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电催化氮还原体系反应界面的不同组分调控及其合成氨性能研究

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摘　要

氨作为一种无碳绿色燃料以及重要的工农业原料，在日常生活中发挥了巨大的作用。目前，氨的工业生产主要通过哈伯－博施法进行，这一工艺过程需要高温高压严苛的反应条件，在消耗大量化石燃料的同时也给环境带来了极大的负担。电催化氮还原合成氨(NRR)方法由此崭露头角，其在常温常压的温和条件下以氮气和水为原料，以可持续能源(太阳能、风能等)发电为驱动力合成氨，可以实现绿色、零排放的预期效果。然而，在研究过程中始终存在以下三个问题，一是氮气化学性质稳定，N≡N键断裂需要较大的能量；二是在常用的水系电解液中倾向于发生较强的析氢反应(HER)，使电催化氮还原的选择性较低；三是由于氮气在水中的溶解度低，扩散动力学缓慢，反应界面氮气供应不足。因此，针对这三种科学问题，从电催化剂、电解液及工作电极的角度出发，探索并设计有效的优化方案，对进一步推进电催化氮还原反应的实际应用具有重要意义。

关键词

氮还原合成氨，电催化剂，电解液，工作电极

Study on the Regulation of Different Components at the Reaction Interface of the Electrocatalytic Nitrogen Reduction System and Its Synthetic Ammonia Performance

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Abstract

As a carbon free green fuel and an important industrial and agricultural raw material, ammonia plays a huge role in daily life. At present, the industrial production of ammonia is mainly carried out through the Haber Bosch process, which requires harsh reaction conditions of high temperature and high pressure. Thus, this process consumes a large amount of fossil fuels, and also brings great burden to the environment. The method of electrocatalytic nitrogen reduction (NRR) to synthesize ammonia has temporarily emerged. It synthesizes ammonia using nitrogen and water as raw materials under mild conditions of normal temperature and pressure, driven by sustainable energy sources such as solar and wind power, and can achieve the expected effects of green and zero emissions. However, it is found that the following three problems always exist in this process. First, the chemical property of nitrogen is stable, N≡N fracture requires a large energy. Second, in commonly used aqueous electrolytes, strong hydrogen evolution reaction (HER) tends to occur, resulting in lower selectivity for NRR. Third, due to the low solubility and slow diffusion of nitrogen in water, nitrogen supply at the reaction interface is always insufficient. Therefore, exploring and designing effective optimization schemes from the perspectives of electrocatalysts, electrolytes, and working electrodes for these three scientific issues is of great significance for further promoting the practical application of electrocatalytic nitrogen reduction reactions.

Keywords

Nitrogen Reduction for Ammonia Synthesis, Electrocatalysts, Electrolyte, Working Electrode

1. 引言

工业时代以来，化石燃料为人类社会的进步发展奠定了基石。然而，其燃烧过程中释放的大量二氧化碳加剧了日益严峻的气候问题，引起了人们的广泛关注和深刻思考[1]-[4]。自中央经济工作会议和两会提出“碳达峰”“碳中和”的概念，能源存储与转化相关产业的深度变革成为当下热门议题[5] [6]。发展高能量密度的储能设备和可再生能源技术是确保实现“碳达峰”“碳中和”目标的重要途径。氢含量高达17.6%的氨由此以一种新的方式进入了学者的视野。它具备高能量密度、高热值、低污染、易液化储运等优点，是一种良好的储氢材料，被视为新一代能源载体，是近年来具有重要研究价值的热点之一[7]-[10]。长久以来，氨作为一种重要的工农业原料，为推动世界科技进步和工业化发展作出了重大贡献。它是农业化肥的基本成分，氨的产量决定了化肥的供给，为世界持续增长的人口提供了坚实的粮食基础[11]。在众多工业领域，也发挥了巨大的作用，包括应用于多种纤维、塑料、涂料、炸药生产过程中等多方面。因此，合成氨工业是现代化工和国民经济的重要支柱[12]-[14]。

目前，Haber-Bosch工艺是工业合成氨的主要手段。1909年，弗里茨•哈伯(Fritz Haber)首先发现增加反应体系的压力，能降低氮气分解所需的温度，并且在非常高的压力下，反应体系可以输出可观数量的氨。而且，通过引入合适的催化剂，可以进一步提高产量，达到工业级产量的水平。最终，他成功设计并制造出连续流动的液氨。随后，冶金学家兼工程师卡尔•博施(Carl Bosch)致力于完善这种氨合成工

