $\text{NO}_3^-$  removal rate,  $\text{NO}_2^-$  selectivity and current efficiency of Cu-N-C-800 electrocatalytic nitrate reduction process under different electrolytic time

Reyter et al.<sup>[49]</sup> used the ball milling method to grind Cu powder under two different gas conditions of air and argon to form Cu nanoparticle catalysts with different structures, and conducted research on nitrate reduction to  $\text{NH}_3$ . After ball milling, ordinary copper powder can significantly improve the copper electrocatalytic nitrate reduction to  $\text{NH}_3$ . Compared with the Cu nanoparticles ground in argon,

the Cu nanoparticles ground in air have smaller size, irregular shape and a large number of surface defects, which are conducive to nitrate adsorption and  $\text{NH}_3$  reduction. Therefore, the nitrate reduction rate of Cu nanoparticles ground in air is 10 times higher than that of Cu nanoparticles ground in argon.

In general, Cu has a high overpotential to HER and can provide a large number of adsorbed hydrogen atoms in front of HER, which is conducive to the reduction of  $\text{NO}_3^-$ . However, Cu still has problems of high overpotential and low current density in its application<sup>[48]</sup>.

### 3.2 Ferrous metals and their compounds

The active sites of Fe in Haber Bosch catalyst (iron based catalyst) and nitrogenase (mainly containing Fe-Mo cofactors) are affected<sup>[56-57]</sup>. Fe series metals and their compounds have shown potential in electrocatalytic nitrate production of ammonia. Ke et al.<sup>[58]</sup> used elemental Fe,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  as catalysts in the experiment of electrocatalytic nitrate reduction to ammonia reaction, and the research results showed that the difference in NARR activity of the three catalysts was likely related to the valence state of Fe atoms. The reduction of  $\text{NO}_3^-$  first requires the adsorption of  $\text{NO}_3^-$ , and the adsorption strength of  $\text{NO}_3^-$  with negative charge on Fe atom should be related to the charge density on the surface of Fe atom, that is, the greater the positive charge density of Fe atom, the stronger the adsorption. Therefore, Fe(111) is conducive to promoting the adsorption of  $\text{NO}_3^-$ , that is,  $\text{Fe}_2\text{O}_3$  has the highest activity. Although  $\text{Fe}_3\text{O}_4$  also has Fe(111), under the premise that the number of Fe sites remains the same, part of Fe(111) is replaced by Fe(11), so the activity is reduced. Due to the presence of only Fe(0), elemental iron has the lowest positive charge density and is the most unfavorable to the adsorption of  $\text{NO}_3^-$ , so the electrocatalytic nitrate reduction to ammonia production has the worst macroscopic activity.

Wu et al.<sup>[59]</sup> used  $\text{SiO}_2$  powder as a hard template to synthesize Fe-SAC (single-atom catalyst) by transition metal salt-assisted carbonization method. DFT calculation shows that Fe single-atom catalyst can effectively prevent the shortage. The N-N coupling step required for  $\text{N}_2$  caused by the absence of adjacent metal sites is used to improve the selectivity of ammonia products. The same synthesis method is used to prepare Co SAC and Ni SAC. The  $\text{NH}_3$  yield of Co SAC and Ni SAC is slightly lower, and the activity of atomic sites is only 1/3 and 1/4 of that of Fe SAC. This indicates that the Fe atomic center has a unique activity.

$\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  have good catalytic stability. Considering that -0.83V is the best voltage for electrocatalyzing nitrate ammonia production for Fe and  $\text{Fe}_3\text{O}_4$  (FE  $\text{NH}_3$  is the largest), the electrolytic voltage is selected as -0.83V, the electrolyte is updated after continuous electrolysis for 6h, and the  $\text{NH}_3$  produced in the electrolyte after each cycle is detected (Fig. 2a-Fig. 2c).

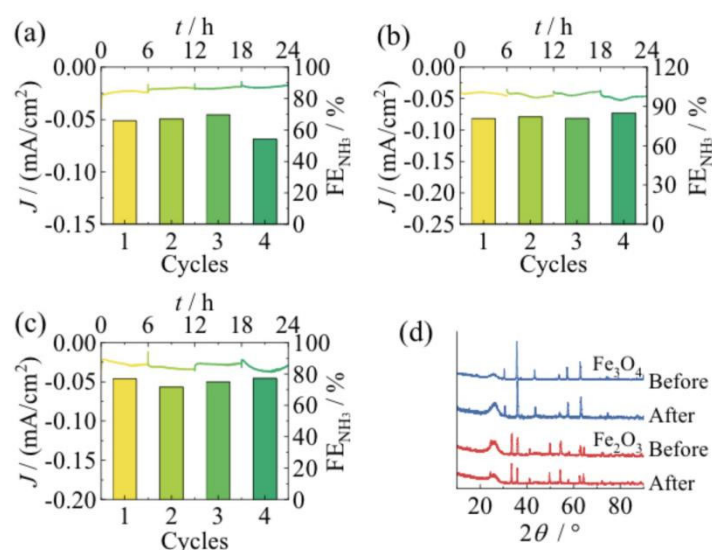


Figure.2 The J-t curves and the corresponding FE  $\text{NH}_3$  per cycle of Fe (a),  $\text{Fe}_2\text{O}_3$  (b) and  $\text{Fe}_3\text{O}_4$  (c) at -0.83 V; (d) comparison of XRD patterns for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  before and after the reaction

