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Recent research progress of electrocatalytic reduction technology for nitrate wastewater: A review

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ABSTRACT

Nitrate pollution is becoming more severe and affects the nitrogen cycle globally. With the advancement of nitrate treatment technology, electrocatalytic nitrate reduction stands out due to its high efficiency and distinct advantages. Herein, this review critically examines the current state of research on the electrocatalytic reduction of nitrate wastewater. First, a brief explanation of the reduction mechanism was provided. Second, factors influencing the electrocatalytic reduction of nitrate in the continuous flow reaction were investigated, including cathode material, cell design, initial nitrate concentration, current density, initial pH, co-existing ions, chloride ion concentration and additives. Third, the cathode material's stability was widely discussed. After that, we discussed current state of industrialized technology for treatment of nitrate. Finally, there are outlook and conclusion on the current state of research in this field. This review aims to provide guidance for electrocatalytic nitrate reduction technology, and it is hoped that large-scale applications of electrocatalytic nitrate reduction for industrial wastewater will be realized in the near future.

1. Introduction

The rapid development of urbanization, industrialization, agricultural activities, and the rising human population has resulted in severe nitrate pollution in water bodies, resulting in eutrophication, which damages aquatic ecosystems and endangers human health, particularly infant health [1,2]. The United States Environmental Protection Agency (US EPA) and World Health Organization (WHO) have declared that the maximum contaminant levels (MCL) of nitrate in drinking water should be less than 10.0 mg N/L [3,4]. However, some water effluents have nitrate concentrations that far exceed the standard, reaching tens or even hundreds of mg/L [5,6]. Nitrate is a type of non-ligand oxygen anion with high mobility and solubility in water [7]. Nitrate occurs naturally in some geological formations.

Nevertheless, nitrate pollution in surface and groundwater is caused by various anthropogenic activities, including fertilizers runoff from agricultural fields, surface runoff of stormwater from municipalities, as

well as discharge of sewage or wastewater [7,8]. There is currently much interest in converting nitrate to non-toxic gaseous nitrogen (N₂) without producing other by-products such as nitrite and ammonium [9]. The biological or chemical conversion of the nitrate ion (NO₃⁻) to the chemically inactive dinitrogen (N₂) is a common method for nitrate pollution remediation. Although the biological approach is one of the most effective methods for dealing with nitrate pollution, it is rather slow and sensitive to changes in environmental variables [10,11]. At the same time, chemical reduction typically results in excessive production of ammonium nitrogen (NH₄⁺) and necessitates the use of hydrogen (H₂) as a reductant or electron donor in the chemical reduction process, while the transport of pressurized H₂ poses a safety hazard [12–14]. Electro-flocculation is a wastewater pollution removal technology that electrolyzes anodes (usually made of iron or aluminium), applies an electric current for a redox reaction, and agglomerates the contaminants through the electrodes (coagulants) [15–17]. However, the main disadvantage of electrocoagulation is the tendency for passivated

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membranes to form on the electrode surface over time, interfering with the pollutant degradation process. The high operating costs and excessive metal hydroxide sludge production are also disadvantages of electrocoagulation [18,19]. Electrodialysis is an emerging electrochemical membrane method for concentrating and separating pollutant ions in wastewater [20]. Electrodialysis, on the other hand, is not well suited for very dilute solutions due to its high resistance, high energy consumption, and polarisation [21]. Therefore, it is necessary to investigate environmentally friendly and sustainable remediation techniques for nitrate pollution. An electrocatalytic reduction is an alternative approach that combines electrochemical and catalytic technologies to treat wastewater. By applying an electric current to the cathode, nitrate undergoes an electrochemical reduction reaction, converting it to harmless N_2 or economically valuable ammonia (NH_3) as a chemical or hydrogen carrier [10,13,22].

The oxidation states of nitrogen for NH_3 , N_2H_4 (hydrazine), NH_2OH (hydroxylamine), N_2 , N_2O (nitrous oxide), NO (nitrogen monoxide), NO_2^- (nitrite), N_2O_4 (dinitrogen tetroxide), and NO_3^- are -III, -II, -I, 0, +I, +II, +III, +IV, and +V, respectively. Regarding these oxidation states, the highest oxidation state is nitrate (+V), the highest reduced state is ammonia (-III), while N_2 has the most stable zero oxidation state [23]. To a certain extent, reducing nitrate ions to their most stable zero oxidation state is difficult. The research on the reduction performance of NO_3^- via electrochemical denitrification or in combination with other novel techniques has received increased attention. Li et al. [24] established experimental results for nitrate removal using electrocatalytic systems, indicating an up to 88.3% removal efficiency for NO_3^- .

Additionally, the effect of the electrode modification technique on the selectivity of NO_3^- reduction products has been extensively discussed. Yao et al. [25] investigated the electrochemical reduction of nitrate in wastewater and its efficiency and N_2 selectivity. The results indicated that the current efficiency was 63.9%, and the removal efficiency was 82.1% when the N_2 selectivity was 81.3%.

Meanwhile, Kirujika et al. [26] demonstrated that copper cathodes could remove nitrate with an efficiency of 72%, and there is a considerable expectation of removing nitrate using other electrodes. Metallic catalysts have received considerable attention recently, and the development of high-performance metallic cathode catalysts for electrocatalytic denitrification is a hot topic [27]. To enhance the electrocatalytic activity and selectivity of harmless nitrogen, it will be necessary to conduct additional research on the composition and structural design of suitable cathode materials [28].

The novelty of this literature review is that it presents the systematic investigation of the effect of different initial concentrations of nitrate wastewater on nitrate reduction and compares the stability of cathodes in the electrocatalytic reduction of nitrate. The factors affecting catalytic selectivity in the electrocatalytic process, as well as the mechanisms by which these factors affect catalytic selectivity, will be comprehensively and systematically discussed in this review paper. Simultaneously, the novelty of this review is that it examines the state of the art in dynamic electrochemical denitrification research. It should be noted that previous reviews of the literature have primarily focused on the feasibility and functionality of cathodic nitrate reduction [29]. Meanwhile, the majority of nitrate wastewaters examined in other reviews have a fixed initial nitrate concentration and a low initial nitrate concentration [30, 31]. Thus, this review aims to close a gap in the literature on electrocatalytic nitrate reduction by combining the investigation of electrocatalytic nitrate reduction of wastewater with varying initial concentration values and the stability of the cathode in electrocatalytic nitrate reduction.

This review also identified potential directions for electrocatalytic reduction technology advancement. Furthermore, this review will enhance the electrocatalytic reduction technology system and provide innovative and sustainable development opportunities for electrocatalytic reduction technology. The following sections summarise the recent research progress on electrocatalytic reduction technology for

nitrate wastewater:

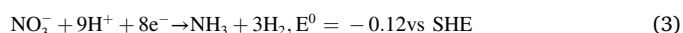
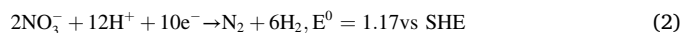
- 1) The effect of initial nitrate concentrations on electrocatalytic reduction efficiency.
- 2) The factors affecting catalytic efficiency in electrocatalytic processes are investigated, as well as the effect of these factors on catalytic selectivity.
- 3) The investigation of the electrochemical denitrification research progress under dynamic conditions and the use of a continuous flow reactor.
- 4) Comparative analysis of cathode stability in electrocatalytic nitrate reduction.

2. Pathways and mechanisms of electrochemical reduction of nitrate

Typically, the mechanism of electrocatalytic nitrate reduction is investigated by detecting the intermediate products formed during denitrification and thus analyzing the intermediate steps. This enables kinetic studies and a theoretical foundation for optimizing the electrocatalytic denitrification treatment technology.

It is critical for researchers to understand the mechanism of complex electron transfer and pathways involved in nitrate reduction. The process of nitrate reduction is complicated by the fact that elemental nitrogen has a wide range of valence states between -3 and +5. Besides, the instability of nitrite, a critical product in the entire process, results in the formation of numerous intermediate products. There are many intermediate products in nitrate reduction, including nitrogen, nitrite (NO_2^-), ammonium (NH_4^+), and some unstable/short-lived products NO_2 , NO , N_2O , NH_2OH , NH_2NH_2 .

Ammonia (NH_3) and nitrogen (N_2) are the most thermodynamically stable forms of nitrogen, particularly at neutral pH [29]. Thus, NH_3 and N_2 are frequently the final products of electrocatalytic reactions of nitrates, where NH_3 is dissolved in water, forming ammonium (NH_4^+) (Eq. (1)).



Nitrite is the primary quasi-stable intermediate formed during the electrochemical reduction of nitrate before it is completely reduced to ammonia or nitrogen gas [7]. Thus, the oxidation of nitrate (NO_3^-) to ammonium (NH_4^+) can be divided into two steps: the conversion of nitrate (NO_3^-) to nitrite (NO_2^-) and the conversion from nitrite (NO_2^-) to ammonia (NH_3)/ nitrogen (N_2) (Eq. (2), Eq. (3)). Fig. 1 shows the intermediate reactions and electron transfer during the electrolysis of nitrate to ammonia and nitrogen. Both pathways go through an adsorption step and a rate-limiting step for the reduction of nitrate to nitrite occurring at the cathode surface. Nitrite ends up forming different intermediate products of ammonia and nitrogen and is influenced by many factors.

2.1. Nitrate adsorption

Adsorption of nitrate is a fast and reversible process subject to competitive adsorption effects [32]. The more chlorine ion, sulfate ion, and other competitive anions present, the lower the efficiency of nitrate adsorption and the slower the nitrate removal rate [33]. Additionally, the process is kinetic and unaffected by the nitrate reduction to intermediate nitrogen products [34]. The equation for the reaction is shown in Eq. (4).



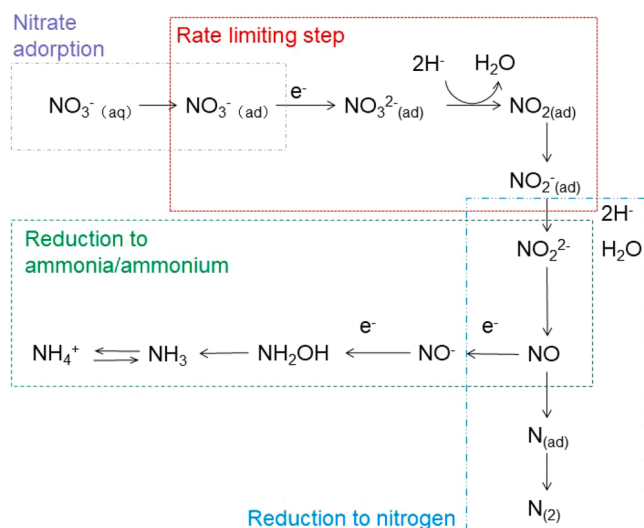


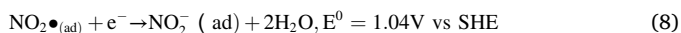
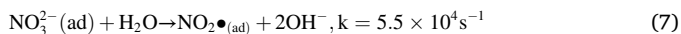
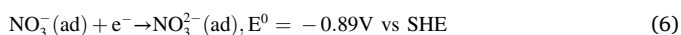
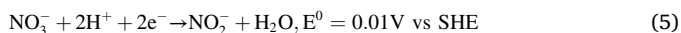
Fig. 1. Process of nitrite reduction.

2.2. Electrochemical reduction of nitrate to nitrite

The rate-limiting step is the nitrite generation process. The rate of the nitrate reduction reaction is determined by the first electron transfer process (Eq. (5)). In the rate limiting step, the nitrate adsorption rate is hindered by other anions. [35]. Some scholars suggested that it is the high energy of the lowest unoccupied molecular π^* orbital (LUMO π^*) of nitrate which limits the charge injection and affects the rate of conversion of nitrate to nitrite [29]. Eq. (5) describes the total electron transfer process for this step.

The formation of nitrite occurs via an electrochemical-chemical-electrochemical (ECE) mechanism in this process [7]. The nitrite formation is accompanied by a primary charge transfer of two electrons (Eq. (5)). When the reaction (Eq. (7)) occurs quickly enough, the entire two-electron process becomes irreversible [36]. $\text{NO}_{2(\text{ad})}$ is the oxidant produced temporarily during the re-reduction process.

Short-lived intermediates are formed as a result of basic charge transfer reactions involving one electron at a time, including nitrate dianion radical ($\text{NO}_3^{\bullet 2-}$) as well as NO_2^- (Fig. 1). Nitrite first receives one electron before forming the short-lived ($\sim 20 \mu\text{s}$) nitrate dianion radical ($\text{NO}_3^{\bullet 2-}$) (Eq. (6)) [7]. Finally, a second electron transfer occurs during the conversion of NO_2^- which is produced during the hydrolysis of $\text{NO}_3^{\bullet 2-}$ to NO_2^- (Eq. (7), Eq. (8)).



2.3. Electrochemical reduction of nitrite to ammonia

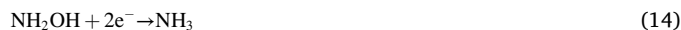
The general chemical equation is shown in Eq. (9):



Additional nitrite reduction may result in the formation of ammonia or nitrogen. As shown in Fig. 1, nitric oxide controls the selectivity of the end product. Ammonia is one of the most stable forms in standard thermodynamics. Due to the electrode type and point position, different electrodes may react differently, producing intermediate products such as nitrous oxide or nitric oxide before the final product is produced [37].

The charge transfer of nitric oxide (NO) as an intermediate product will be discussed in this section, assuming the final product is ammonia. Nitrite is highly reactive on transition metal surfaces and thus rapidly produces chemisorbed nitric oxide (NO) [35]. It is inferred that further reduction of NO (ads) results in the formation of NH_2OH and NH_3 .