艺，使之能够在世界范围内使用[15]-[17]。现今，普遍采用铁基催化剂，在高温高压的条件下(300℃~500℃, 20~30 MPa)以氢气和氮气为反应原料合成氨。该工艺固有效率高，总转化率高达97%，是合成氨领域的主流生产工艺，全球90%以上的氨是由此产生的[18]-[20]。但是，Haber-Bosch工艺始终面临严峻的能耗和环境问题。严苛的反应条件需要消耗大量的化石燃料提供能量，反应原料氢气一般来自天然气蒸汽重整过程，也会消耗大量的化石燃料。据统计，Haber-Bosch工艺的能耗高达全球能源总消耗的1%~2% [21]-[23]。同时，化石燃料过程中排放出大量的温室气体，加剧了全球气候问题[15] [24] [25]。因此，探索绿色可持续的合成氨工艺路线，克服Haber-Bosch法高能耗、高污染的不足至关重要[26]-[28]。

电催化氮还原合成氨(NRR)是以可再生电能为驱动力，以水和氮气为原料，在常温常压的温和条件下实现氨的绿色合成的新工艺[7] [29]-[31]。与传统的Haber-Bosch工艺相比，温和条件下的电催化氮还原方法在降低能源消耗，减少碳排放和简化反应器设计等方面具有可行性，是目前氮还原合成氨领域的重点研究方向之一[32]-[34]。然而，在实际研究过程中，人们也发现了一些棘手的难题。首先N≡N三键稳定性极高，从N_2制得NH_3的过程要克服极高的能量壁垒[35]-[37]；其次，常温常压下氮气在水中的溶解度较低，液相中的传质速率有限，反应物供给不足[38]-[40]；同时，由于析氢电位和氮还原的电位非常接近而水溶液中存在大量质子，析氢反应(HER)作为主要的竞争反应，致使电催化氮还原反应的选择性和氨产率大大降低[41]-[43]。针对这些问题，人们从多方面对电催化氮还原进行了深入的研究并取得了一定的成果，但在提高电催化活性和法拉第效率方面仍存在巨大的提升空间[44]-[47]。

2. 电催化氮还原概述

2.1. 电催化氮还原反应机理

电催化氮还原以水和氮气为原料，反应的总反应式如下(1)所示：

$$\text{总反应：}N_2 + 3H_2O \rightarrow 3/2O_2 + 2NH_3 \tag{1}$$

水相体系中，NRR过程通常包含5个步骤：I) N_2溶解于电解液并扩散到催化剂表面；II) 催化剂活性部位氮吸附；III) 进行电化学合成氨反应；IV) 产物氨的解吸；V) 氨从催化剂表面扩散到体相[2] [12] [48] [49]。当电解液酸碱性质不同时，由于质子的存在形式不同，阴阳极反应存在差异[50]-[52]。具体的反应式如下(2)至(5)所示：

$$\text{阴极反应(酸性)：}N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \tag{2}$$

$$\text{阳极反应(酸性)：}3H_2O \rightarrow 3/2O_2 + 6H^+ + 6e^- \tag{3}$$

$$\text{阴极反应(碱性)：}N_2 + 6H_2O + 6e^- \rightarrow 2NH_3 + 6OH^- \tag{4}$$

$$\text{阳极反应(碱性)：}6OH^- \rightarrow 3H_2O + 3/2O_2 + 6e^- \tag{5}$$

由于反应过程中质子－电子转移过程多，中间产物多，NRR的反应机理至今尚未完全阐明[53] [54]。目前，人们普遍认可的反应机制分为两种：解离机制和缔合机制(图1) [55]-[57]。解离机制中，N_2分子吸附到催化剂表面后，N≡N键在氢化反应之前断裂，在活性位点上产生两个孤立的氮原子，经连续质子化最终产生NH_3 [58]-[60]。由于N≡N键十分稳定，这一机制需要消耗大量的能量。在缔合机制中，N_2分子被氢化时，两个氮原子仍保持彼此结合的状态，N≡N键在第一个NH_3分子释放的同时被断开[61]-[63]。根据加氢顺序的不同可进一步分为远端途径和交替途径。远端缔合途径中，加氢反应优先发生在远离催化剂表面的氮原子上。当第一个NH_3分子形成并释放时，结合在催化剂表面附近的氮原子开始加氢并产生第二个NH_3分子；而在交替反应途径中，N_2分子中的两个氮原子同时氢化，加氢过程在两个N原子间交替进行，第一个NH_3分子被释放后，第二个NH_3分子紧接着被释放[64]-[66]。因此，一般认为相比解离机制，缔合机制的能耗更低，更容易进行。在酶促加氢路径中，N_2分子的两个N原子均吸附在催化剂