The experimental results show that the three catalyst materials still maintain a high level of FE  $\text{NH}_3$  during the entire electrolysis process, especially  $\text{Fe}_2\text{O}_3$  (Fig. 2b), and the corresponding FE  $\text{NH}_3$  can reach 80.8% after electrolysis for 6h, and remain above 81% in the following three cycles. After 24 hours of continuous work, FE  $\text{NH}_3$  showed no signs of decay, which indicates that  $\text{Fe}_2\text{O}_3$  has very good catalytic stability and recyclability. Since the reduction potential applied in the electrocatalytic nitrate reduction process of ammonia production may cause the reduction reaction of high-valence Fe ions in the catalyst, the XRD patterns of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  electrodes before and after electrolysis were tested and compared (Fig. 2d). The results showed that the diffraction patterns of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  had no significant changes, and no formation of new species was observed, indicating their stability in the catalytic process<sup>[58]</sup>.

Hu et al.<sup>[60]</sup> successfully prepared an Fe foil-supported Fe/ $\text{Fe}_3\text{O}_4$  composite material for nitrogen reduction of ammonia synthesis by using a two-step preparation method of high-temperature calcination and in-situ electrochemical reduction. The experimental results showed that the interface site between Fe and  $\text{Fe}_3\text{O}_4$  nanocrystals was the active site for  $\text{N}_2$  reduction. Because the two relative reaction intermediates (such as  $^*\text{N}_2\text{H}$ ,  $^*\text{NH}_2$ ) have different binding abilities, they have a synergistic effect and improve the ammonia production activity of the catalyst. Therefore, the construction of composite materials with heterogeneous structure is an effective strategy to improve catalyst activity. Interface effects in heterogeneous structures can not only overcome the weaknesses of each material, but also generate some new properties and functions<sup>[62]</sup>.

Fe-based catalysts are widely used due to their low price and high  $\text{NO}_3^-$  reducing activity<sup>[62]</sup>. Combined with the basic national conditions of China as a resource country<sup>[63]</sup>, the application of iron series metals and their compounds has good advantages.

### 3.3 Nickel series metals and their compounds

Nickel foam material is a porous three-dimensional electrode material. Due to its good electrical conductivity, thermal conductivity and catalytic activity, it has been widely used as an electrode material for electrocatalyzing nitrate ammonia production<sup>[64]</sup>. The new Ni foam has a strong inhibition effect on HER. A.IARCHUK et al.<sup>[65]</sup> prepared the new nickel foam catalyst by dynamic hydrogen bubble template assisted electrodeposition process. The optimized nickel foam exhibited a rather high Faraday efficiency ( $\text{NH}_3$ ) under ideal electrolyte conditions, and hydrogen was the only by-product of nitrate reduction. No other nitrogen-containing by-products were produced, indicating that nickel foam could achieve 100% selective conversion of nitrate to ammonia.

Liu et al.<sup>[66]</sup> prepared a new NiO/ $\text{TiO}_2$  bimetallic nanoelectrode by anodic oxidation method and chemical water bath method. The surface of the electrode has a relatively uniform nanoporous honeycomb structure. The presence of NiO not only increases the contact area between nitrate and the surface of the plate, but also increases the number of active sites, thus increasing the electrochemical activity of the electrode.

Zheng et al.<sup>[67]</sup> conducted a study with a self-activated nickel cathode, and the activated cathode's ability to treat actual wastewater was improved. When the mass concentration increased from 241mg/L to 2527mg/L, the nitrate conversion rate exceeded 92.0%, and the main product was ammonia. The cathode corrosion and chemical oxidation of nickel electrode form  $\text{Ni}(\text{OH})_2$  particles of nanometer size on the surface of the Ni electrode, which is the reason for the high conversion rate of the electrode. Unlike other electrodes, the original nickel foam electrode shows relatively low activity for electrocatalytic nitrate reduction to ammonia production, but the cyclic electrode significantly amplifies the activity. The nickel electrode can self-activate after continuous cycle in the electrocatalytic nitrate reduction process to ammonia production, showing high selection, lifetime and Faraday efficiency in the conversion of nitrate to ammonia<sup>[48]</sup>.

