元素掺杂材料在电催化反硝化中的研究进展

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摘要:电催化反硝化是处理硝酸盐废水技术之一。本文综述了电催化反硝化的最新研究进展,分析了电催化反硝化直接电子转移和原子氢(H^*)介导间接还原两种反应机理,总结了电催化反硝化的决速步是将NO_3^-还原为NO_2^-以及决定产物选择性的关键中间体是NO。在此基础上,总结了元素掺杂方法及其对电极材料催化活性中心和电催化反硝化反应路径的调控效应,提出了元素掺杂是提高电极材料催化活性、产物选择性和长期稳定性的有效手段。此外,还讨论了其他因素如水质特征、运行参数等对电催化反硝化效果的影响,明确了水中共存卤素离子如Cl^-和Br^-等可显著提高N_2选择性以及大多数电极材料在中性条件下还原效果最佳。面向日益增长的硝酸盐废水处理需求,指出了电能消耗高和实际废水水质成分复杂导致副反应多是限制电催化反硝化大规模应用的关键瓶颈。由此,展望了电催化反硝化技术研究未来需要针对多种实际废水的理化性质开展长期中试试验,除了提高还原速率和产物选择性外,还要重点关注电能消耗并对处理尾水的安全性进行监测,以促进电催化反硝化技术的进一步发展和实际应用。

关键词:电催化反硝化;硝酸盐废水;元素掺杂;选择性还原;电能消耗

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Progress in electrocatalytic denitrification using element-doped materials

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Abstract: Electrocatalytic denitrification is one of the promising technologies for the treatment of nitrate wastewater. This review comprehensively summarizes the recent advances in electrocatalytic denitrification. Two reaction mechanisms of direct electron transfer and atomic hydrogen (H^*)-mediated indirect reduction in electrocatalytic denitrification are analyzed. It is concluded that the rate-limiting step of electrocatalytic denitrification is the reduction of NO_3^- to NO_2^- and the key intermediate determining product selectivity is NO. On this basis, the element-doping method and its regulation effects on the catalytic active centers and the electrocatalytic denitrification pathways are summarized, and it is suggested that element doping is an effective method to improve the catalytic activity, product selectivity and long-term stability of electrode materials. In addition, the influence of other factors such as water quality characteristics and operating parameters on the electrocatalytic denitrification performance is discussed. It is confirmed that the coexistence of halogen ions in water, such as Cl^- and Br^-, can significantly improve the N_2 selectivity, and most electrode materials exhibit- the best performance under neutral conditions. Facing the increasing demand of nitrate wastewater treatment, it is pointed out that

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the key bottlenecks limiting the large-scale application of electrocatalytic denitrification are the high electric energy consumption and the complex composition of the actual wastewater which leads to side reactions. Therefore, it is expected that the future research of electrocatalytic denitrification technology needs to conduct long-term pilot-scale tests based on the physicochemical properties of various actual wastewater. In addition to improving the reduction rate and product selectivity, it is also necessary to pay attention to the electric energy consumption and monitor the safety of treated water to facilitate the further development and practical application of electrocatalytic denitrification technology.

Keywords: Electrocatalytic denitrification; Nitrate wastewater; Element doping; Selective reduction; Electric energy consumption

0 引言

硝酸盐在水中溶解度高，且硝酸根（NO_3^-）中氮处于最高价态，在氧环境中稳定性良好，是水体中普遍存在的污染物[1]。人体摄入过量 NO_3^- 会导致高铁血红蛋白症（蓝色婴儿综合症）[2]。世界卫生组织规定饮用水中硝酸盐氮（NO_3^--N）最大浓度为 10 mg · L^{-1}。近年来，化肥大量使用与硝酸盐工业废水排放等造成了多地地表水与地下水硝酸盐含量严重超标。我国 9.6%的河流中 NO_3^--N 浓度高于 10 mg · L^{-1}[3]。长春地区地下水自 2008 至 2022 年一直存在严重的硝酸盐污染[4]。