表面，进行独特的侧端配位模式，加氢过程交替进行。

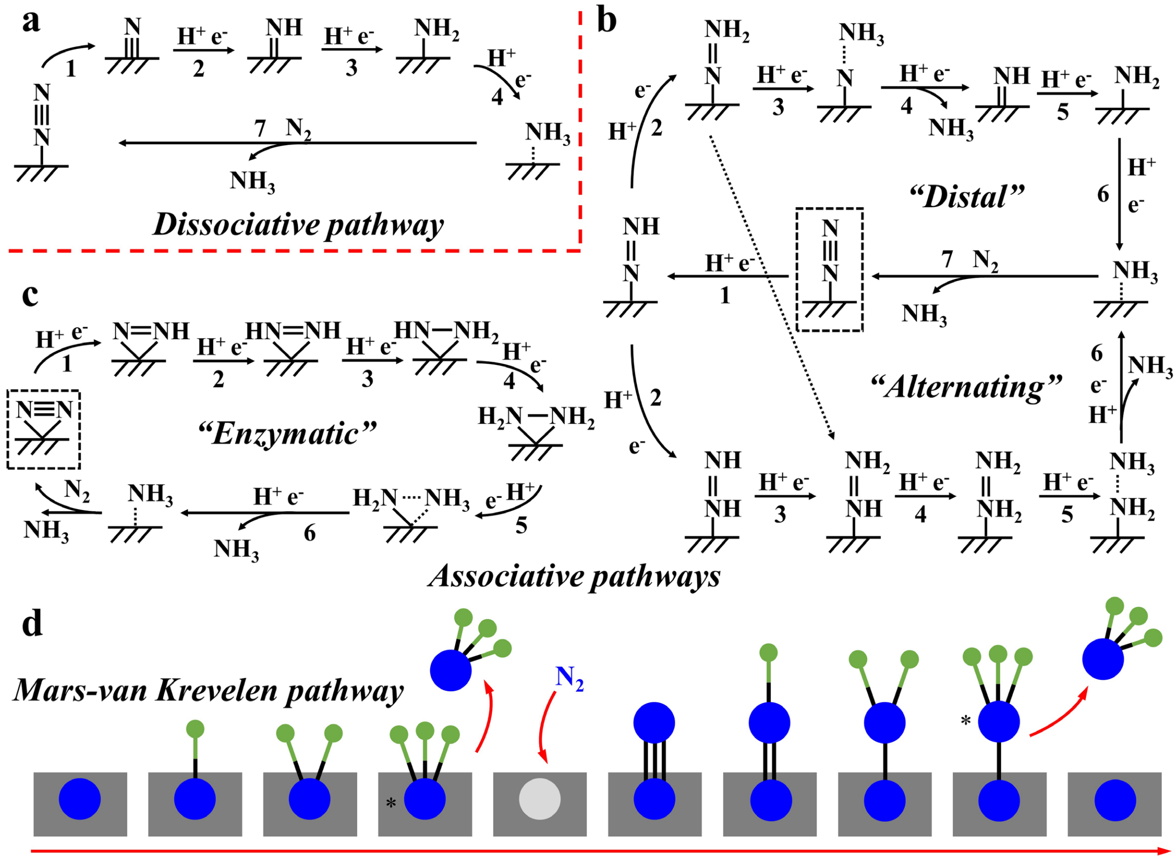

Figure 1. Schematic diagrams of (a) dissociative pathway, (b) associative distal and alternating pathways, (c) associative enzymatic pathway, and (d) Mars-van Krevelen pathway [70]
图 1. (a) 解离路径，(b) 缔合远端及交替加氢路径，(c) 缔合酶促加氢路径，和(d) Mars-van Krevelen 路径的示意图[70]