Liu et al.<sup>[68]</sup> developed a new Ni- $\text{TiO}_2$  nanotube array bimetallic nanoelectrode, which could increase the removal rate of nitrate by 66.8% compared with the nano-electrode prepared by the traditional  $\text{TiO}_2$  method.



Table2 Nickel-based metal and compound electrodes for electrocatalytic reduction of nitrate to ammonia in wastewater<sup>[48]</sup>

Electrode type	Electrode preparation method	Electrolyte	NH <sub>3</sub> /NH <sub>4</sub> <sup>+</sup> formation rate	Potential	Reactor	Faraday efficiency	Removal rate	Selectivity	References	
Nickel series metals and compounds	Nickel foam	Dynamic hydrogen bubble template assisted electrode position	100 mmol NO <sub>3</sub> <sup>-</sup> -N, pH=14	—	-0.1~0.3 V vs. RHE	Two-compartment cell	95%	—	100%	(65)
	Ni(OH) <sub>2</sub> @Ni	—	2000 mg/L NO <sub>3</sub> <sup>-</sup> -N+ 0.1 mol/L Na <sub>2</sub> SO <sub>4</sub>	—	(3.67±0.08)V	Single cell	90.4%	97.8%	97.1%	(67)
	Ni(OH) <sub>2</sub> @Ni	—	500 mg/L NO <sub>3</sub> <sup>-</sup> -N+ 0.1 mol/L Na <sub>2</sub> SO	—	(3.88±0.12)V	Single cell	74.3%	—	96.7%	(67)
	Ni(OH) <sub>2</sub> @Ni	—	200 mg/L NO <sub>3</sub> <sup>-</sup> -N+ 0.1 mol/L Na <sub>2</sub> SO <sub>4</sub>	—	(4.02±0.15)V	Single cell	64.4%	95.3%	95.5%	(67)
	<u>Ni-NSA-VNi</u>	—	200 mg/L NO <sub>2</sub> <sup>-</sup> -N+ 0.2 mol/L Na <sub>2</sub> SO <sub>4</sub>	—	1.2 V vs.RHE	Two-compartment cell	88.9%	73.4%	77.2%	(69)

Because the three-dimensional structure of Ni foam makes it have a large specific surface area, it provides more active sites for the deposition of metal component Cu, which can promote the activity of nitrate nitrogen electrocatalytic reduction reaction. Guo et al.<sup>[70]</sup> compared the nitrate removal effect of the four electrodes at 2.5h, and the results showed that the curve change of the Ni foam electrode and the stainless steel electrode was relatively stable, indicating that the removal effect of the two electrodes on nitrate nitrogen was not obvious. Compared to the removal rate of the stainless steel /Cu electrode, the removal rate of the Ni foam/Cu electrode was improved by about 34% under the same conditions (Fig.3a).

Guo et al.<sup>[70]</sup> took Ni foam/Cu as the cathode and Ti/RuO<sub>2</sub>-Ir<sub>2</sub>O<sub>3</sub> electrode as the anode. Under the conditions of pH=7, electrolyte Na<sub>2</sub>SO<sub>4</sub> concentration of 0.5g/L and electrolytic current density of 4mA/cm<sup>2</sup>, NARR treatment was carried out on wastewater with different concentrations of NO<sub>3</sub><sup>-</sup>-N, as shown in (Fig. 3b). With the increase of the initial concentration of nitrate, the 2.5h electrolytic removal of nitrate nitrogen first increased and then decreased. When the solution concentration was 100mg/L and 150mg/L, the nitrate nitrogen removal rate was significantly higher than 50mg/L, and when the solution concentration was 200mg/L, the nitrate removal rate was significantly reduced. The reason is that the increase of nitrate in a certain concentration range can adsorb NO<sub>3</sub><sup>-</sup> ions on the cathode surface, so that the reaction rate and removal rate can be improved. However, when the concentration is higher than a certain value, the cathode adsorption capacity will reach saturation, hindering the mass transfer of nitrate, slowing down the rate of reaching the electrode surface, and reducing the rate of reaction removal.

In the electrochemical test conducted in the H-type electrolytic cell, the current of Cao et al.<sup>[71]</sup> is larger in the solution containing NO<sub>3</sub><sup>-</sup> than in the solution without NO<sub>3</sub><sup>-</sup>, and the difference between the two increases with the increase of voltage, indicating that NO<sub>3</sub><sup>-</sup> has a chemical reaction on the working electrode. In the solution containing NO<sub>3</sub><sup>-</sup>, the current of NiPd<sub>50</sub>Cu<sub>50</sub> is larger than that of NiPd, indicating that NiPd<sub>50</sub>Cu<sub>50</sub> has the best catalytic NO<sub>3</sub><sup>-</sup> electric reduction performance. It can be seen from (Fig.3c) that the NH<sub>3</sub> yield and Faraday efficiency of NiPd<sub>50</sub>Cu<sub>50</sub>, which has undergone several cycles, remain stable, indicating its good catalytic stability.