氮气（N_2）是氮元素的无害存在形式。将 NO_3^- 通过反硝化作用转化为 N_2 是处理硝酸盐废水的典型思路。生物反硝化法耗时长且处理条件难以控制[5-6]，化学混凝法需要投加大量药剂且会产生污泥，需要进行二次处理，严重限制了其实际应用[7]。电催化反硝化反应速率高，无需投加化学药剂，是一种极具前景的硝酸盐废水处理方法[8]。

氮元素存在低至-3，高至+5 的多种氧化态，因此电催化反硝化过程中可能会产生不同价态的多种还原产物，如 NO_2^-、N_2O、N_2、NH_3 等[9]。此外，在高电位条件下，电催化反硝化过程常伴随显著的析氢反应（HER），使得法拉第效率降低。电催化反硝化反应的速率与选择性很大程度上取决于阴极材料性能以及废水特征如 pH、NO_3^- 浓度等[10-15]。因此，选择合适的电极材料和反应条件，对电催化反硝化反应至关重要。

1 电催化反硝化反应机理

电催化反硝化产物复杂多样，N_2 是对环境最友好的产物。电催化反硝化通过 $5e^-$ 转移生成 N_2，实现硝酸盐废水无害化处理（式 1），其标准电极电位 $E^\theta = 1.17$ V（vs. RHE）。研究电催化反硝化机理，能够指导电极材料以及电位、pH 等条件的选择，为选择性生成理想产物 N_2 提供理论依据，对开发高效率、高选择性电极材料具有关键意义。

$$2NO_3^- + 10e^- + 12H^+ \longrightarrow N_2 + 6H_2O \qquad (1)$$

研究者通过多种表征方式研究了电催化反硝化的不同反应路径，发现其主要涉及两种机理（图 1）。一种是在阴极直接进行电子转移实现 NO_3^- 直接还原，另一种是通过裂解水分子产生的活性氢（H^*）进行间接还原[16]。由于叔丁醇可以清除反应体系中的 H^*，通过叔丁醇淬灭反应可以计算间接还原对电催化反硝化的贡献率[17]。

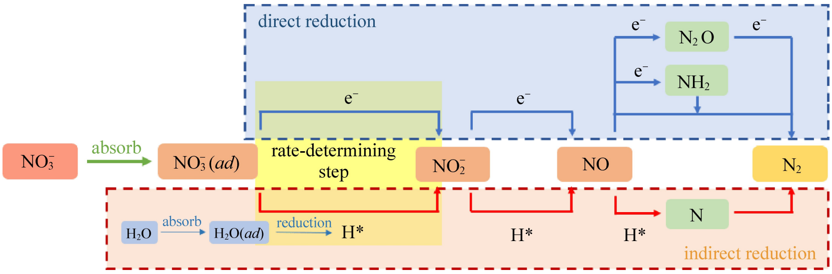


图 1 电催化反硝化机理

Fig. 1 Mechanism of electrocatalytic denitrification

阴极电子转移直接还原机理包含多步质子化过程。首先，NO_3^- 被电极吸附为 NO_3^-（ad）（式 2）[17-18]。LIU 等[18]通过计算得到 Pd-Au(311) 对 NO_3^- 的吸附能（-0.17 eV）显著低于 Au(311) 对

NO_3^-的吸附能(0.16 eV),因此通过构建特殊结构合金强化 NO_3^-吸附。在此过程中,H_2O 分子同样容易被吸附从而占据催化活性中心(式 3),并伴随 HER 副反应(式 4)[20-21],降低反应的法拉第效率[22]。接着,NO_3^-(ad)在电极界面上得电子,同时从 H_2O 中攫取质子,还原生成 NO_2^-(ad)(式 5)[23]。在中性或碱性条件下,由于 NO_3^-中存在大π键结构并位于 NO_3^-正电中心 N 外围,e^-难以接近 N 中心,导致还原反应动力学缓慢。此外,从分子轨道角度来看,NO_3^-的 LUMOπ^* 轨道能量高,十分不利于 e^-进攻和 NO_3^-还原[24],因此该步骤是整个电催化反硝化反应的决速步。当 NO_3^-还原为 NO_2^-后,NO_2^-(ad)继续在电极界面上还原生成 NO(ad)(式 6)[13,15,25],该步骤生成的 NO(ad)可以在进一步的电还原反应过程中,通过两条不同的反应路径生成 N_2。一是经历 HN_2O_2中间体,还原产生 N_2O(式 7~8),N_2O 被进一步还原最终生成 N_2(式 9)[26],二是经历形成 NH_2(ad)中间体,与 NO(ad)结合产生 NH_2NO,脱去 H_2O 生成 N_2(式 10~12)[27]。