The final reduction of nitrite to ammonia is an electrochemical-electrochemical (EE) mechanism involving a succession of direct charge transfer reactions. Nitric oxide is first reacted to form nitroxyl acid azanone (HNO) (Eq. (8)), which is then reduced to NH_2OH . After a rapid reduction to NH_2OH , two electrons are eventually gained to form ammonia (NH_3). At high pH, ammonium is rapidly converted to ammonia; conversely, nitrogen is more stable in the form of ammonium (Eq. (1)).



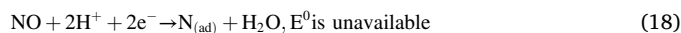
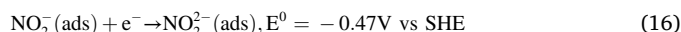
2.4. Electrochemical reduction of nitrite to nitrogen (N_2)

The general chemical equation is shown in (Eq. (15)):



Since the electro-reduction of NO species happens with a conventional ECE mechanism in the potential range of 0.78 V to Ep [38] under alkaline conditions, this would produce the typical ECE reaction. Under alkaline conditions, the primary intermediates in this process are $\text{NO}_2^{\bullet 2-}$ and $\text{H}_2\text{N}_2\text{O}_2$ [39]. Thus, the electro-reduction mechanism of nitrite ions can be represented by the following reaction equations (Eq. (16), Eq. (19)) [40].

Nitrite accepts one electron via a direct charge transfer reaction to produce $\text{NO}_2^{\bullet 2-}$ (Eq. (10)), which is then hydrolyzed to form nitric oxide (NO) at the next step (Eq. (17)). As the core of selective by-product formation, nitric oxide is most commonly reduced to adsorbed atomic nitrogen ($\text{N}_{(\text{ad})}$) (Eq. (18)). The nuclear bonding of two nitrogen atoms integrates to form a triple bond of nitrogen (Eq. (19)) to produce harmless nitrogen gas.



2.5. Other reactions

Under strongly acidic conditions, all mechanistic pathways are possible. For instance, under such highly acidic conditions ($\text{pKa}=3.4$) and at nitrate reactant concentrations above 1.0 M and below 4.0 M, due to the high concentration of hydrogen ions, nitrite may be converted into weak nitrite acid, and the nitrite may also be further oxidized to form nitric oxide (NO) [7]. In the first case, nitrite (HNO_2) and nitrate (NO_3^-) react to form dinitrogen tetroxide (N_2O_4), and two nitrogen dioxides (NO_2) are rapidly released. Due to the electroactive nature of nitrous acid (HNO_2), the rate of nitrate reduction reactions increases as the concentration of nitrous acid (HNO_2) increases [7].

Thus, the electrochemical reduction of nitrate is a highly complex process that produces a diverse range of products. The primary end products are ammonia and nitrogen gas. Naturally, stable intermediate

products can be formed under certain environmental conditions. Additionally, by adjusting the applied spot position and the electrode material, it is possible to selectively reduce nitrate to different products [41].

3. Factors influencing the performance and selectivity of electrochemical reduction of nitrate

3.1. Cathode material

The electrochemical reduction of nitrate reaction cells comprises three basic units: a cathode, an anode, and a reaction tank. The electrolyte and electrodes are the primary components of the reaction that allow the current to circulate. Nitrogen is the ideal product of electrocatalytic nitrate reduction, while ammonia, nitrite, and other substances are the intermediate products. Nitrogen atoms' valence changes from +5 to -3 throughout the process, and they gain electrons during the reduction reaction. Thus, the cathode material selected directly affects the electrocatalytic activity and selectivity of the nitrate reduction reaction. Several decades of research have been conducted on various electrode materials, including non-metallic electrodes, single metal electrodes, polycrystalline electrodes, and composite electrodes, and it has been discovered that the performance of different materials for nitrate electrocatalytic reduction varies significantly.

3.1.1. Non-metallic material electrode

Firstly, the non-metallic material electrodes are a more popular area of research today due to their high melting point, high hardness, high corrosion resistance, and metal-like characteristics, as well as their superior electrocatalytic reduction efficiency of nitrate. Such as Boron-doped diamond (BDD) [42,43], activated carbon [44], charcoal [27], carbon paper [45], along with others. As is shown in Table 1, under the same conditions, nitrate shows the best reduction efficiency on GF (Graphite felt) electrodes compared with $\text{Cu}_{90}\text{Ni}_{10}$ and Ti metal electrodes [46]. Charcoal is more efficient at reducing nitrate than graphite, and this may be because it has a higher sp^3/sp^2 ratio than graphite, which enhances the electron transfer kinetics of nitrate reduction on the charcoal cathode. In addition, charcoal is an electromagnetic storage material that can provide more active sites to boost the electrocatalytic reduction activity of the cathode by charging and discharging C-O and other oxygen-containing functional groups [27].

3.1.2. Metallic electrodes

Among metal electrodes, different metallic materials exhibit a range of physical and chemical properties and contribute to the electrocatalytic reduction of nitrate in a variety of ways, and there are significant differences in reduction efficiency and product selectivity, implying that they have a diverse range of application scenarios. Noble metals such as Pd [47], Pt [48], Ag [49], and Au [50], along with others, which have high corrosion resistance and high electrocatalytic activity can effectively reduce nitrate in wastewater as cathodes, but their high cost prevents their use on a large scale. Non-noble metal materials such as Cu [51], Fe [23], Al [52], Ni [53], Ti [54], along with others, also have excellent electrochemical performance and lower cost, thus, non-noble metal research is one of the primary research directions for metal electrodes today. Amongst non-noble metals, Cu electrodes have attracted much attention from researchers due to their high catalytic performance [55–57]. In order to obtain better nitrate reduction efficiency and corresponding products, adjusting the surface nanostructure of the electrode is an economical and effective method [58–63]. For example, Ma et al. [64] demonstrated in their experiments that the nitrate electroreduction efficiency of the surface-treated nano titanium electrode reached 94.6%, significantly higher than the 65.8% of the untreated nano titanium electrode, while the normal titanium electrode had only 37.9% reduction efficiency under the same conditions. This may be the result of surface nanostructure reconfiguration, the surface

of the treated nano titanium electrode appeared to deformation and fracture, and the nanopores changed, which increased the specific surface area of the electrode and promoted the formation of a double electric layer during electrolysis, all of which could affect the ion adsorption process and mass transfer efficiency on the electrode surface. Recently, 3D Cu nanobelt electrodes have been found to have excellent nitrate removal efficiency, approaching 100%, which is much higher than the efficiency of nitrate reduction using foam copper under the same conditions. Because the 3D Cu nanobelt electrodes have a larger surface area and higher charge transfer capability, which facilitates the nitrate transfer and accelerates electrocatalytic kinetics. In addition, the 3D Cu nanobelt electrode preferentially reacts with nitrate, whereas the pristine foam Cu electrode is more likely to react with dissolved oxygen to form hydrogen peroxide, which directly inhibits the nitrate reduction process [65]. The Cu cathode exhibits better nitrate removal efficiency in a shorter period of time, and the Ni cathode has a higher level of N_2 selectivity despite its lower nitrate reduction efficiency, so the Cu/Ni alloy may have both higher nitrate catalytic efficiency and nitrogen selectivity.

Combining different metallic materials through synergistic interactions between two or more different metals has become a popular and effective approach for optimizing the performance of metallic catalysts. Fe/Cu foam electrodes prepared by cathodic electrodeposition were used as cathode materials for electrocatalytic reduction of nitrate nitrogen, and Fe/Cu achieved 98.6% nitrate nitrogen removal efficiency in 90 min compared to 24.3% for copper foam and 76.0% for iron cathode [66]. At $E = -1.20$ V vs. Hg/HgO potential, $\text{Cu}_{80}\text{Ni}_{20}$ and $\text{Cu}_{90}\text{Ni}_{10}$ showed superior performance in the reduction of nitrate nitrogen and nitrite compared to Cu and Ni electrodes because the alloys had a slower current decay rate, supported a higher current and faster ion exchange rate [67]. In addition, $\text{Cu}_{80}\text{Ni}_{20}$ almost exclusively produced NH_3 at a selection rate of 96%, which is consistent with Wang et al. [68] work. The electronic structure studies revealed an upshifting of the d-band center toward the Fermi level, a feature that enhances intermediate adsorption energies. By replacing 50% Cu with Ni, the performance of NO_3RR -to- NH_3 was significantly improved, which has greater significance for the targeted reduction of nitrate to ammonia. Compared with Cu and Fe cathode, Cu-Bi bimetallic cathode improves nitrate electrocatalytic reduction performance and reduces the generation of by-products like nitrite and ammonia. The nitrogen selectivity of Cu-Bi cathodes is also better than that of Cu cathodes [69]. By covering the Ti substrate with the Cu-Sn-Bi metal layer and adjusting the Bi content to 3.18%, a nitrate removal rate of 88.43% and a nitrogen selection rate of 77.8% were obtained [43]. Su et al. [37] used electrodeposition to load Cu, Pd-Cu onto stainless steel, and cyclic voltammetry results showed that the Pd-Cu/SS electrode significantly increased the nitrite reduction reaction activity and obtained a higher nitrate reduction efficiency than Cu/SS. As shown in Fig. 2(a) and (b), the surface morphology of Cu/SS and Pd-Cu/SS synthesized under the same conditions showed a significant difference, Cu/SS has a smooth polyhedral morphology, while Pd-Cu/SS is relatively rough and forms dendrites, which may be due to the presence of Pd, which changes the surface conformation, and this difference in conformation, altering the reaction mechanism and process of nitrate electrocatalytic reduction to some extent, which is one of the reasons why Pd-Cu/SS has better performance. Fig. 2(c) and (d) shows the XRD patterns of Cu/SS and Pd-Cu/SS electrodes, respectively. No Pd peak was detected at the Pd-Cu/SS electrode. It is hypothesized that there was formation of Cu_3Pd phase on the electrode surface. Fig. 2(e) characterizes the chemical morphology of Cu/SS and Pd-Cu/SS electrode surfaces by XPS. As shown in Fig. 2(f), for the Cu/SS electrode, a reduction peak can be observed at all scan rates without a corresponding oxidation peak, indicating that an irreversible reduction reaction occurs at the electrode. From Fig. 2(g), (h), (i), it can be seen that the acidate reduction step changed when the Pd-Cu/SS electrode was used, and further studies revealed that Pd-Cu/SS was more favorable for the N_2 production. The result was

Table 1
Performance of different cathode materials in nitrate electrocatalytic reduction.