近期，尤尼斯・阿布古伊(Younes Abghoui)和埃吉尔・斯库拉松(Egill Skúlason)提出在过渡金属氮化物表面比常规的解离机制和结合机制更有利的 Mars-van Krevelen 机制。该机制与传统的解离机制和结合机制不同的地方在于认为金属氮化物表面的晶格氮原子被还原为 NH_3 产生氮空位后，化学吸附的氮分子进行补充使电催化氮还原反应连续发生。经此机制预测的 N_2 还原和生成 NH_3 的过电位要小于缔合机制预测的结果[67]-[70]。需要注意的是，当催化剂的类型、结构及反应条件不同时，电催化氮还原产氨所经历的反应过程也存在差异，在考虑应用机理时，仍需要根据具体情况具体分析。

2.2. 电催化氮还原反应影响因素

在目前的研究过程中，众多研究者将研究重点放在 NRR 的催化剂上，而忽视了整个电催化反应体系的影响。在实际反应过程中，NRR 性能的关键在于电催化剂与反应系统的协同作用，包括电极电位，溶剂效应、电解液 pH 值等多种因素[18] [71]-[74]。因此，提高 NRR 性能不仅要合理设计催化剂，还要从整体上考察整个反应系统，选择合适的电极电位、合理设计电解池结构、优化电极结构等[74]-[76]。

电催化氮还原反应只有在施加电势低于平衡电极电势时才会发生，因此，在反应过程中施加电位的大小对于 NRR 至关重要。有研究发现，环境条件下不使用任何电催化剂时，电催化 NRR 所需的最低电势为 1.17 V，比析氢反应的过电位至少大 0.5 V。通常情况下，不同反应条件下的最佳电势也不同，当施

加电位超过最佳电势时，析氢反应此时占主导电位，NH_3 产率和法拉第效率均会下降。但当选择合适的工作电势时，NRR 也会占主导地位[66] [77]。具体来说，NH_3 的生成速率随施加电位的增加而增加，直到趋于平稳。在施加电位较高时，HER 完全占主导电位[78]。因此，在实验过程中需要根据具体情况，尝试选择电催化 NRR 的最佳反应电位。室温条件下水溶液的电催化氮还原体系中，根据电解池结构的不同，主要有以下几种：背靠背电解池、质子交换膜型(PEM)电解池、H 型电解池和单室电解池(如图 2 所示) [12] [72] [79] [80]。背靠背电解池中间由固态电解质聚合物膜隔开分为阴阳两极，两侧为阴极室和阳极室，都带有催化剂和气体扩散层。因质子交换膜 Nafion 能在室温下高效传递质子，实验室研究中用得较多(图 2(a))。PEM 型电解池中，阳极室以水为电解液，加入参比电极使电极电位的测定更加精准(图 2(b))。