$$NO_3^-(aq) \rightleftharpoons NO_3^-(ad) \tag{2}$$

$$H_2O(aq) \rightleftharpoons H_2O(ad) \tag{3}$$

$$2H_2O(ad)+2e^- \longrightarrow H_2+2OH^- \tag{4}$$

$$NO_3^-(ad)+2e^-+2H_2O \longrightarrow NO_2^-(ad)+2OH^- \tag{5}$$

$$NO_2^-(ad)+e^-+H_2O \longrightarrow NO(ad)+2OH^- \tag{6}$$

$$2NO(ad)+e^-+H_2O \longrightarrow HN_2O_2(ad)+OH^- \tag{7}$$

$$N_2O_2^-(ad)+e^-+H_2O \longrightarrow N_2O(ad)+2OH^- \tag{8}$$

$$N_2O(ad)+2e^-+H_2O \longrightarrow N_2+2OH^- \tag{9}$$

$$NO(ad)+4e^-+3H_2O \longrightarrow NH_2(ad)+4OH^- \tag{10}$$

$$NH_2(ad)+NO(ad) \longrightarrow NH_2NO(ad) \tag{11}$$

$$NH_2NO(ad) \longrightarrow N_2+H_2O \tag{12}$$

H^*介导的间接还原以 H^*为还原剂实现间接电子转移。该机理的关键中间体 H^*由吸附在电极界面上的 H_2O 裂解产生(式 13),接着通过连续的脱氧反应产生 NO_2^-(ad)、NO(ad)等中间体(式 14~16),最终生成 N(ad)并偶联生成 N_2(式 17)[28-30]。

$$H_2O(ad)+e^- \longrightarrow H(ad)+OH^- \tag{13}$$

$$NO_3^-(ad)+2H(ad) \longrightarrow NO_2^-(ad)+H_2O \tag{14}$$

$$NO_2^-(ad)+H(ad) \longrightarrow NO(ad)+OH^- \tag{15}$$

$$NO(ad)+2H(ad) \longrightarrow N(ad)+H_2O \tag{16}$$

$$2N(ad) \longrightarrow N_2 \tag{17}$$

阴极还原往往会生成 NH_4^+(式 18),但是在 Cl^-存在的条件下能耦合阳极氧化产生 HClO(式 19~20),继而氧化 NH_4^+产生 N_2(式 21),提高 N_2选择性。由于反应关键中间体 NO_2^-也有显著的还原性,HClO 的氧化效应会在一定程度上抑制 NO_2^-还原反应的进行,降低 NO_3^-的去除率(式 22),但这也能大大降低电催化反硝化处理后的污水中 NO_2^-的检出率。

$$NO_3^-+8e^-+10H^+ \longrightarrow NH_4^++3H_2O \tag{18}$$

$$2Cl^--2e^- \longrightarrow Cl_2 \tag{19}$$

$$Cl_2+H_2O \rightleftharpoons HClO+Cl^-+H^+ \tag{20}$$

$$3HClO+2NH_4^+ \longrightarrow N_2+3Cl^-+3H_2O+5H^+ \tag{21}$$

$$NO_2^-+HClO \longrightarrow NO_3^-+Cl^-+H^+ \tag{22}$$

2 元素掺杂电极材料对电催化反硝化的调控效应

电催化反硝化的速率与 N_2选择性受多种因素影响,其中电极材料的影响最为关键。电极材料主要包括金属电极与非金属电极,其中金属电极应用较多。Ru、Pt、Ir 等贵金属由于其优良的催化活性与强大的抗腐蚀能力得到了研究者的青睐,但价格昂贵、储量不足将成为该类电极最大缺点。Cu、Fe 等非贵金属电极凭借其高性价比与较为优良的性能,具有极大的应用潜力。然而,由于金属离子析出,非贵金属电极往往难以达到优良的稳定性,限制了其应用。相较而言,碳基电极如碳纳米管等具有储量高、成本低、酸碱耐受度高等显著优势,是潜力极大的电极材料[31-35]。但不可否认的是,非金属电极在电催化活性等方面仍难以企及金属电极(见表 1),鲜有非金属电极具备优良性能的报道。综上所述,各类型电极材料存在不同的弊端,亟需通过一定的手段对其结构和性能进行调控。