Cathode	Concentrations	J (mA/cm ²)	T (min)	pH ₀	S (N ₂)	S (NH ₄ ⁺)	R (NO ₃)	R (TN)	Ref.
GF	2 mM NO ₃ ⁻	N/A	120	N/A	36.4%	34.5%	70%	N/A	[46]
Charcoal	110 mg/L NO ₃ ⁻	N/A	120	N/A	N/A	98.5%	91.2%	N/A	[27]
Si/BDD	350 mg/L NO ₃ ⁻	35.7	120		Over 80%	N/A	About 100%	N/A	[86]
	500 mg/L NaCl								
	0.05 mol/L Na ₂ SO ₄								
Fe	41.61 mmol/L NO ₃ ⁻	28.571	180	7.0	N/A	N/A	51%	N/A	[23]
	26.72 mmol/L NH ₄ ⁺								
	12 mmol/L Cl ⁻								
Cu	51 mM Na ₂ SO ₄	10	90	N/A	N/A	70%	63%	N/A	[87]
	1.5 mM NO ₃ ⁻								
Ti	2 mM NaNO ₃	N/A	120	N/A	32.7%	21.8%	8%	N/A	[46]
Al	50 mg/L NO ₃ ⁻	15	240	N/A	N/A	33%	78%	N/A	[24]
	0.5 g/L Na ₂ SO ₄								
Ni	50 mg/L NO ₃ ⁻	15	240	N/A	N/A	25%	36%	N/A	[24]
	0.5 g/L Na ₂ SO ₄								
Nickel Foam	0.5 g/L Cl ⁻	5	240	6.2	99.86%		28.16%	N/A	[81]
	50 mg/L NO ₃ ⁻								
Ni-TNTA	0.3 g/L NaCl	30	90	11	Over 90%	N/A	93.4%	N/A	[88]
	50 mg/L NO ₃ ⁻								
	0.5 g/L Na ₂ SO ₄								
Cu/Ni	100 mg/L NO ₃ ⁻	25	60	N/A	N/A	N/A	99.2%	N/A	[89]
	0.05 M Na ₂ SO ₄								
Cu ₅₀ Ni ₅₀	100 mg/L NO ₃ ⁻	N/A	N/A	N/A	N/A	99%	N/A	N/A	[68]
	1 M KOH								
Cu ₇₀ Ni ₃₀	0.1 M NO ₃ ⁻	N/A	480	N/A	N/A	95.9%	86.8%	N/A	[90]
	1 M KOH								
Cu ₈₀ Ni ₂₀	20 mM NO ₃ ⁻	N/A	480	N/A	N/A	88%	50%	N/A	[67]
Cu ₉₀ Ni ₁₀ (Cu based)	2 mM NaNO ₃	N/A	120	N/A	41.8%	30.9%	58%	N/A	[46]
Fe/Cu	100 mg/L	25	90	N/A	N/A	N/A	98.6%	N/A	[66]
	NO ₃ ⁻ -N								
Cu-Bi	100 mg/L NO ₃ ⁻	6	240	N/A	60.8%	N/A	87.5%	N/A	[69]
Ni-Fe ⁰	0.5 g/L Cl ⁻	5	240	6.2	85.79%	N/A	45.95%	N/A	[81]
	50 mg/L NO ₃ ⁻								
Cu/Ni-Foam (Ni-based)	100 mg/L NO ₃ ⁻	25	90	N/A	About 100%	N/A	100.0%	N/A	[91]
	0.05 mol/L Na ₂ SO ₄								
	1 g/L Cl ⁻								
TiO ₂	50 mg/L NO ₃ ⁻	38	120	N/A	17.7%	N/A	94.6%	N/A	[64]
	0.5 g/L Na ₂ SO ₄								
TiO ₂	50 mg/L NO ₃ ⁻	37	90	N/A	N/A	78.6%	74.4%	N/A	[92]
	0.5 g/L Na ₂ SO ₄								
TiO ₂	600 mg/L NO ₃ ⁻	40	90	N/A	N/A	N/A	97.8%	N/A	[93]
	0.035 M g/L Na ₂ SO ₄								
Fe ₂ O ₃	100 mg/L NO ₃ ⁻	10	180	7	N/A	50.0%	99.0%	N/A	[77]
	0.05 M Na ₂ SO ₄								
Co ₃ O ₄ nanosheet	50 mg/L NO ₃ ⁻	5.72	180	N/A	N/A	80.0%	84.0%	N/A	[94]
	0.5 M Na ₂ SO ₄								
Co ₃ O ₄ -TiO ₂ /Ti	50 mg/L NO ₃ ⁻	10	120	7.0	About 100%	N/A	89%	N/A	[95]
	0.1 M Na ₂ SO ₄								
	2 g/L NaCl								
Fe ₂ O ₃ /Ti	100 mg/L NO ₃ ⁻	10	180	7.0	50%	50%	98%	49%	[77]
	0.05 mol/L Na ₂ SO ₄								
Co ₃ O ₄ /Ti	100 mg/L NO ₃ ⁻	10	180	7.0	68%	32%	99%	66%	[77]
	0.05 mol/L Na ₂ SO ₄								
Co ₃ O ₄ /Ti	100 mg/L NO ₃ ⁻	20	120	N/A	N/A	59.3%	N/A	40.7%	[80]
	0.05 M Na ₂ SO ₄								
CuO-Co ₃ O ₄ /Ti	100 mg/L NO ₃ ⁻	20	120	N/A	N/A	46.3%	N/A	53.7%	[80]
	0.05 M Na ₂ SO ₄								
CuO-Co ₃ O ₄ /Ti	100 mg/L NO ₃ ⁻	20	120	N/A	About 100%	N/A	N/A	About 100%	[80]
	0.05 M Na ₂ SO ₄								
	1000 mg/L Cl ⁻								
Ni-Fe ⁰ @Fe ₃ O ₄	0.5 g/L Cl ⁻	5	240	6.2	88.80%	N/A	90.19%	N/A	[81]
	50 mg/L NO ₃ ⁻								
P _{2.1} -Co ₃ O ₄ /NF	2500 mg/L Cl ⁻	N/A	120	7.0	About 100%	N/A	N/A	95%	[96]
	50 mg/L NO ₃ ⁻								
	0.05 M Na ₂ SO ₄								
P _{2.1} -Co ₃ O ₄ /NF	50 mg/L NO ₃ ⁻	N/A	120	7.0	21%	N/A	N/A	20%	[96]
	0.05 M Na ₂ SO ₄								
ENTE(Ti-based)	0.5 g/L Na ₂ SO ₄	38	60	N/A	Over 95%	N/A	94.6%	N/A	[64]
	50 mg/L Nitrate								
	1.5 g/L NaCl								
Pd/activated carbon fiber	135.5 mg/L NO ₃ ⁻	2	N/A	6.0–6.5	95%	N/A	76%	N/A	[97]
3D Pd-Cu(OH) ₂ /CF (Cu Foam)	50 mg/L NO ₃ ⁻	N/A	60	N/A	About 100%	N/A	N/A	98.7%	[98]
	0.1 M Cl ⁻								
YMGO/CB-CC	100 mg/L NO ₃ ⁻	7	180	5.26	95.87%	N/A	96.48%	N/A	[72]
	25 mM Na ₂ SO ₄								
	5 mM NaCl								

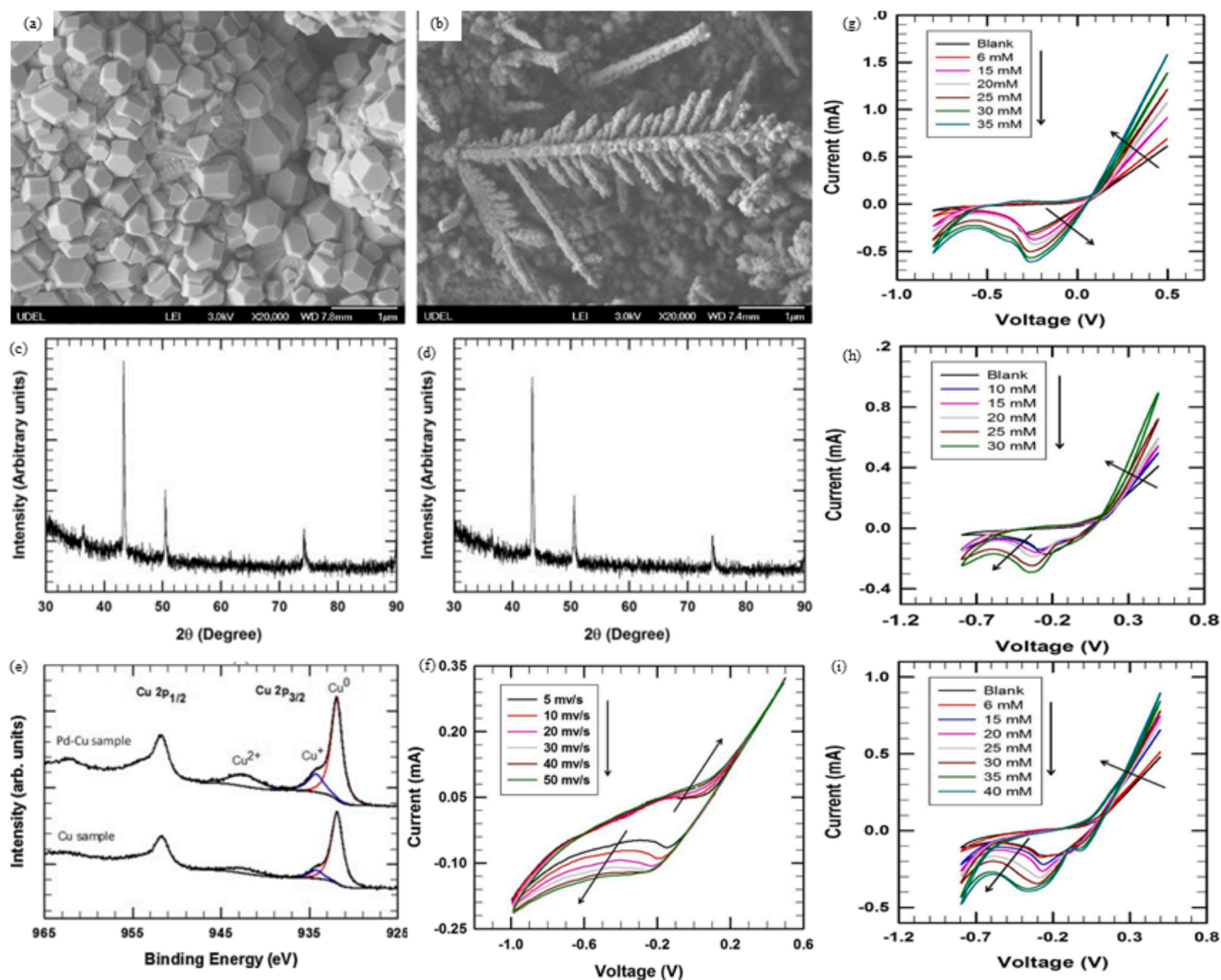


Fig. 2. The surface SEM images of (a) Cu/SS cathode and (b) Pd-Cu/SS cathode. The XRD patterns of (c) Cu/SS electrode and (d) Pd-Cu/SS electrode. (e) XPS spectrum of Cu/SS and Pd-Cu/SS electrodes. (f) The CV (cyclic voltammetric) curves of the Cu/SS electrode recorded at varying scan rates (from 5 to 50 mV/s) for a 0.6 mM NaNO₃ solution in the presence of 0.01 M NaClO₄ electrolyte. (g) CV curves for various concentrations of nitrate (from 6 to 35 mM) in 0.05 M NaClO₄ electrolyte scanned at a rate of 10 mV/s at the Cu/SS electrode. (h) CV curves for varying concentrations of nitrite (from 10 to 35 mM) in 0.05 M NaClO₄ electrolyte solution scanned at a rate of 10 mV/s at the Cu/SS electrode (i) CV curves on Pd-Cu/SS electrode scanned at a rate of 10 mV/s for various nitrite concentrations (from 6 to 40 mM) in 0.05 M NaClO₄ electrolyte solution.

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likely due to the surface coverage of N-species, namely N* and NO*, on Pd monometallic sites as reported by De Vooy et al. [32]. This further illustrates that the electrode material is important in nitrate reduction, and changing the surface structure of the electrode material can significantly change the nitrate reduction process and products.

According to extensive research, the performance of bimetallic catalysts in reducing nitrate is highly dependent on the metal ratio [70–73]. By adjusting the amount of B on the Fe-based electrode, it was possible to increase the nitrate conversion of boron-iron nanochains to 80% and nitrogen selection to 99% in a mixed electrolyte system containing Cl⁻ and SO₄²⁻ ions [74]. Changing the mass ratio of Pd/Cu on TiO₂ nanofibers in the preparation of Pd-Cu/TiO₂ NFs catalysts could change the performance of the electrode, and the highest nitrate removal and N₂ selection rates of the catalyst were obtained at Pd: Cu = 1:1 (IS-1:1), 91.5% and 80.0%, respectively. This data was obtained at other mass ratios of IS-0.5:1 (84%, 73.2%), IS-2:1 (72.7%, 70.8%), and IS-4:1 (56.8%, 57.1%), respectively. At IS-0.25:1, the catalyst removed only 7% of nitrate, confirming the claim that the bimetallic catalyst metal

ratio significantly affects the nitrate reduction performance [75]. Due to the poor performance of Pd-Cu/SS in terms of nitrogen selectivity, they focused their efforts on multi-metal electrodes. By adjusting the ratio of Sn/Pd and changing the electrodeposition procedure, Su et al. [76] prepared electrodes with a batch of solutions containing SnCl₂ and PdCl₂ with a molar ratio of 4–1, which were close to 100% efficient at reducing nitrate and reached 81% efficient in nitrogen selectivity, which may be due to the reduced microcrystal size and increased surface roughness showed in Fig. 3. Thus, additional research is required to understand the effect of the electrode preparation method on the surface morphology of metal electrodes in order to control the reaction process and product selection rate by altering the structure and surface morphology.

3.1.3. Metal oxide electrodes

Mixed metal oxide electrode plays a crucial role in the electrocatalytic reduction of nitrates. By comparing the performance of Ti, Cu, Fe₂O₃/Ti and Co₃O₄/Ti cathodes in nitrate reduction. The result shows that the Cu cathode maintained a significantly higher electrocatalytic

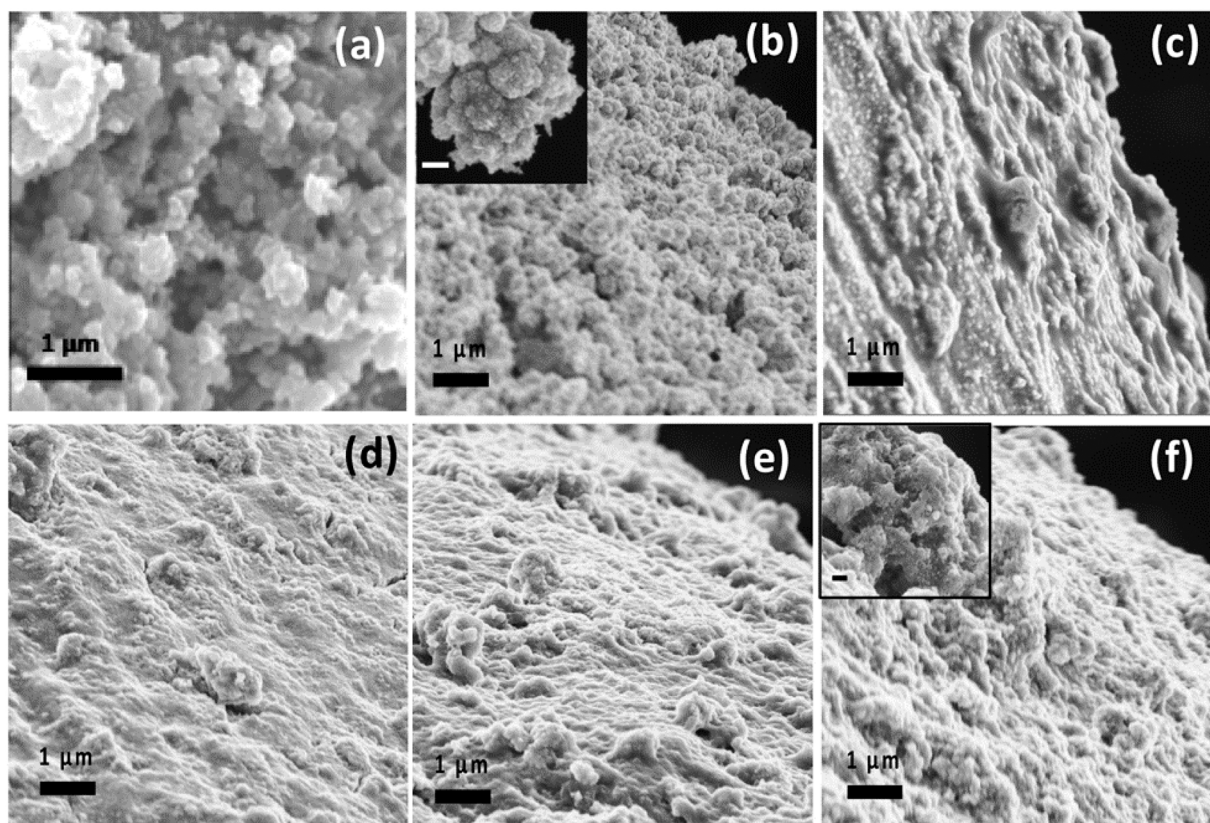


Fig. 3. Micrographs of HRSEM of SS/Sn_{0.8}Pd_{0.2} electrodes at various N values, where N is the overall number of Sn deposited segments + Pd deposited segments. (a) N = 1; (b) N = 2 (100 nm scale); (c) N = 3; (d) N = 4; (e) N = 5; (f) N = 14 (100 nm scale). Reproduced with permission from [76]. Copyright 2019 Elsevier.

performance than the Ti cathode but was significantly less efficient than the Fe₂O₃/Ti and Co₃O₄/Ti cathodes. After three hours of electrolysis, both Fe₂O₃/Ti and Co₃O₄/Ti achieved close to 100% nitrate removal efficiency, whereas Cu and Ti cathodes removed nitrate at only 68% and 18%, respectively [77]. Compared to its Co₃O₄ counterparts, ZnCo₂O₄ nanosheet array could obtain a faraday efficiency of 98.33% and provide nearly twice the NH₃ yield in alkaline media [78]. The oxygen chemical environment on the Cu₂O surface was regulated by Ar plasma treatment to promote the formation of oxygen vacancies and hydroxyl groups on the Cu₂O surface to facilitate the adsorption of nitrate and proton transfer on the Cu₂O surface, thereby increasing the nitrate reduction efficiency and ammonia selectivity [79].