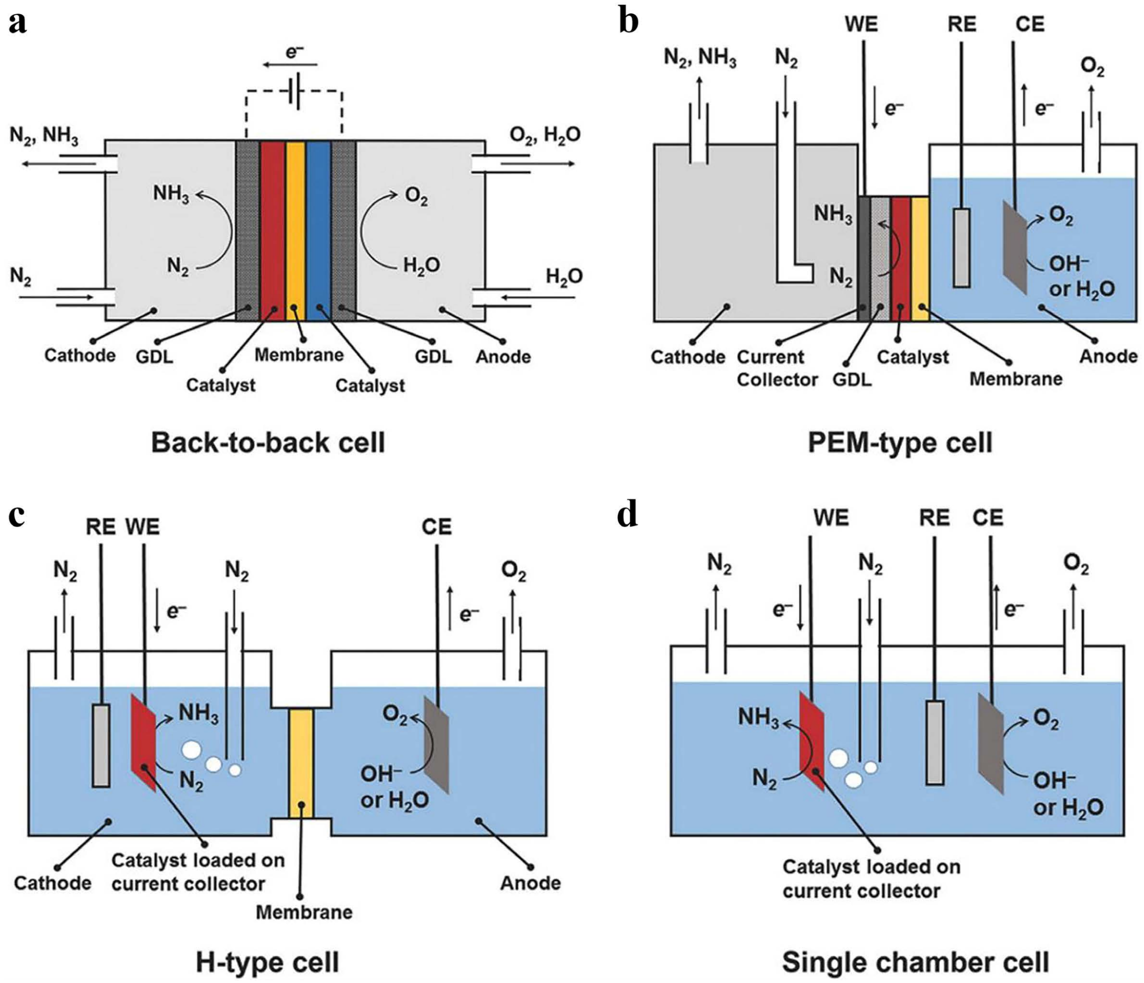

Figure 2. Schematic diagrams of (a) back-to-back cell, (b) proton exchange membrane (PEM) cell, (c) H-type cell, and (d) single-chamber cell [80]
图 2. (a) 背靠背电解池，(b) 质子交换膜型电解池，(c) H 型电解池，和(d) 单室电解池的示意图[80]

H 型电解池是目前研究最广泛的类型，由两个单室池分别作为阴极室和阳极室，中间用交换膜隔开，防止阴极室还原产生的 NH_3 扩散到阳极室中被氧化(图 2(c))。采用三电极体系，对电极位于阳极室，在此发生氧化反应。阴极室中发生还原反应，参比电极与工作电极均在此室，使施加电位更加准确。通常情况下，工作电极采用催化剂沉积的碳衬底，参比电极为 Ag/AgCl 电极、饱和甘汞电极等，对电极使用碳棒或铂丝。单室电解池中阴、阳极室相通，两电极处于同一电解液环境中(图 2(d))。虽然装置简单，易于

操作，但阴极上生成的 NH_3 分子容易扩散至阳极发生氧化。H 型电解池中两极室被交换膜隔开，离子在极室间选择性交换，两极相对独立，能够更加简便、灵活地调控电极环境。因此，H 型电解池是当前应用最多的一类电催化反应装置[81]。针对 PEM 型电解池实验过程中部分阴极生成的氨透过膜扩散到阳极室被氧化，影响合成氨产率和效率等问题，Chen 等对 PEM 型电解池结构进行优化设计(图 3)，将一层气体扩散层添加到催化剂层和膜之间，阻止合成的氨在膜两侧的穿透[82]。同时，气体扩散层的存在使质子的传输受到限制，使阴极析氢副反应也受到了抑制。

电解池的结构及形式决定了电极和电解液的分布，也对体系中反应物的传递途径及反应区间产生一定的影响。同时，使用不同电解池进行 NRR 测试过程中，电解池的各项参数如电解液体积、阴阳极室体积、各个电极、质子交换膜、气密性等对实际产氨的浓度和收集效率会产生较大的影响[33] [83]。因此，在实际应用过程中，需要根据具体体系合理选择并设计电解池的形式、结构及参数[84]-[90]。