元素掺杂是提升电极材料电催化反硝化活性的重要手段[59],研究者使用多种合成手段,向不同电极材料中掺杂多种非金属元素和金属元素以构建元素掺杂电极材料。元素掺杂能够增加电极比表面积,增强电极导电性和稳定性,从而克服电极材料原有弊端,获得优良催化性能。元素掺杂通过调控催化活性中心电子结构、改变 NO_3^-与反应中间体的吸附能或降低反应决速步能垒提升反应效率。此外,元素掺杂材料还能够影响电子转移路径以及反应活性中间体 H^*的生成,进而调控反应路径和提升还原选择性。

表 1　电催化反硝化的电极材料及性能

Table 1 Electrode materials and their performance on electrocatalytic denitrification

电极材料	NO_3^--N 浓度/(mg·L^{-1})	NO_3^--N 去除率/%	N_2选择性/%	参考文献
Cu/Fe@NCNF	100.00	74.00	96.00	[36]
生物炭	100.00	75.80	90.00	[37]
Cu@Pd	50.00	81.90	90.70	[38]
Fe/Fe_3O_4-Ni	50.00	80.09	90.00	[39]
Pd/TiO_2	20.00	91.70	/	[40]
Fe-氧化石墨	100.00	90.00	/	[41]
CuPd-CNTs	100.00	95.00	95.00	[42]
Fe(Ⅱ)/Fe(Ⅲ)-OH	35.00	96.80	99.60	[43]
Fe@Gnc	100.00	96.00	96.00	[44]
Pd NPs	100.00	99.00	87.50	[45]
YMGO/CB-CC	100.00	96.48	95.87	[46]
Sn/Ni	50.00	99.00	65.00	[47]
Cu-NPC	50.00	100.00	63.10	[48]
P/Co_3O_4-NF	50.00	98.00	100.00	[49]
FeS_x@FF	50.00	94.96	98.88	[50]
Cu/TNTA	50.00	84.30	/	[51]
$Co@Cu_2(OH)_2CO_3$	100.00	81.92	97.11	[52]
$LaMn_{0.6}Co_{0.4}O_3$	25.00	78.40	/	[53]
Cu-BDD	50.00	71.00	45.00	[54]
Fe@N-C	50.00	83.00	100.00	[55]
$Ti/CuZn_5O_x$	150.00	92.30	33.70	[56]
CuO/Cu_2O NWs	100.00	99.90	86.90	[57]
Co-PBAs	50.00	100.00	97.89	[58]

2.1　元素掺杂对催化活性中心的调控效应

2.1.1　非金属元素掺杂

非金属元素能够有效调控电极材料空间结构与电子结构。根据电极材料的基底类型以及非金属元素的化学性质,研究人员使用 B、N、P、S 等多种非金属原子对电极材料进行掺杂,合成具有高选择性与高稳定性的电催化反硝化电极。

B 元素能够激活含 N 物种(如 NO_3^-等),有效抑制 HER 副反应发生。LUO 等[60]合成了具有优良电催化活性的 B-MoS_2纳米片阵列,并通过密度泛函理论(DFT)计算与分子动力学(MD)模拟表明 B 掺杂促进了 NO_3^-吸附与活性中间体的生成。N 原子的配位效应能够在一定程度上使金属原子(如 Zn)带有一定的正电荷,使其获得对 NO_3^-适宜吸附能力[61]。通过 N 掺杂调控材料金属活性中心,有助于优化电子传递路径,降低 NO_3^-转化为 NO_2^-的反应能垒,实现高效催化。XU 等[42]合成的 CuPd-CNTs 杂化纳米阵列,通过电子-金属-载体相互作用造成了 Cu 位点电子的缺失,增强了对 NO_3^-的吸附能力。