Similarly, Yang et al. [80] prepared two metal oxide composite catalytic electrodes, Co₃O₄/Ti and CuO-Co₃O₄/Ti, by modifying Ti electrodes with Cu and Co, thereby increasing nitrate reduction efficiency of Ti electrodes from 55.9% to nearly 100%. CuO-Co₃O₄/Ti composite electrodes perform exceptionally well in terms of total nitrogen removal and nitrogen selectivity performance. This may be due to the unclosed d-orbital shells of CuO and the unoccupied π* orbital, which make it easier for nitrate to be adsorbed onto CuO and then reduced to nitrites, thereby speeding up the nitrate reduction process. While the nickel cathode exhibits superior nitrogen selectivity, but its nitrate reduction efficiency is unsatisfactory. After nickel foam was loaded with Fe⁰ and Fe₃O₄ nanoparticles, the catalytic and reduction performance of the nanoparticles, due to their ionic synergistic effect, substantially enhanced, increasing the nitrate electrocatalytic reduction efficiency to 90.19%, and the nitrogen selection rate reached 88.8% [81]. Compared with Ti/CuOx, Ti/Cu₅ZnOx electrode can provide more active sites for the degradation of intermediate N products, particularly in highly alkaline solutions; the presence of Zn increases the efficiency of nitrite reduction to N₂, and the preparation of Cu-Zn oxide composite

cathode compensates for the absence of Cu elements' ability to degrade nitrite and achieves reduction performance comparable to that of precious metals such as Pd [82].

The investigation of metal oxide electrodes reveals a low-cost method for electrocatalytic nitrate reduction. Polymetallic electrodes and metal oxide electrodes show higher reduction efficiency than monometallic electrodes in nitrate electrocatalytic reduction due to their more diverse physicochemical properties, higher specific surface area and high catalytic activity, and different reduction efficiencies and product selectivity can be obtained by adjusting the conditions of metal types, metal ratios and synthesis methods, but leaching of metal particles and electrode corrosion are still a difficult problem to solve.

3.1.4. Composite electrode

To address some of the shortcomings of metal electrodes, researchers are pursuing a new direction: composite nanocatalytic electrodes. Composite electrodes combine the benefits of multiple materials synthesized via chemical and physical methods from various substances, including metals, non-metals, and metal oxides. For example, inorganic materials such as graphene and phosphorus are loaded onto metals such as Cu and Ti to further increase the electrode's stability, specific surface area, and electrocatalytic reduction efficiency. Carbon-based Pt/Ru materials also exhibit excellent electrocatalytic reduction performance. As with metal catalysts, the performance of carbon-based composites is also highly dependent on the metal ratio, with a moderate Pt/Ru ratio being optimal for electrocatalytic reduction of nitrate [14]. Polypyrrole coated copper electrode (Ppy-Cu) is a copper electrode with a polypyrrole coating: the coating has no effect on the product type compared to a blank copper electrode, but has a larger effect on the product ratio. When Ppy-Cu is used as an electrocatalyst, in the low electrode potential region between 0.4 V and 0.8 V, Ppy adsorbs protons from the solution

and electrons are transferred to Ppy to produce atomic hydrogen, which promotes the conversion of nitrate to ammonia. The disappearance of nitrite and ammonia in the solution with Ppy-Cu as catalyst supports this idea, which improves the selectivity of ammonia in this system [83]. Carbon-based electrodes are among the most commonly used base electrodes for composite electrodes. DOW 3 N-Fe/Pd (Dow 3 N: DOWEX™ M4195, a kind of dowex ion-exchange resin) was a composite electrode composed of chelating resin loaded with Fe/Pd bimetallic nanoparticles, and the catalyst exhibited > 95% nitrate reduction efficiency and 69.2% nitrogen selectivity under neutral conditions [84]. The nitrate reduction activity and N₂ selectivity of the electrode were improved by loading Cu-modified Pt (100) nanoflowers on the carbon cloth surface using an electrochemical deposition process [85]. The bimetallic catalyst was loaded onto a grape seed activated with phosphoric acid. By adjusting the metal ratio, the 100 mg/L nitrate solution was reduced to levels below the European drinking water standard while maintaining a high N₂ selection rate [44].

In summary, current researchers have focused on the aspect of cathode materials for electrocatalytic reduction of nitrate systems, including non-metallic materials, metallic materials, metal oxide materials and composite materials. Non-metallic materials have remarkable points such as low cost, high mechanical strength and stability, but in electrocatalytic applications, their shortcomings such as insufficient activity and slow kinetic rate lead to their low catalytic efficiency. Without considering energy consumption and time, appropriate increase in current density and catalytic time can significantly improve the performance of non-metallic materials in electrocatalytic applications. Research on metal electrodes and metal oxide electrodes has matured. As mentioned earlier, researchers have directly improved the reduction efficiency of nitrate by changing the metal surface structure which increases the metal specific surface area and active sites. By changing the metal ratio of multi-metal electrodes, the treatment of nitrate wastewater can effectively regulate the product selection rate through the synergistic effect between two or more metals. Compared with non-metal and metal electrodes, metal oxide electrodes have stronger adsorption capacity for nitrate and stronger ion exchange capacity. In the process of nitrate electrocatalytic reduction, metal oxide electrodes will be reduced in situ to form active phase electrodes and the nitrate reduction efficiency is significantly improved, but the stability of metal oxide electrodes is generally poor, and the shedding of metal oxide nanoparticles and electrode corrosion still need to be addressed. Compared to metal and metal oxide electrodes, composite electrodes have improved performance in electrocatalytic reduction of nitrate under the same conditions and can effectively increase the selection rate of nitrogen by modifying the cathode material. However, the preparation method of composite electrodes is usually complicated and the preparation success rate is low, so the large-scale preparation and use of composite electrodes will still be a challenge.

3.2. Cell design

The electrolysis structure of cells, arrangement, and distance between the electrode sheets may all affect the nitrate electrocatalytic reduction process. The two most frequently used electrocatalytic reduction devices are single-chamber and dual-chamber cells. A single-chamber cell is a reaction cell in which the cathode and anode coexist in the same electrolyte environment, allowing rapid and unrestricted ion transfer. In a dual-chamber cell, the cathode and anode are typically separated by an ion-exchange membrane, resulting in two distinct reaction cells with restricted ion transfer depending on the membrane type. Cation exchange membranes are the most frequently used membrane type in electrocatalytic nitrate reduction. The dual-chamber cell removes more nitrate than the single-chamber cell. This is most likely because adding a cation exchange membrane to the dual-chamber cell significantly alters the process and outcome of electrocatalytic nitrate reduction [46]. The reaction mechanism is distinct between

single-chamber and dual-chamber cells, as shown in Fig. 4. The cation exchange membrane will prevent the nitrite generated at the cathode from contacting the anode, which prevents the nitrite from being oxidized to form new nitrate, leading to a decrease in nitrate removal efficiency, while ammonium ions will be transferred from the cathode chamber through the cation membrane to the anode chamber due to the concentration gradient, where they will be oxidized to produce nitrogen gas. Due to the absence of nitrite, only the oxidation of ammonia will occur at the anode, which will effectively improve the reduction efficiency and nitrogen selection rate of the reaction system [7,99]. Ding et al. [46] used a two-chamber electrolytic cell to reduce nitrate for 120 min, resulting in a pH of 3 at the anode and 10 at the cathode, suggesting that the cathode and anode form separate reduction and oxidation zones due to the presence of a cation exchange membrane.

However, there are limitations to the dual chamber electrolytic cell, as the above studies were carried out at a low initial nitrate concentration. For example, Ding et al. [46] used an initial nitrate concentration of 2 mM and Beltrame et al. [99] used an initial nitrate concentration of 135 mg/L. The reduction of nitrate was carried out by myself in a single-chamber electrode and an H-type dual-chamber cell with a cation exchange membrane at 1000 mg/L. The reduction efficiency of the dual-chamber cell was slightly higher than that of the single-chamber cell, but more electrical energy was consumed, which probably because using an ion-exchange membrane increases the ohmic resistance of the reaction system, increases energy consumption, and reduces the Faraday efficiency of the system. Li et al. [24] also conducted experiments with nitrate solutions of 100 mg/L and 1000 mg/L using a two-chamber electrode, and the reduction rate was reduced from 2.2 h⁻¹ to 0.9 h⁻¹, and the nitrate removal rate was only 88.3% at an initial concentration of 1000 mg/L, which is similar to my results. In addition, the pH of the solution will rise rapidly after energization and the service life of the cation exchange membrane will be affected by the strong alkaline environment. Therefore, when the nitrate concentration is below 200 mg/L, it may be better to use a dual chamber electrolytic cell. Using a dual-chamber cell under the same conditions can produce more nitrogen and reduce the ammonia produced by nitrate reduction. When the nitrate concentration is higher, factors such as ion exchange membrane, power consumption and reduction efficiency need to be taken into account to select a suitable electrolytic cell.

3.3. Initial nitrate concentration

The mechanism of nitrate reduction indicates that the process of nitrate reduction is highly dependent on the initial concentration of nitrate [2,100]. Nitrate removal efficiency is generally greater at lower initial nitrate concentrations (200 mg/L), whereas it is lower at higher initial nitrate concentrations (>200 mg/L) under the same conditions. Su et al. [77] investigated the change in the efficiency of electrocatalytic reduction of nitrate by Co₃O₄/Ti cathode at initial nitrate concentrations of 50–500 mg/L. With increasing concentrations of nitrate removal and ammonia production at the same current density and spotting time, the efficiency of nitrate removal and ammonia production decreased. The removal of nitrate and ammonia production increased, indicating that more electrical energy can be used for electrocatalytic reduction of nitrate. As shown in Table 2, the reduction of nitrate at concentrations of 100, 250, 500, and 1000 mg/L using a Fe cathode in a dual-chamber cell energized for 2.5 h at a current density of 15 mA/cm² resulted in nitrate removal rates of 99.4%, 98.3%, 97.8%, and 88.2%, respectively, which further demonstrates the feasibility of electrocatalytic reduction of nitrate even at high concentrations [24]. As the initial nitrate concentration increases, the cation exchange membrane becomes more likely to be blocked and corroded, which result in a concentration of nitrate ions in the cathode cell. Meanwhile, the high nitrate concentration means more by-products like nitrite and ammonia are produced, which leads to a decrease in the nitrate adsorption capacity of the cathode due to other ions, and thus a decrease in the nitrate removal efficiency is inevitable.

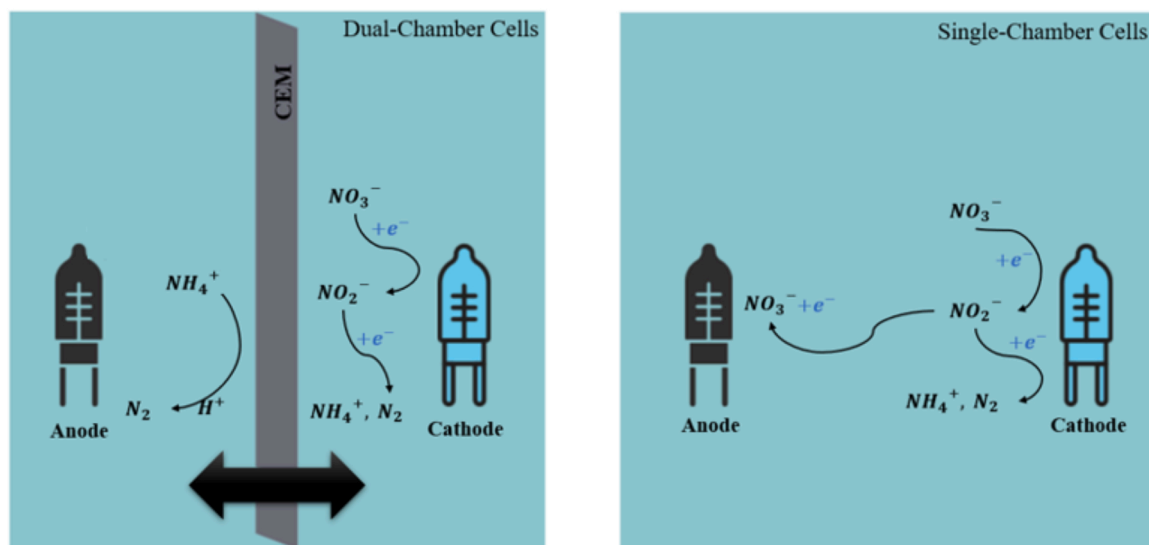


Fig. 4. The mechanism of nitrate reduction in SCC and DCC.