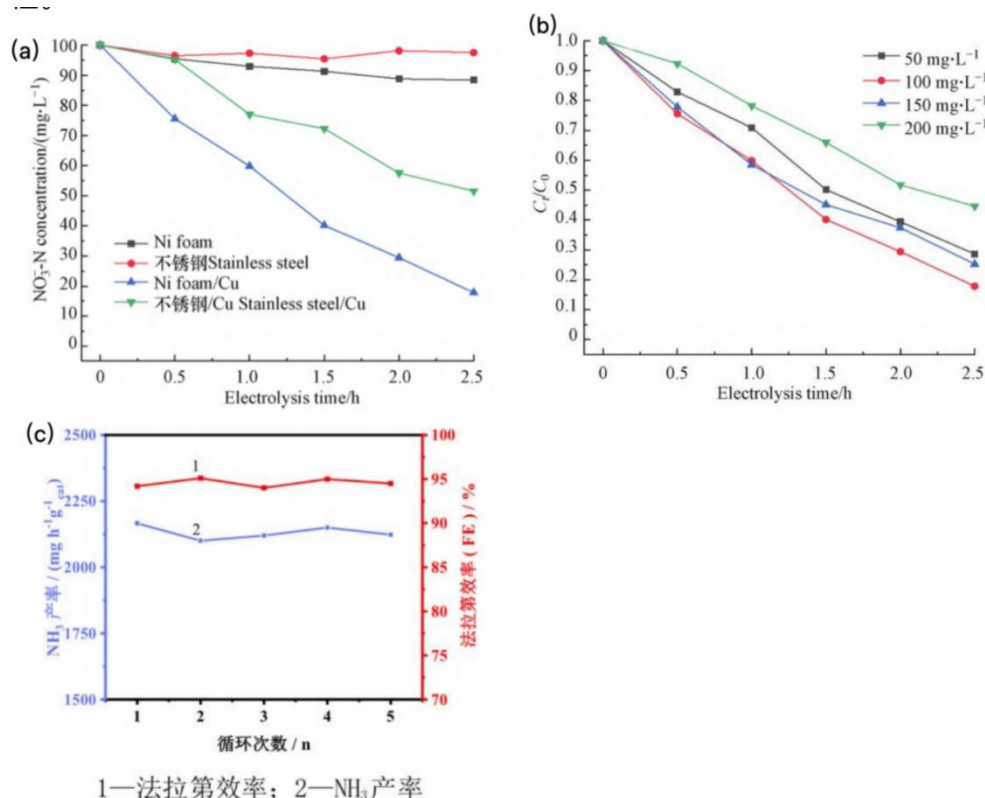


Figure.3 (a)Influence of different electrodes on reduction of nitrate nitrogen; (b)Influence of initial concentration of nitrate nitrogen on reduction of nitrate nitrogen; (c) NiPd<sub>50</sub>Cu<sub>50</sub> cycle stability test

#### 4. Conclusion and Prospect

This paper reviews the recent domestic and foreign literature on electrocatalytic nitrate reduction to ammonia, and summarizes the research progress of transition metals Cu, Fe and Ni as electrode materials. Due to its unique electronic structure and abundant resources, transition metals show excellent performance in electrocatalyzing nitrate to ammonia. However, electrocatalytic reduction method still has the disadvantages of harsh electrode material conditions, stable control and large scale NH<sub>3</sub> production ability compared with Haber-Bosch method.

The adsorbed hydrogen atom provided by Cu before the hydrogen evolution reaction is conducive to the reduction of NO<sub>3</sub><sup>-</sup>, but there are problems of high potential and low current density in the application process. China is a big country of iron resources, and Fe<sub>2</sub>O<sub>3</sub> has very excellent catalytic stability and high Faraday efficiency of ammonia generation, so Fe as electrocatalytic nitrate ammonia electrode material has good prospects for development. Because of its unique structure, the foam nickel can achieve 100% selection of ammonia, and the self-activation of the nickel electrode, so that it has quite high selectivity and Faraday efficiency.

Future research on electrocatalytic nitrate reduction of ammonia production should focus on the following aspects :1) Research on new electrodes to prepare more innovative electrode materials; 2) The mechanism of electrocatalytic nitrate reduction to ammonia production should be further studied to reduce the generation of intermediate by-products. A more suitable and effective catalyst is selected to make the reaction proceed in the direction of generating the target product. 3) Strengthen the study of electrode stability and energy consumption, so that it meets the needs of actual production; 4) The use of renewable energy and the development of low-cost catalysts, the preparation of lower-cost catalysts, so that it is in line with economic benefits.

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