P、S 是第三周期元素,原子半径较大,电负性较低,且与 N 类似,具有一定的配位能力。GAO 等[49]合成的 P/Co_3O_4-NF 电极材料与未掺杂 P 原子的电极相比还原速率提高了 8.45 倍,并在 2 500 mg·L^{-1} Cl^-存在的情况下获得了 100% N_2选择性。研究表明,该掺杂阴极材料的主要优势在于 P 取代了部分晶格氧,造成了 Co 空 d 轨道增强,从而提高了对 NO_3^-的吸附能力,提高反应活性。LI 等[62]构建了锚定有 Fe 原子的 N、S 掺杂碳电极,其反应活性高于单一 N 掺杂电极,在 Cl^-存在的高电位条件下实现了 100%的 N_2选择性。S 掺杂改变了单原子中心的配位环境,产生了大量高导电性缺陷,对提高催化活性起到了关键作用。WANG 等[50]研究了 S 掺杂泡沫铁阴极,S 原子掺

杂显著调整了 Fe 电子密度，促进 NO_3^- 向 NO_2^- 的快速转化，在低电能消耗下，实现了高 NO_3^- 去除率（89.08%）和高 N_2 选择性（98.88%）。

2.1.2　金属元素掺杂

金属基电极往往存在稳定性较差、金属离子析出严重等问题，但金属的优良催化性能是其他材料难以完全替代的。因此，将金属原子掺杂于其他电极材料中，能够在发挥金属材料优势的同时，有效避免金属离子析出问题。此外，掺杂金属与电极材料（如氧化物）之间形成的特殊电子效应（如造成 d 带中心偏移）能促进反应活性中间体的产生与吸附[63-65]。

Cu 基电极性能优良，但长期运行会导致 Cu^{2+} 析出，运行稳定性不佳。SONG 等[51]使用一种 Cu 掺杂的 TiO_2 纳米管阵列进行电催化反硝化 12 h，对 NO_3^- 去除率达到了 84.3%。同时，该电极稳定性良好，在稳定性测试（10 次电催化反应循环）中无 Cu^{2+} 析出。电化学表征表明 Cu 掺杂能够促进电子转移，降低反应能垒，进而表现出优良的电催化活性。YU 等[52]利用 CO_2 辅助气泡共沉淀法合成 Co 掺杂孔雀石纳米片，在中性条件下实现了 97.11% 的 N_2 选择性，其优良的电催化性能源自于对电子结构的调节以及对反应中间体吸附的促进作用。

钙钛矿型金属氧化物稳定性好，缺陷可控，设计弹性大，是一种有前景的电极材料。ZHANG 等[53]向 $LaCoO_3$ 中掺杂适量 Mn 离子，制得了催化活性与稳定性优良的材料。Mn 掺杂增大了电极的比表面积，改变了不同氧化态 Co 的比例。研究人员推测 Mn 掺杂够提高电极对 NO_3^- 的吸附能力并加速电子转移，从而实现高效催化。

2.1.3　耦合掺杂

金属元素具有优良的电催化活性，非金属元素能够对电极结构产生有效的调控效应，而非金属基材料本身拥有良好的稳定性，且能同金属原子形成独特电子结构从而直接影响反应效率[66-67]（图 2）。研究人员将金属元素与非金属元素耦合掺杂于非金属材料基底（如碳纳米管），形成催化活性中心，优化电子传递路径，构建出了多种高稳定性的高效电极材料。