Table 2

Nitrate converted to nitrite and ammonia by Fe cathode in dual-chamber configuration, 15 mA/cm², 0.5 g/L Na₂SO₄.

Initial nitrate concentration (mg/L)	Nitrate concentration (mg/L)	Nitrite concentration (mg/L)	Ammonia concentration (mg/L)	TN concentration (mg/L)	Nitrate removal rate
100	0	0	16	16	99.4%
250	10	0	40	50	98.3%
500	20	0	100	120	97.8%
1000	120	0	200	320	88.2%

However, the absolute nitrate removal increases with the initial nitrate concentration increases, whether in a single-chamber or dual-chamber cell, when other conditions are held constant, indicating that more electrical energy is used to reduce nitrate. Due to the extensive electrochemical processes, the Faraday efficiency of nitrate electrocatalytic reduction system is consistently maintained at a considerable level regardless of the nitrate concentration [2].

3.4. Applied potential and current density

Applied potential and current density are important factors affecting the rate of electrochemical reduction. According to the reaction mechanism analysis, the nitrate removal efficiency tended to increase with increasing applied current, higher current density would hydrolyze to produce more H⁺, and increased hydrogen supply could promote nitrate reduction, however, the promotion effect was weakened when the current density was too high. Too high current density promotes the formation of N-H and inhibits the formation of N≡N, leading to an increase in NH₄⁺-N production and a decrease in the selection rate of nitrogen, which is consistent with the study of [101]. For example, By varying the applied potential, nitrate was selectively reduced to various products, indicating that the selectivity of electrocatalytic nitrate reduction is highly dependent on the current density and applied potential [37]. At low electrode potentials (−0.6 V vs Hg/HgO), electrons are indirectly mediated by Cu to convert NO₃⁻-N to NO₂⁻-N, and subsequently to N₂, with N₂ being the major product with a selection rate of 55.6%; while at higher electrode potentials (i.e., less than −0.6 V vs Hg/HgO), NO₃⁻ is over-reduced by the hydrogen group to produce NH₄⁺, and when the electrode potentials reaches −1.2 V vs Hg/HgO, NH₄⁺ becomes the major product with 89.1% production [89]. Li et al. [24] investigated the nitrate removal efficiency in a double-chamber cell separated by a cation exchange membrane at different current densities with different product selection rates. As the current density increased continuously

from 5 to 20 mA/cm², the nitrate removal efficiency continues to increase, but from 15 mA/cm² to 20 mA/cm², the removal efficiency increased slowly, and the best nitrogen selection rate was observed at a current density of 15 mA/cm². While increasing the current density improves nitrate removal efficiency, an excessive current density not only increases the electrocatalytic system's energy consumption and decreases Faraday efficiency but also accelerates electrode corrosion and dissolution [102]. In addition, the process of electrocatalytic reduction of nitrate generates a large amount of oxygen due to the hydrolysis reaction, generating a large amount of bubble, current density directly affects the amount of bubble produced, which in turn affects the electrode's ion exchange and mass transfer efficiency [103]. Therefore, the reaction rate and the reaction process can be regulated by appropriately adjusting the applied potential and current density.

In short, current density is one of the most critical factors affecting the nitrate reduction rate. From the physicochemical level, the higher the current density, the faster the nitrate reduction rate, the more nitrate is reduced per unit time, and the more ammonia is oxidized simultaneously by the anode, so increasing the current density, without considering other factors, can significantly improve the nitrate removal rate, total nitrogen removal rate and nitrogen selection rate of the NER (nitrate electrocatalytic reduction) system.

3.5. Initial pH

The pH of a solution has an effect on the form of metal ions, the reaction process, and the solubility of the products [104]. At different pH, the surface of the metal electrode is covered with different substances including hydrogen compounds in acidic conditions and hydroxide or oxide in basic conditions, depending on the reactive groups present in the solution [1]. As a result, changes in the pH of the solution may affect the nitrate removal efficiency. Beltrame et al. [99] reported in their study that the pH of the cathode cell was alkaline and the pH of

the anode cell was acidic in a dual-chamber cell with multiple cathode materials tested. Katsounaros [30] also mentioned that in a single-chamber cell, the pH on the surface of the cathode plate is alkaline, and the pH on the surface of the anode plate is acidic. This change is related to the reactions occurring at the electrodes, where OH^- is formed near the cathode and H^+ near the anode, which results in a gradual increase in the pH near the cathode as the electrolysis time increases. Therefore, the electrocatalytic reduction of nitrate takes place mainly under alkaline conditions. It has been demonstrated that altering the initial pH has little effect on the kinetics and efficiency of nitrate reduction [105–107]. Under acidic conditions, a high concentration of H^+ present in the solution facilitates the hydrogenation and nitrate reduction reactions [108]. The pathway of oxidation of ammonia differs in different solutions. In alkaline solutions, ammonia is adsorbed by the anode and oxidised to nitrogen mainly by direct electrolytic reaction. In neutral and acidic solutions, ammonium ions can be indirect oxidation by OH^- radical, rather than by direct electrode reactions, so the rate of decomposition is much lower than in alkaline solutions [109]. In addition, hypochlorite produced under alkaline conditions can aid in ammonia oxidation, while the instability of free chlorine under acidic conditions can also indirectly affect the rate of ammonia degradation [110]. The nitrate reduction on the surface of Cu single crystals in acidic and alkaline solutions was investigated using electrochemical methods and in-situ characterization techniques. The results indicated that Cu electrodes generate NO and ammonia preferentially in acidic media. In contrast, nitrate is more readily reduced to nitrite in alkaline media, which then converts to hydroxylamine, and the selectivity of intermediates varies according to the configuration of Cu single crystals [111]. The BDD, as a bipolar electrode, acts as a cathode to reduce nitrate while efficiently producing a large number of hydroxyl radicals,

which also accelerates the oxidation of nitrite and ammonia. The pH of the solution increases rapidly from initially neutral to 11–12, which due to the high production of OH^- [86].

However, other studies have found that under acidic conditions, the proton donor is a hydrated hydrogen ion, and the reduction rate of nitrate is expected to be proportional to the concentration of the hydrated hydrogen ion [112]. A high pH (>11) reduces the rate of N_2 selection via nitrate reduction, whereas a weakly acidic environment increases the rate of N_2 selection via nitrate reduction but reduces the efficiency of nitrate removal. Thus, while the effect of initial pH on nitrate reduction efficiency and mechanism remain unknown, adjusting the pH to increase the catalytic selection rate of N_2 is one possible method [99].

3.6. Co-existing ions

The nitrate wastewater usually contains not only nitrate ions but also sulfate, phosphate, chloride, halide, and various cations, so it is also necessary to examine the effect of different ions on nitrate reduction. Katsounaros et al. [113] studied the effect of cations and halide anions on nitrate reduction. In the presence of a cationic electrolyte, the voltammetric curve is shown in Fig. 5(a), where the reduction current increases significantly in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$, and Fig. 5(b) shows a steady-state electrolysis experiment performed at -1.8 V , confirming the increase in the reduction rate. When NH_4^+ and multivalent cations such as Ca^{2+} and La^{3+} are present, the reaction rate is higher than that of alkali metals. As shown in Fig. 5(c)(d), the decreasing order of the reduction rate of nitrate by halide ions is $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ due to the tendency of these anions to adsorb specifically on the electrode surface. The specifically adsorbed anions reduce the active surface area of the electrode, thus inhibiting nitrate reduction. Tong et al. [33] studied the

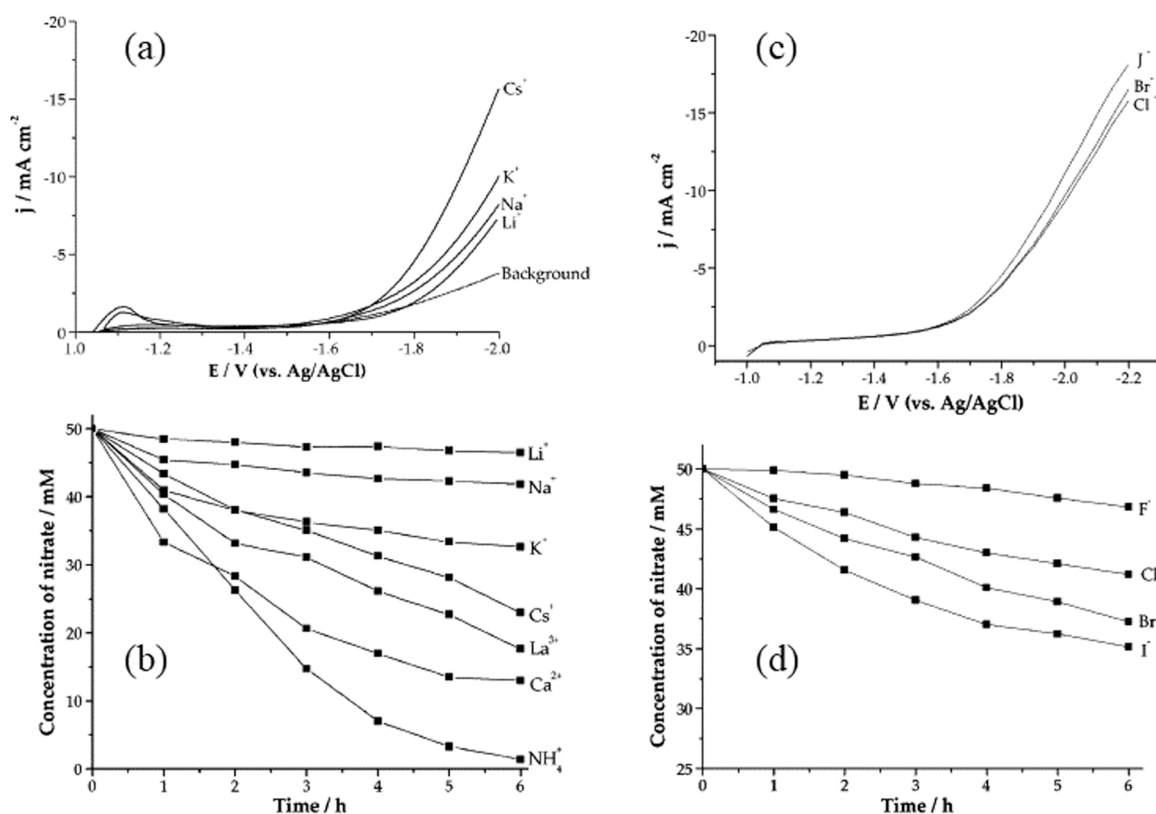


Fig. 5. (a) Voltammetric curves in $0.1\text{ M Cl}^- + 0.05\text{ M NO}_3^-$ at a scan rate of 5 mV/s , in which M: Li^+ , Na^+ , K^+ , or Cs^+ . (b) Concentration curves of nitrate in the existence of various cations at ionic strength of 0.15 M at -1.8 V versus Ag/AgCl . (c) Voltammetric curve obtained in a solution containing $0.1\text{ M CsX} + 0.05\text{ M CsNO}_3$ at a scan speed of 5 mV/s , in which X: Cl^- , Br^- or I^- . (d) Concentration curve of nitrate at -1.8 V versus Ag/AgCl in a solution containing $0.1\text{ M NaX} + 0.05\text{ M NaNO}_3$, in which X: Cl^- , Br^- , or I^- .

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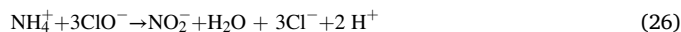
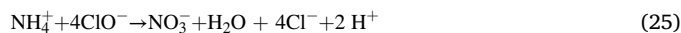
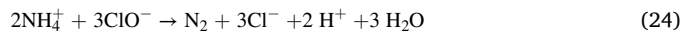
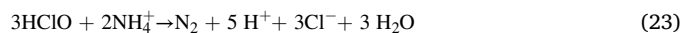
effect of different concentrations of PO_4^{3-} , SO_4^{2-} , Cl^- , ClO_4^- on electrocatalytic reduction of nitrate, the co-existing anions below 50 mg/L had less effect on the electrocatalytic reduction of nitrate, while the concentration of coexisting anions reached 200 mg/L, the reduction efficiency of nitrate decreased significantly in the order of $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{ClO}_4^-$. Compared to monovalent anions, higher valence anions have a stronger competitive adsorption capacity and inhibit the adsorption of nitrate by the cathode, which is similar to the conclusion obtained from the study of Huang et al [115]. Unlike other ions, chloride ions are commonly found in natural waters bodies, industrial wastewater, and domestic wastewater, and the effect of chloride ions on the reduction of nitrate is multifaceted. Therefore, the effect of chloride ions on the electrocatalytic reduction of nitrate is discussed comprehensively in Section 3.7.

Manzo-Robledo et al. [114] used real-time on-line differential electrochemical mass spectrometry combined with chronoamperometry in reduction of nitrate on boron-doped diamond (BDD) electrodes. By steady state voltammetry, they found that the presence of K^+ causes a moderate HER reaction in nitrate wastewater, which favors the reaction of nitrate and H_2 and promotes N_2 production. In contrast, HER kinetics are stronger in electrolytes containing Na^+ , which inhibits the production of N_2 .

In conclusion, the reduction process and reduction products of nitrate are affected by co-existing ions to different degrees, both promoting and inhibiting, and all co-existing ions in the electrolyte should be thoroughly considered when electrochemical reduction of nitrate moves from experimental to practical applications and faces actual wastewater with complex composition.

3.7. Chlorine

Breakpoint chlorination is a widely used drinking water treatment method, where NH_4^+ can be effectively oxidized by free chlorine [91]. In an electrolytic cell, chloride ions are oxidized on the anode to form Cl_2 , ClO^- , and HClO , which can react with NH_4^+ to form chloramine compounds. When there is sufficient free chlorine in the electrolytic cell, it oxidizes NH_4^+ to N_2 , NO_2^- , NO_3^- , etc. Almost all nitrate electrocatalytic reduction systems consider using chlorine ions to enhance total nitrogen removal and improve nitrogen selectivity. The mechanism of ammonia oxidation in the presence of chloride ions is shown in Fig. 6. The specific reaction equations are as follows (Eqs. (20)-(27)): [1,31,72].



The Cu/Ni-Foam electrode has excellent potential for large-scale application due to its near-100% removal of nitrate at 100 mg/L and near-100% nitrogen selection rate when energized for 90 min in the presence of 1 g/L Cl^- [91]. Ghazouani et al. [86] explored the effect on nitrate reduction in the presence of 500 mg/L and 1000 mg/L of chloride ions. The results showed that the addition of chloride ions significantly increased the selection rate of nitrogen and reduced the production rate of ammonia and nitrite, but some of the ammonia and nitrite were oxidised to nitrate, which reduced the reduction kinetics of nitrate. A similar situation was found by Pérez et al. in their study of the kinetic effects of chloride on nitrogen species [116]. In the electrocatalytic reduction of nitrate, the nitrate concentration remains constant as the chloride ion concentration increases, but the production of NH_4^+ gradually decreases. This is because chlorine radicals ($\text{Cl}\cdot$) are generated on the anode surface and then combine with chloride ions (Cl^-) to form chlorine. The active chlorine substance formed during chlorine hydrolysis will indirectly oxidize NH_4^+ . For the $\text{P}_{2,1}\text{-Co}_3\text{O}_4/\text{NF}$ electrode, the TN removal rate increases from 20% to 95% and the N_2 selection rate increases to nearly 100% in the presence of 2500 mg/L chloride ions [96]. The cyclic voltammetry analysis of cathode and anode materials in NaCl presence reveals that when ammonia is present, the hypochlorous acid in the solution is rapidly consumed in ammonia oxidation, accelerating the generation of chloride ions to hypochlorous acid. As a result, the presence of ammonia can compensate for the effect of NaCl on the rate of nitrate reduction. However, an excessive concentration of NaCl will still reduce the efficiency of nitrate removal because the competitive adsorption of excess chloride ions in the solution will inhibit nitrate adsorption, and the hypochlorite and hypochlorite generated at the anode will also cause some interference with the system's redox potential [10,117]. For solutions containing high concentrations of Na_2SO_4 , a slight increase in nitrate removal occurred as the

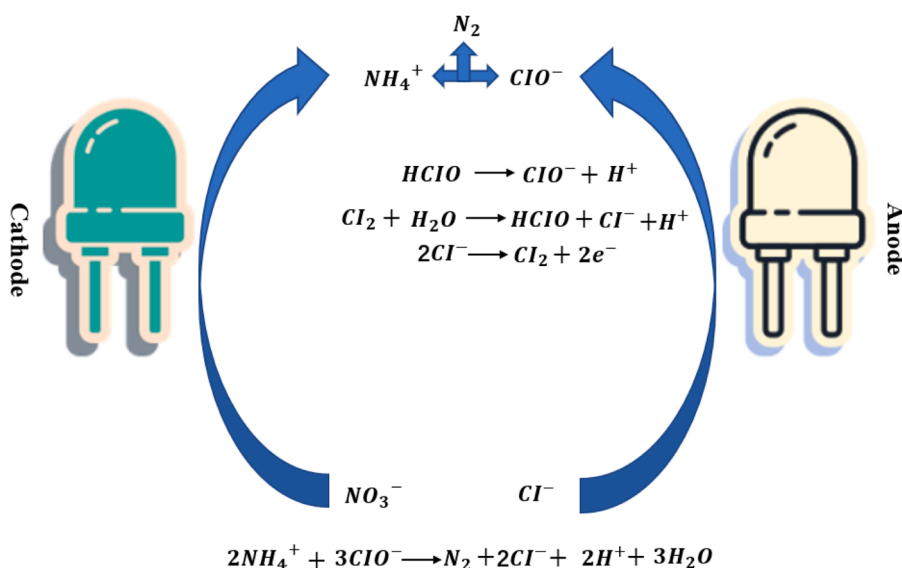


Fig. 6. Schematic diagram of the effect of chloride ions on N_2 selectivity.

concentration increased, whereas a decrease in nitrate removal occurred as the concentration increased of NaCl, and a similar trend was observed in other studies [115,118,119].

As mentioned in 3.6, the presence of Cl⁻ affects the reduction efficiency of nitrate, and some of the ammonia and nitrite is re-oxidized to nitrate, which reduces the reduction kinetics of nitrate. Chlorine ions and nitrate ions can form competing adsorptions, resulting in fewer active sites for nitrate reduction, which in turn affects the efficiency of nitrate reduction. However, the chlorine ion dosing is still an effective way to improve the nitrogen selectivity and total nitrogen removal in the NER system. Considering the pollution and toxicity of residual chlorine, we prefer to increase the current density and electrolysis time to improve the total nitrogen removal in the NER system.

3.8. Additives

Additives play a significant role in determining the efficiency of removing nitrate. With appropriate additives, the removal efficiency of nitrate can be increased, and the selection efficiency of ammonia and nitrogen can be precisely controlled to obtain specific target products. Using a microbubble hydrogenation-catalyzed nitrate reduction process, the time required to reduce the nitrate concentration to less than 25 mg/L was reduced from 240 to 120 min [120]. The addition of Pd-Cu/ γ -Al₂O₃ catalyst to the electrocatalytic system increased the nitrogen selection rate from 30% to more than 80% at a Pd loading of 5 wt%, while the nitrate conversion rate of the electrocatalytic system increased from 0.20 to 0.51 mg/L min to a level of 1.08 mg/L min. With the presence of HAs, Ni-Fe/Fe₃O₄ electrode doubles the efficiency of nitrate reduction and achieves a selectivity of 95.63% for nitrogen [121]. Additionally, different nitrogen and ammonia selection rates could be obtained by varying the Pd loadings while maintaining a high nitrate removal efficiency, providing a novel approach to the electrocatalytic reduction nitrate system's targeted product selection [122].

In contrast, NaIP₆ (sodium inositol phytate) acted as an inhibitor or protector in the reaction system. Not only did the Pt-Cu cathode perform well in the electrocatalytic reduction of nitrate and nitrite in the

presence of NaIP₆, but it also exhibited improved stability. After fifty operation cycles, the Pt-Cu electrode's cyclic voltammetric curves showed no significant decrease in current density. As illustrated in Fig. 7 (g), the presence of the NaIP₆ protective membrane prevented the Cu atoms on the electrode surface from being oxidized [123]. Fig. 7(a-c) shows the FE-SEM images of Pt-Cu electrode freshly fabricated Pt-Cu (a), after prolonged cycling in the presence of inhibitor NaIP₆ (b) and in the absence of inhibitor (c). After extended cycles (50 cycles) in the presence of inhibitors, the copper morphology did not change significantly compared to the freshly deposited morphology. The copper particles appeared uniform on the Pt substrate. In contrast, the surface of the electrode changed considerably in the absence of inhibitors. Randomly formed needle-like structures, probably copper (II) hydroxide, can be clearly seen on the surface. The appearance of such structures indicates that corrosion has occurred on the copper surface. The corresponding EDX spectra in Fig. 7(d,e) show a high percentage of copper (96.9 wt%) and a relatively low percentage of oxygen (1.9 wt%) in the presence of the inhibitor. This further confirms that less copper oxidation occurs. In the absence of inhibitor, the percentage of copper decreases from 96.9% to 91.9 wt% while oxygen increases from 1.9% to 5.2 wt%, which further confirms that less copper oxidation occurs in the material in the presence of inhibitor. Fig. 7(f) shows the XRD spectrum of the Pt-Cu electrode in the presence and absence of the inhibitor NaIP₆. There is no peak shift observed, indicating that the Cu crystals did not change after oxidation.

In general, the most critical factors affecting the nitrate electrocatalytic reduction efficiency are cathode material and current density. Since the solution pH increases with the reaction, the initial pH change has less effect on the nitrate reduction efficiency, while the applied potential, chloride ion concentration, electrolyzer type and other additives mainly affect the product selection rate of the system. For different concentrations of nitrate wastewater, a good nitrate removal efficiency can be obtained by adjusting the current density. For systems with higher ammonia production, the nitrogen selection rate can be improved by changing the applied potential and electrolyzer type at lower concentrations, while some additional chloride ions can be added to oxidize

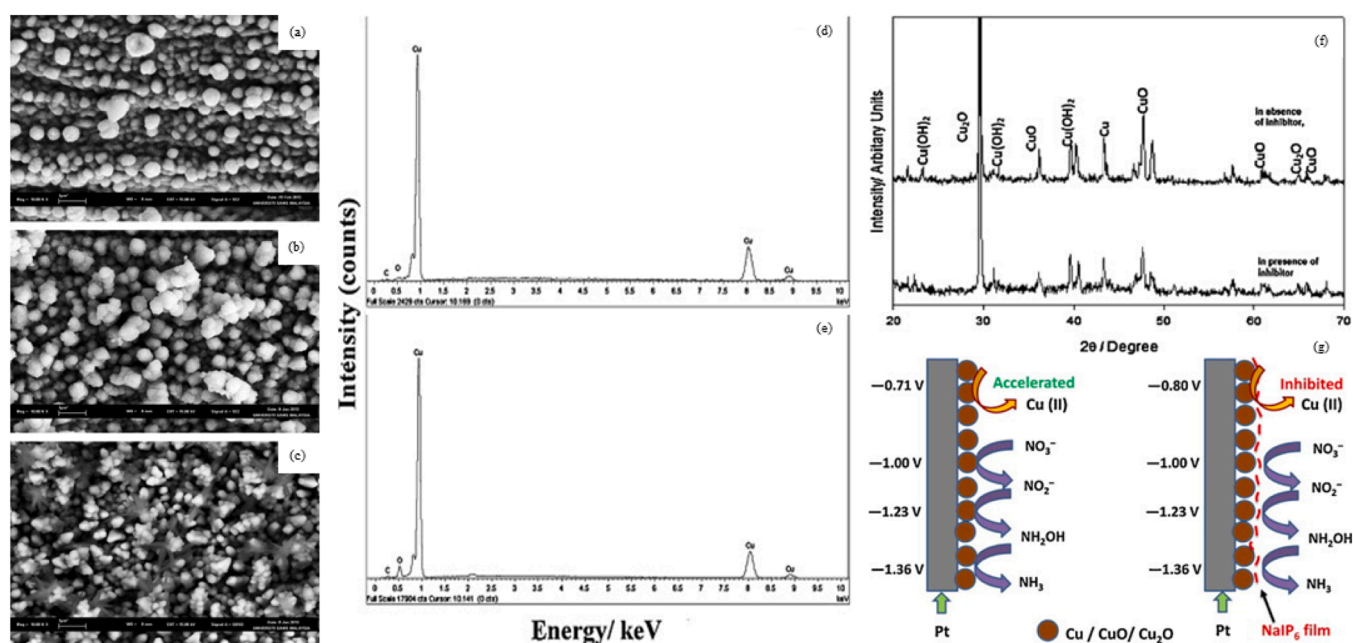


Fig. 7. FE-SEM images of Pt-Cu electrode samples in 0.01 M NaOH; freshly prepared (a), in the presence (b) and in the absence (c) of 0.01 M NaIP₆ after 50 cycles. (Note the presence of needle like structures in c). EDX spectra of Pt-Cu electrode surface in the presence (d) and absence (e) of 5 mM NaIP₆. (f) XRD pattern of Pt-Cu surface in presence and absence of inhibitor, 5 mM NaIP₆, prepared after cycling up to 50 cycles in 0.01 M NaOH. (g) Schematic diagram of the summary of nitrate (0.01 M) reduction reaction in the presence and absence of 5 mM NaIP₆ in 0.05 M NaOH.

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ammonia to obtain more nitrogen at higher concentrations. Considering the potential secondary contamination of chloride ions, the addition of oxidants without secondary contamination such as ozone and hydrogen peroxide might also be effective in reducing ammonia in solution. In addition, it is also feasible to reduce the total nitrogen content of the effluent by adding mature ammonia removal methods such as anaerobic ammonia oxidation, negative pressure evaporation, and blow-off ammonia removal after the electrocatalytic reduction system.

4. Continuous flow reactors

Although the electrocatalytic nitrate reduction in a continuous flow reactor has received little attention, it is critical to advance electrocatalytic nitrate reduction from the laboratory to practical application. By adjusting experimental conditions such as hydraulic residence time, influent pH, current density, and other variables, it is anticipated that high concentration nitrate wastewater will be treated continuously in a continuous flow reactor, resulting in a lower nitrate concentration or even a lower total nitrogen concentration in the effluent water. Abdallah et al. [124] used modified graphite felt Cu electrode for continuous flow electrocatalytic reduction of nitrate wastewater in a 1 L reaction chamber with a controlled flow rate of 2 mL/min, a feedwater nitrate concentration of 3 g/L, pH = 7.2, and a current ratio $R_i = 1.73\%$ nitrate removal and 96% NH_4^+ selectivity was obtained. This study provides a new idea for electrocatalytic reduction of nitrate continuous flow reactor, but there are still many shortcomings: (I) The preparation of modified graphite felt Cu electrode is very complicated, with the success rate of preparation is low, which is still difficult in practical application; (II) Although the effluent water contains a low concentration of nitrate, it contains a high concentration of ammonia and total nitrogen. While the ammonium solution may have some potential use, its toxicity is unknown, and converting nitrate to harmless N_2 is clearly a better direction; (III) Because the modified electrode was not subjected to a long-term pressure test, its stability remains unknown. The continuous flow reactor was also investigated by Rajic et al. [125]. Numerous cathode materials were evaluated for their nitrate reduction capability. At a residence time of 30 min, the palladized Fe cathode demonstrated the highest nitrate removal efficiency, but only 53.2%, while other cathode materials achieved only about 30% nitrate reduction efficiency under the same conditions, and the ammonia production rate was maintained at a high level. Fig. 8 shows the continuous flow reactor used by Makover et al. [87] to treat the Donnan dialysis waste stream, where Cu was used as the cathode and DSA as the anode. The optimal residence time was determined to be 90 min, closely related to the electrode's catalytic activity and soluble fraction.