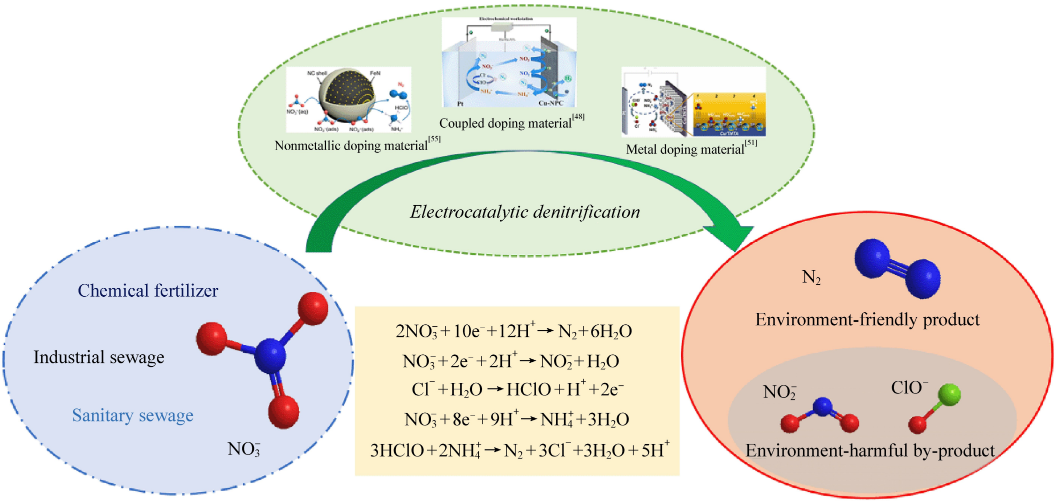


图 2　元素掺杂电极材料用于含硝酸盐废水处理

Fig. 2　Application of element-doped electrode materials in nitrate wastewater treatment

KUANG 等[54]合成了 Cu 修饰 B 掺杂金刚石电极，并将电沉积 Cu 氧化物固结在其表面。研究表明该电极拥有良好的电导率与电化学稳定性，能够显著提升对 N_2 的选择性。DUAN 等[55]合成的一种 N 掺杂石墨碳包裹 Fe 纳米颗粒材料，在 $1.0\ g \cdot L^{-1}$ 的 NaCl 电解液中实现了 83.0% 的 NO_3^- 去除率与 100% 的 N_2 选择性。在 20 天连续运行的电催化反应过程中，电极性能未发生显著改变，这源于石墨炭对 Fe 原子的保护作用以及 N 原子对催化活性中心的调控。

2.2　元素掺杂对电催化反硝化反应路径的影响

前文中指出，电催化反硝化存在两种反应路径，即阴极直接电还原和 H^* 介导的间接还原。研究表明，部分元素掺杂能够改变电极材料对 NO_3^- 和多种含氮中间体的吸附能，使得含氮物种更易于直接在阴极得电子还原；同时，该类电极材料能够抑制 H_2O 在电极界面的吸附，有效抑制 HER 的发生和 H^* 的生成。与此相反，部分掺杂电极材料能够有效促进 H_2O 的吸附与还原，产生 H^* 并介导间接还原反应的发生。值得一提的是，电催化

反硝化未必是通过单一路径进行的，直接与间接两种反应路径往往都对 NO_3^- 还原有一定的贡献度[17]。

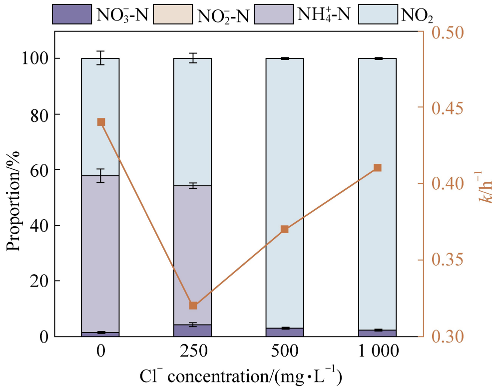
YAN 等[69]研究的 N 掺杂 C 球负载 Cu/Fe 氧化物不能有效促进 H_2O 在电极界面还原产生 H^*，被认为主要反应路径为 NO_3^- 直接还原。YANG 等[56]合成的 $Ti/CuZn_5O_x$ 电极在宽电位范围下均能抑制 HER，并通过抑制 H_2O 在电极界面放电产生 H^* 为 NO_3^- 提供更多反应活性位点，从而使得阴极直接电还原路径更加容易进行。研究人员合成的 S 掺杂泡沫铁加强了对关键中间体 NO_2^- 的吸附，有利于 NO_2^- 在电极界面进行直接还原反应[50]。