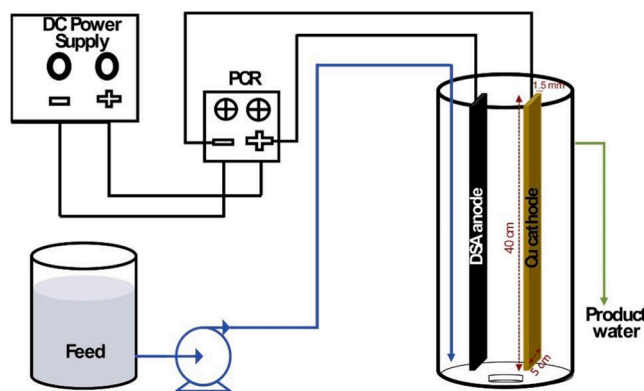


Fig. 8. Electrochemical continuous flow system. Reproduced with permission from [87]. Copyright 2020 Elsevier.

5. Stability of cathodes

Although nitrate removal efficiency is the best indicator of nitrate electrocatalytic reduction performance, electrocatalysis is a highly complex process; loss and corrosion of electrode sheets, changes in electrolyte composition, and changes in pH are all inevitable. Therefore, in order to apply electrocatalysis to actual nitrate industrial wastewater treatment, tests on the stability and durability of electrode sheets are critical to achieving effective nitrate removal.

The iron cathode was continuously energized at a high potential, and after 60 cycles of durability testing, no significant loss was observed on the electrode's surface, the structure remained intact, and the nitrate reduction efficiency remained unchanged, indicating that the Fe electrode is stable in an alkaline environment of pH 10–12 and meets the requirements for sustainable development [23]. It is possible that the change in pH affects the stability of the metal. The leaching of Cu ions was 0.53, 0.24 and 1.97 mg/L for 12 h of electrolysis at pH 1.8, 7.8, and 12, respectively. Meanwhile, the leaching of Zn ions was 1.41, 3.76, and 1.76 mg/L for 12 h of electrolysis at pH 1.8, 7.8, and 12, respectively. These indicate that under acidic conditions, the metal cathode suffered the least corrosion [126]. To maintain the activity of Cu-DSA and prevent cathode deactivation, Makover et al. [87] performed periodic current reversal of the cathode and anode by a reverse polarization timer to extend the service life of the cathode material. The frequency of periodic current reversal is once every half residence time, with an average loss of 1 mg of Cu per reversal. The new copper cathode weighs 280 g a piece and can be used more than 7000 times based on a maximum loss of 5% of cathode weight due to reverse polarization. The non-metallic GF (Graphite felt) electrode does not undergo oxidation during electrolysis and exhibits extremely stable and excellent electrochemical performance with high nitrate removal efficiency. In Tafel and EIS tests, the Ti electrode showed better chloride resistance than $\text{Cu}_{90}\text{Ni}_{10}$. In SEM micrographs, as shown in Fig. 9, the GF surface was very smooth, whereas the $\text{Cu}_{90}\text{Ni}_{10}$ surface produced some pits with a diameter of 5 μm [46].

Cu/Ni-foam electrodes remove over 95% of nitrate and maintain their performance after eight stress tests at the same level [91]. The BDD (Boron-doped diamond) electrode was energized at a constant high potential for 40 h with no noticeable changes to the electrode plate's surface, whereas the Cu electrode was pressure tested under the same conditions and demonstrated poor stability, with the electrode plate's surface gradually becoming rougher with increasing energizing time. Meanwhile, Raman spectroscopy revealed that the chemical composition and structure of the BDD electrode remained unchanged before and after electrolysis, whereas the Cu electrode's Raman spectrum revealed diffraction peaks of CuO and Cu_2O after electrolysis, indicating that the Cu surface was corroded and covered in copper oxide, whereas the BDD electrode retained its stability [42]. Under the same conditions, the stability of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ is significantly greater than that of Co_3O_4 , which is most likely due to the electrode-stabilizing effect of TiO_2 [95]. However, the cathode has not been subjected to prolonged stress, and its stability has not been established. After 1000 cycles of cyclic voltammetry, the peak current of NF-Cu/Pd remained constant, and the cathode's redox potential remained constant [127]. The nitrate reduction efficiency of Cu/Fe catalysts was improved by employing a special method of doping Fe and Cu into metasequoia-like nanocrystal, which demonstrated excellent stability after four consecutive tests [128]. Wang et al. [75] evaluated the stability and sustainability of Pd/Cu- TiO_2 NFs prepared in-situ (IS) and via impregnation (IM) methods. After four cycles of use, the electrodes prepared by in-situ retained an 81.7% nitrate removal efficiency, whereas the electrodes prepared via the impregnation method showed a greater performance decline, as well more Pd and Cu leaching. In addition, ICP and TEM-EDX characterization results indicated that the IS-1:1 Pd/Cu- TiO_2 NFs electrodes prepared by the in-situ exhibited no significant changes in their physicochemical properties, and the particle aggregation phenomenon

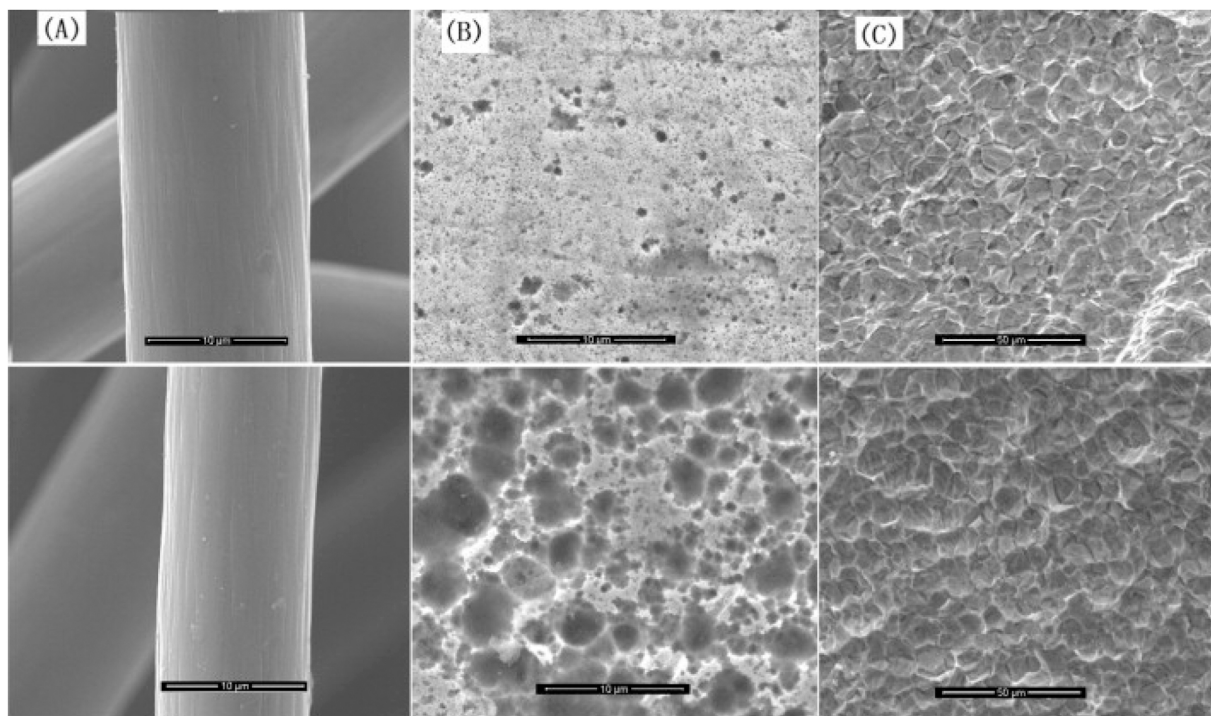


Fig. 9. The SEM images of the cathode of applied GF (A), Cu90Ni10 (B) and Ti (C) electrodes (the upper part of the picture is before use, the lower part of the picture is after 24 hours of electrolysis).

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of bimetallic NPs was much less than that in the IM-1:1 samples. This may be due to the partial embedding of bimetallic nanoparticles into the titanium dioxide nanoparticles during electrostatic spinning, providing excellent support and immobilization. Therefore, the preparation of composite catalysts using active nanoparticles as carriers is one of the feasible methods to increase electrode stability. Fe (20%) @N-C is a carbon-based composite electrocatalyst. As shown in Fig. 10 (a), after 20 cycles, Fe (20%) @N-C still maintained greater than 75% nitrate removal. Fig. 10 (b) indicates that the Fe nanoparticles remained tightly wrapped by the graphite shell after 20 cycles, and the Fe nanoparticles exhibited almost no leaching during the experiment. Fig. 10 (c) shows a comparative XRD plot before and after 20 cycles of Fe (20%) @N-C; as indicated by the shape of the fronts, the electrode chemistry did not change significantly, comparing the LSV curve of Fe (20%) @N-C cathode running from 0 to 1.4 V for 5000 cycles reveals only a slight change (Fig. 10 (d)), confirming that the Fe (20%) @N-C cathode has excellent stability [129]. This study demonstrates that it is possible to load active nanoparticles onto chemically stable carriers to create efficient and stable electrocatalytic materials (Table 3).

As illustrated in Fig. 11, the composite electrodes fabricated following in-situ electrochemical exfoliation and a one-step simultaneous graphene oxide reduction and Cu deposition, named Cu/rGO/GP, showed good stability during the CV cycle and eight cycles of electrolysis. It is possible that strong interactions exist between rGO and the copper NPs. This study shows that graphene-based composite electrodes have good stability performance in electrocatalytic nitrate reduction [130]. The FeNi/graphitized mesoporous carbon/Ni Foam (FeNi/g-mesoC/NF) is a unique and novel carbon-based alloy nanocatalytic electrode. After thirty days of continuous electrocatalytic testing, the nitrate catalytic efficiency of the composite cathode remained high. In the 24-hour electrolytic solution, the iron leaching was detected at less than 0.01 mg/L, indicating that this composite cathode has good stability [131].

Thus, non-metallic electrodes have higher stability than metallic electrodes, whereas the stability of composite electrodes is determined

by the combined properties of the base electrode and nanomaterials. Additionally, as previously stated, the presence of additives may improve the electrodes' stability and lifetime. The simpler the structure of the electrode material, the more stable it should be, but there may be fewer active sites on the electrode surface, resulting in a low electrocatalytic reduction efficiency of nitrate. As a result, a balance between stability and reduction efficiency must be found, or new stable and efficient composites must be developed for commercial application.

6. Current state of industrialized technology for treatment of nitrate

Electrocatalytic reduction for nitrogen removal is currently not widely used in industrial applications. In industrial applications for nitrogen reduction or elimination, the primary categories are separation-based nitrate reduction technology and elimination-based nitrate removal technology [132]. Among separation-based nitrate reduction technologies, reverse osmosis is one of the most widely used treatment technologies in industrial applications. It is a process in which the wastewater is pressurized and forced to pass through a semi-permeable membrane, allowing the wastewater to penetrate and thereby allowing the contaminants to be blocked by the membrane. Nitrates can be removed by Reverse osmosis at a range of pressures from 2000 to 10,000 kPa. While Reverse osmosis can be applied to treat wastewater containing high nitrate concentrations with nitrate removal rates of 59–95%, reverse osmosis is not a selective approach to nitrate removal [133]. In elimination-based nitrate removal technology, biological methods (such as activated sludge method) are known to be effective in removing nitrate from wastewater. In conventional nitrate removal processes, the wastewater is treated by nitrification and denitrification. However, when there is not enough organic carbon source in the wastewater for denitrification, this could negatively affect the denitrification efficiency [134]. Biological denitrification can selectively reduce nitrate to harmless nitrogen without the need for treatment streams and remineralization stages and the biological approach can

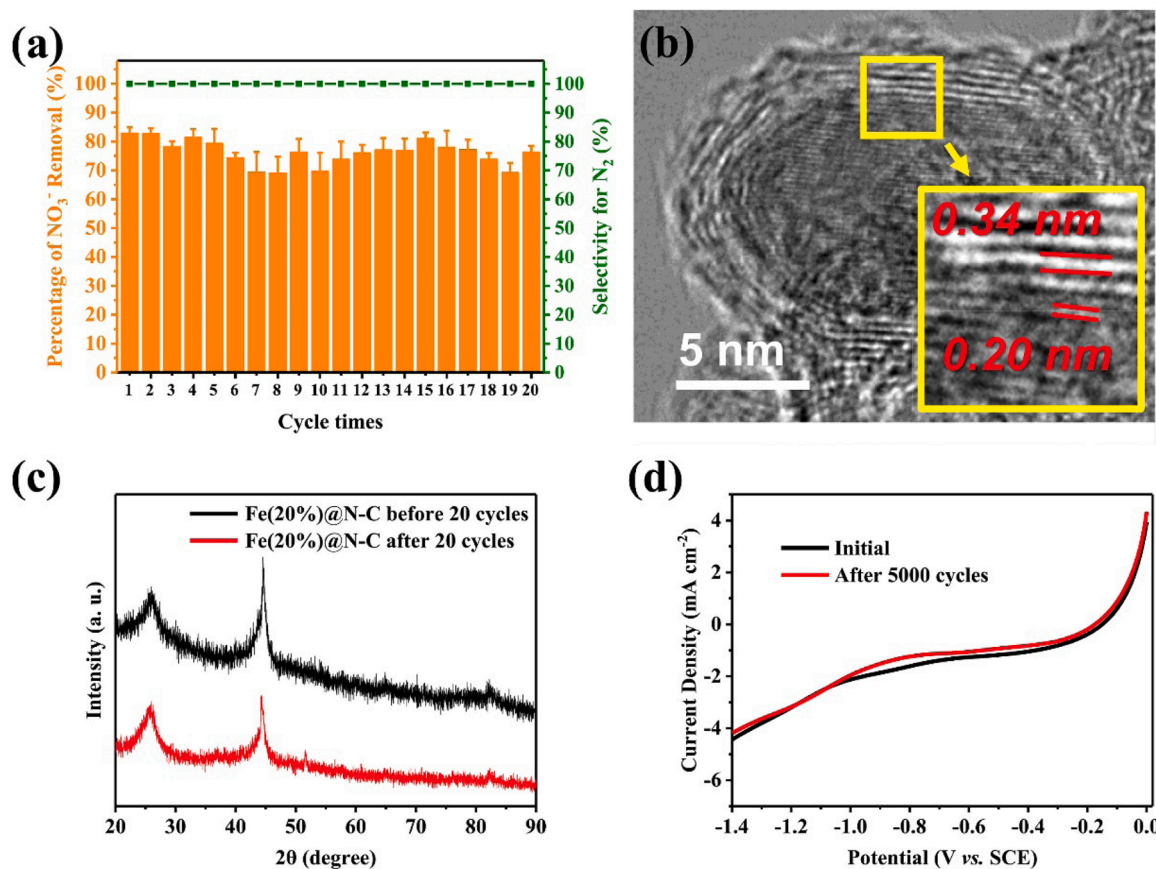


Fig. 10. (a) Nitrate removal recorded over 20 cycles using Fe(20%)@N-C cathode (reaction conditions of 50 mg /L NO₃-N, 24 h of operation per cycle, plus a potential of -1.3 V). (b) The HRTEM of Fe(20%)@N-C after 20 cycles of electrolysis tests. (c) The XRD pattern of Fe(20%)@N-C before and after 20 cycles of electrolysis tests. (d) LSV profiles of Fe(20%)@N-C cathode before and after 5000 cycles (from 0 to -1.4 V in N₂-saturated 50 mg/L NO₃-N solution with a scan rate of 100 mV/s).

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utilize little biomass to create waste sludge under anaerobic conditions [135]. Nevertheless, the biological treatment technology also has some disadvantages: (1) The potential contamination of treated water by microorganisms and their metabolic by-products used for biological denitrification; (2) The long hydraulic retention time (HRT) of the biological denitrification process [133].

Economic issues are important influencing factors in the industrial use of nitrogen removal. Alguacil-Duarte et al. [136] analyzed the cost of reverse osmosis technology compared to biological denitrification by treating 1 m³ of wastewater. The results showed that although the biological treatment method required more human resource costs, overall the total cost of the biological treatment method was 30% lower than that of reverse osmosis. The cost of treating 1 m³ of wastewater with the reverse osmosis method is €1.1619, while with the biological method is €0.8116. Although many industrial methods have been applied for nitrogen removal, new technologies that are more eco-friendly and economical are still needed to develop the wastewater treatment industry.

7. Outlook

Although researchers have conducted extensive research on materials and influencing factors of nitrate electrocatalytic reduction, some issues remain unresolved. The following are some of the current issues in the study and the research outlook.

- (1) Until now, research on the nitrate mechanism has concentrated on the surface of metal catalysts, with little work on the reaction

in the liquid phase. Due to the formation of numerous unstable intermediates during the nitrate reduction process, the conversion mechanism and influencing factors are also unknown. Advanced in-situ and characterization techniques can be applied to the reaction system in order to design the optimal system for electrocatalytic nitrate reduction [29], which is crucial for the development of electrocatalytic nitrate reduction technology.

- (2) Although the research on cathode materials has been quite abundant, the advantages and disadvantages of different cathode materials are also very obvious, and researchers still need to invest in the development of cathode materials. In the latest research, a core-shell copper oxides-cobalt oxides heterostructure nanowire arrays [78], a novel Ni foam [137] and a self-supported porous copper oxide nanosheet arrays [138] have been developed for continuous electrocatalytic reduction of nitrates, all of which have efficient performance, high stability and low cost, which is the direction of cathode material development.
- (3) According to recent research, the end product of electrocatalytic nitrate reduction is more ammonia, and researchers prefer to focus on the conversion of nitrate to ammonia in order to pursue subsequent utilization [139–141]. Nitrogen selection was generally low and received little research. Researchers frequently use chloride ions (mostly NaCl) to oxidize ammonia, converting the over-reduced N to harmless nitrogen. However, the widespread use of NaCl increases salinity and residual chlorine in water bodies, which poses a potential threat to human and biological health. As a result, other oxidants such as hydrogen peroxide or ozone can be used to oxidize ammonia. In addition, it

Table 3
Summary of stability of various cathodes.

Cathode	Electrolytes	Test method and conditions	Parameter	Stability	Evaluation	Ref.
Fe	41.61 mmol/LNO ₃ 26.72 mmol/LNH ₄ ⁺ 12 mmol/L Cl ⁻	60times durability test	High applied potentials	Good stability	Little change in surface and structure	[23]
Cu	1.5 mM NO ₃ Low, moderate, and high salinity	Reverse polarization and PCR	Residence time: 90 min Current density: 10 mA/cm ²	Support 7000times of use	1 mg average loss per PCR applied	[87]
GF Cu ₉₀ Ni ₁₀ Ti	0–10 mM NO ₃ 10 mM Cl ⁻	Tafel plot, EIS and SEM	DCC reactor 140 mL	Best Normal Better	GF is more stable than metallic cathodes	[46]
Cu/Ni-foam	100 mg/L NO ₃ 0.05 mol/L Na ₂ SO ₄	8times durability test	Current density: 25 mA/cm ² Electrolysis time: 90 min	Good stability	Maintain a high removal efficiency of > 95.0%	[91]
Cu BDD	50 mg/L NO ₃	40 h durability test	High applied potentials	Poor Good	Surface change into rough No significant variation	[42]
Co ₃ O ₄ Co ₃ O ₄ -TiO ₂ /Ti	50 mg/L NO ₃ 0.1 M Na ₂ SO ₄	Dissolution test	Current density: 10 mA/cm ² pH ₀ = 7.0 Electrolysis time: 120 min	Poor Good	Dissolved Co: 0.2 mg/L Detected	[95]
Pd/Cu-TiO ₂ IS = 1: 1	30 mg/L NO ₃	Four repeated cycles	pH ₀ = 3.2 Electrolysis time: 180 min	Good	Maintain a high nitrate removal: 81.7% Dissolved Pd: 0.03% Dissolved Cu: 2.90%	[75]
Pd/Cu-TiO ₂ IM = 1: 1				Poor	Low NO ₃ removal: 34.7% Dissolved Pd: 0.10% Dissolved Cu: 5.56%	
3D Pd-Cu (OH) ₂ /CF (Copper Foam)	50 mg/L N NO ₃	Four repeated cycles	Electrolysis time: 60 min potential -1.2 V vs Ag/AgCl	Good	Maintain a high nitrate and TN removal: 98.7% and 92.8%	[98]
Fe/Cu (Cu foam based)	100 mg/L NO ₃	8 repeated cycles	pH ₀ = 6 Current density: 25 mA/cm ² Electrolysis time : 180 min	Good	Maintain a high nitrate and TN removal: over 90% leaching iron: less than 0.89 mg/L	[66]
Fe(20%)@NeC	50 mg/L NO ₃ 1 g/L Cl ⁻	20 cycles use	Each cycle lasted 24 h	Good	Maintain a good nitrate removal: over 75% No iron leaching	[129]
Cu/rGO/GP	0.01 M NO ₃ and 0.02 M NaSO ₄	50 cycles scan and eight electrolysis cycle	Each cycle lasted 3 h	Good	Maintain a good nitrate removal of 92.4%	[130]
FeNi/g-meso/ NF	50 mg/L NO ₃ 0.05 mol/L Na ₂ SO ₄ , 0.02 mol/L NaCl	1 month recycling test	- 1.3 V (vs. SCE) of applied potential Uninterrupted	Good	Keep stable and low iron leaching	[131]

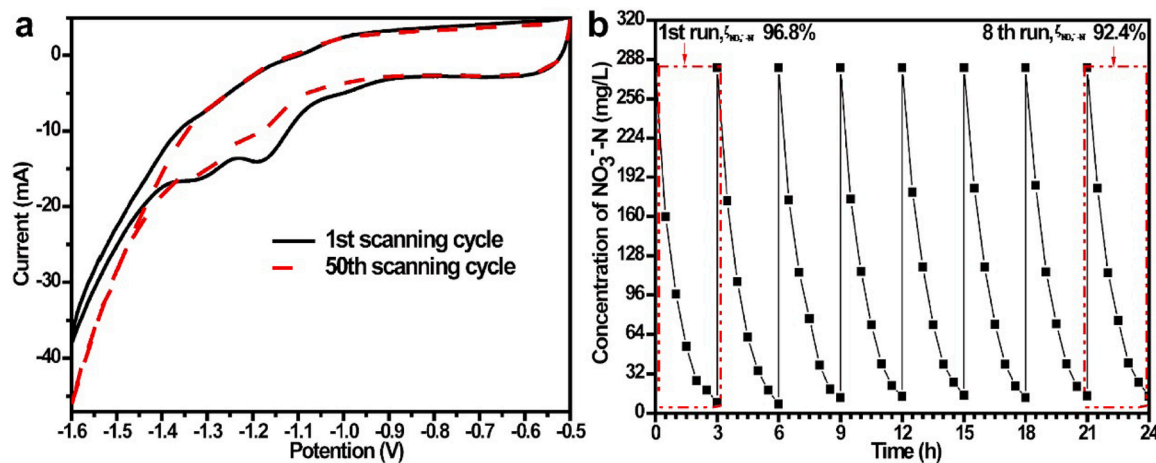


Fig. 11. Experimental stability of manufactured composite electrodes: (a) Cyclic voltammogram of the Cu/rGO/GP electrode in 0.02 M NaNO₃ and 0.5 M NaOH at a scan rate of 20 mV/s between -0.5 and -1.6 V. (b) Massive electrolysis of the Cu/rGO/GP electrode in the absence of 0.01 M NaNO₃ and 0.02 M NaSO₄ for eight cycles at -1.4 V and 3 h of electrolysis time.

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is also feasible to reduce the total nitrogen content of the effluent by adding mature ammonia removal methods such as anaerobic ammonia oxidation, negative pressure evaporation, and blow-off ammonia removal after the electrocatalytic reduction system.

- (4) While additives (such as catalysts, protectants, and oxidants) may improve the electrocatalytic reduction system's N_2 selectivity, catalytic efficiency, and electrode stability, they frequently combine other electrocatalytic reactions into the electrochemical reduction of nitrate, which not only complicates the system's components but also increases the cost of subsequent water body treatment. Additionally, studies have shown that additive by-products can affect the nitrate electrocatalytic reduction reaction process, reducing current efficiency and increasing energy consumption, and the use of additives is still debatable.
- (5) To our best knowledge, there are no well-documented articles on a unified approach to the setup of electrolytic cells, including single-chamber cells and dual-chamber cells (typically separated by a cation membrane between the cathode and anode chambers), and the number and arrangement of electrode plates are also quite different, whether foam electrodes or plate electrodes will be used in continuous flow reactors to achieve a better flow pattern is a matter that needs to be further studied.
- (6) Regarding commercial applications, research on the stability of electrodes is critical, and current research on the stability of electrodes is still relatively scarce. Most researchers will concentrate on the innovation and efficiency of electrodes while overlooking their stability. The electrodes' stability is typically determined after a few minutes or hours [142,143], which is insufficient. In general, the simpler the components of electrode materials are, the more stable they are, and the relative processing efficiency may be slightly affected; however, choosing or locating an electrode with high efficiency and good stability is a concern.
- (7) Before treating actual nitrate wastewater, complex components such as ionic species, organic pollutants, and solid sediments should be fully considered, and pretreatment may be necessary in some cases. Continuous flow reactor research is the first step from the laboratory to practical application, but few researchers are studying continuous flow reactors, and continuous flow reactor research should be strengthened. Additionally, because the treated effluent of electrocatalytic nitrate reduction is predominantly alkaline, extracting valuable by-products such as NaOH from the effluent is a worthwhile direction to investigate in terms of economic rationality. Electrochemical reduction of nitrate wastewater has a wide range of potential applications in the future for reestablishing the N-cycle.

8. Conclusion

In summary, this article discusses the electrocatalytic reduction of nitrate research that has been conducted over the last two decades, with a particular emphasis on the last five years. Electrochemical technology is distinguished by its low operating temperatures, lack of secondary pollution, and high treatment efficiency in comparison to electrocoagulation, electrodialysis, adsorption, catalytic hydrogenation, chemical reduction, biological denitrification and environmental friendliness. Based on previous research, this article begins with a brief overview of the world's current nitrogen environment and nitrate treatment methods, followed by an in-depth analysis of the mechanism of the electrocatalytic reduction of nitrate. Unlike previous review articles, this review considers more comprehensive factors affecting electrocatalytic nitrate reduction, including cathode material, cell design, initial nitrate concentration, current density, initial pH, co-existing ions, chloride ion concentration and additives. Then the current studies on nitrate electrocatalytic reduction continuous flow reactors has been discussed. The stability and durability of the electrode

will be critical factors to consider, and thus the electrode's stability has been reviewed to provide some references for future researchers. Finally, the current state of industrialized technology for treatment of nitrate and the possibility of applying electro catalytic nitrate reduction to actual wastewater treatment has been considered. Despite significant progress in electrocatalysis for nitrate reduction over the last few years, it remains extremely difficult to transition the entire system from the laboratory to practical application. It is believed that the high level of interest in electrocatalysis will accelerate its development, and the transition from the microscopic to the macroscopic world will occur naturally with time.

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.

Data Availability

No data was used for the research described in the article.

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