WANG 等[70]研究了 N 掺杂介孔碳包裹的 Cu/Pd 纳米颗粒的反应机理，NO_3^- 易吸附于 Cu 表面并被还原为 NO_2^-，Pd 则能有效促进 H^* 的产生，并为其提供吸附位点，在 H^* 的介导下，NO_2^- 继续被还原最终生成 N_2，实现了 NO_3^- 的间接还原。

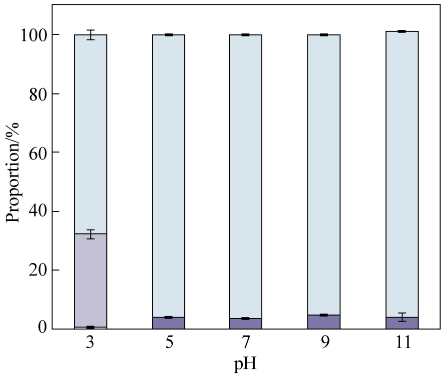
3　其他因素对电催化反硝化的影响

除电极材料外，电催化反硝化的还原效率和产物选择性还受电解质、pH 等其他因素影响，这些反应条件或影响 NO_3^- 吸附，或改变电极材料稳定性，或调控反应中间体的生成，对电催化反硝化的选择性、能耗与长期运行稳定性等产生重要影响。

电催化反硝化常用的电解质有 Na_2SO_4、NaCl、KOH、KNO_3、$NaNO_3$ 等。它们或提供反应物，或调节 pH，或增强导电性，对电催化反硝化过程和产物产生重要影响[50, 71-73]。阳离子对反应的影响很小，但部分特殊阳离子能对某些电极材料产生稳定效应，抑制金属离子析出。KATSOUNAROS 等[74]向电解液中添加 Rb^+、Cs^+，有效抑制了 Sn 阴极腐蚀。阴离子对反应影响相对较为显著，SO_4^{2-} 由于与硝酸根有相对类似的结构，会与硝酸根竞争活性吸附位点，降低反应速率。Cl^- 则能够通过耦合阳极氧化效应大大提升 N_2 的选择性[75-76]（图 3（a））。类似的，溶液中的其他卤素离子如 Br^- 也能够产生相似的效应，其原理基本相同，均基于在阳极生成的强氧化性的 XO^- 物种。ZHANG 等[77]使用生物炭电极进行电催化反硝化反应，以 Na_2SO_4 作电解液时主产物为 NH_3，但向溶液中加入一定浓度的任一卤素离子都能够大大提升 N_2 的选择性（由 7.6% 提升至 88.1%）。自然水体或实际废水中往往有一定浓度的卤素离子，因此会大大提升 N_2 的选择性[78-81]。ZHAO[82]用 Cu 电极处理含 Cl^- 的实际湖水，N_2 选择性从中性 K_2SO_4 溶液的 49.2% 提升至 64.2%。总而言之，卤素离子的存在可以极大地提高 N_2 选择性，并抑制高毒性 NO_2^- 的生成。然而，卤素离子氧化产生的强氧化性中间体 XO^- 可能与水体中部分有机化合物反应产生毒性较高的卤代副产物，需要对 XO^- 物种的残留浓度以及是否存在氯代副产物进行检测，以评估该水处理手段的安全性。



(a) Cl^- 对 Pd-Cu/CeO_2-OVs 电极催化性能的影响[85]



(b) pH 对 Pd-Cu/CeO_2-OVs 电极催化性能的影响[85]

图 3　Cl^- 和 pH 对 Pd-Cu/CeO_2-OVs 电极催化性能的影响

Fig. 3　Effect of Cl^- and pH on catalytic performance of Pd-Cu/CeO_2-OVs electrode

电解液 pH 是影响反应选择性的另一重要因素（图 3（b））。一般来说，酸性条件下 HER 的活性远高于碱性条件[83]，因此电催化硝酸盐还原反应常在中性甚至强碱性条件下进行，以抑制 HER 副反应。不同种类电极的最佳 pH 不同。ZHAO 等[82]使用 Cu_2O 电极于碱性条件下获得了最佳 N_2 选择性，CHEN[84]等使用 Cu/Pd 电极则在 pH = 3 时获得了最佳性能。与此相对应，多数电极的最适 pH 接近 7[85-87]。这可能是由于多数情况下，酸

性条件下反应容易受到 HER 的竞争,而碱性条件下电催化反硝化动力学缓慢。

4　电催化反硝化的关键挑战

随着全球工业发展和化肥施用量的增加,未来硝酸盐废水处理将成为环境治理的重要内容。电催化反硝化将 NO_3^- 还原为 N_2 是一种极具前景的硝酸盐废水处理技术之一,近年来获得广泛关注。目前已有部分研究人员使用实际废水或模拟废水作为电解液对电极活性进行了评估[55, 88-89],但仍未进行大规模长时间的运行试验,因此电催化反硝化处理实际废水仍需进一步研究。

电能消耗过高是目前电化学治污技术面临的主要瓶颈,如果能够实现低能耗运行,电化学技术将成为一种更加卓越的环境治理手段。近年来多项研究关注了 NO_3^- 电还原为 N_2 所带来的电能消耗,能耗高低不尽相同,但绝大多数报道的能耗低于 0.3 kW・h/g NO_3^--N,且随着电极性能的改进与电化学反应条件的优化,能耗进一步降低[17, 50, 89-91],这佐证了电催化还原技术在未来污染物处理中的巨大潜力。然而实际废水化学成分复杂,其处理能耗往往高于实验室模拟废水,GAYEN 等[92]使用 Pd 基电极分别进行了模拟废水与实际废水的电催化还原反应,结果表明实际废水的电耗(1.1~1.3 kW・h/mol)是模拟废水电耗(0.12~0.19 kW・h/mol)的数倍之高。

实际废水化学成分复杂,可能含有多种阴离子(Cl^-,Br^-等)、多种有机化合物以及 Pb、Cd 等重金属。复杂的化学环境会多方面影响电催化反硝化,使得实际处理效果与模拟废水实验相异,尤其是卤素阴离子,通过耦合阳极氧化能显著提升 N_2 选择性[49, 71, 93-95],而重金属离子的存在则会对 NO_3^- 还原效率产生不利影响[81]。此外,在进行实际废水处理之前,往往需进行一定的预处理以去除水体中的部分污染物,该步骤对后续的电催化反硝化过程会产生影响。SU 等[96]使用 Co_3O_4/Ti 阴极处理纺织废水,由于纺织废水 COD 较高,故在进行电催化还原前进行了芬顿反应预处理,该步骤增加了废水中的 Cl^- 浓度,提高了后续电催化反硝化步骤的 N_2 选择性。

5　结论与展望

电催化反硝化是一种新型的绿色高效水处理技术,本文综述了电催化反硝化的最新研究进展,总结了反应的两种路径,明确了反应决速步以及关键中间体,分析了元素掺杂手段对催化活性中心以及反应路径的调控效应,考察了电解液组成及其 pH 对反应的影响,从能耗和实际废水理化性质的角度分析了目前电催反硝化技术面临的关键挑战。综合以上分析,未来研究应当聚焦于以下几个方面:(1)围绕电催化反硝化过程中 NO_3^- 吸附与反应决速步(NO_3^- 还原为 NO_2^-),研发高效、高稳定性的电极材料。(2)通过多种材料复合或改性手段(如元素掺杂),调控电极催化活性中心,提高电子转移效率,促进活性中间体生成。(3)卤素离子(Cl^-、Br^-)能显著提高 N_2 选择性,在实际废水中普遍存在,研究含该类离子废水的电催化反硝化技术具有重要应用前景。(4)电能消耗高是电化学处理法目前面临的主要技术瓶颈,研究能进一步降低能耗的电极材料或反应条件,能够极大地促进电催化反硝化技术迈向实际应用。(5)在研发出高效电极材料的基础上,针对不同类型硝酸盐废水的物理化学特征,研究一体化水处理技术,通过耦合预处理与电催化反硝化协同效应包括 NO_3^- 在内的多种污染物。(6)对于电催化反硝化处理后的水,除关注 NO_3^- 去除率与 N_2 选择性外,还应关注 NO_2^-、ClO^- 等含氯物种以及氯代有机物等可能残留的副产物。

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