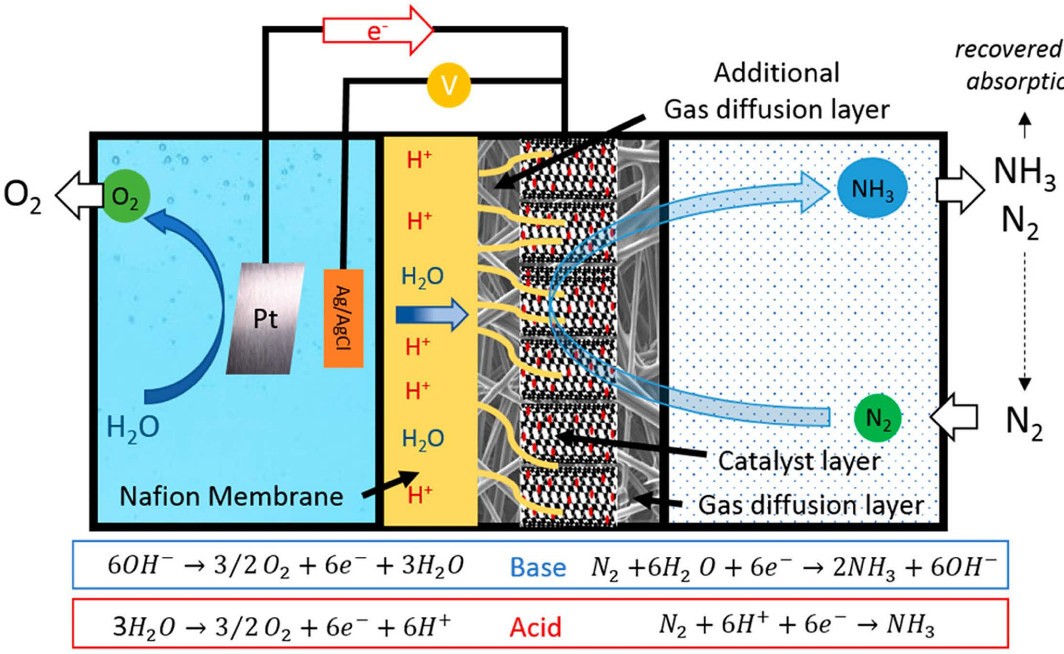

Figure 3. Schematic view of the improved design in the PEM cell for electrochemical ammonia synthesis [82]
图 3. 电化学合成氨的 PEM 型电解池的改进设计的示意图[82]

3. 电催化氮还原研究进展

相较于 Haber-Bosch 工艺，电催化氮还原合成氨的优势主要体现在以下几方面：1) 水作为质子源替代 H_2，减少了化石燃料的消耗，且来源广泛，绿色无污染；2) 电催化氮还原以可再生电能为驱动力，反应条件温和，能耗低，安全性高；3) 根据热力学理论计算结果，电催化氮还原方法比 Haber-Bosch 工艺节能 20%；4) 装置简单，操作灵活，不需要建设昂贵复杂的基础设施，实现氨的按需、精准制备，灵活性和可调谐性优于 Haber-Bosch 工艺。从原料、能源供应、绿色环保还是生产灵活性等方面来看，电催化氮还原相较于 Haber-Bosch 工艺具有明显的优势，是一种低碳、与“碳达峰”“碳中和”目标极其吻合的新型产氨工艺路线，有望替代传统的 Haber-Bosch 工艺实现氨的工业化生产[60] [91] [92]。然而，目前电催化氮还原合成氨工艺还面临着很多技术难关，主要包括以下几方面：1) $N\equiv N$ 三键稳定性极高且氮气的吸附缓慢，电催化氮还原在热力学和动力学上存在巨大挑战；2) 析氢副反应剧烈，电催化氮还原反应选择性差；3) 常温常压下氮气在水中的溶解度低，传质受限，反应界面处反应物供应不足[93]-[95]。基

于此，将电催化氮还原领域的研究分为电催化剂、电解液以及工作电极设计三个部分，下面将具体介绍这三个部分迄今为止的研究进展。

3.1. 电催化氮还原催化剂研究进展

在电催化氮还原体系中，电催化剂是实现高效电催化反应的核心，可以降低反应势垒、提高合成氨产率[47] [96] [97]。对此，研究者对其进行了大量的研究与优化。根据电催化剂的化学组成，主要将其分为贵金属催化剂、非贵金属催化剂和非金属电催化剂。

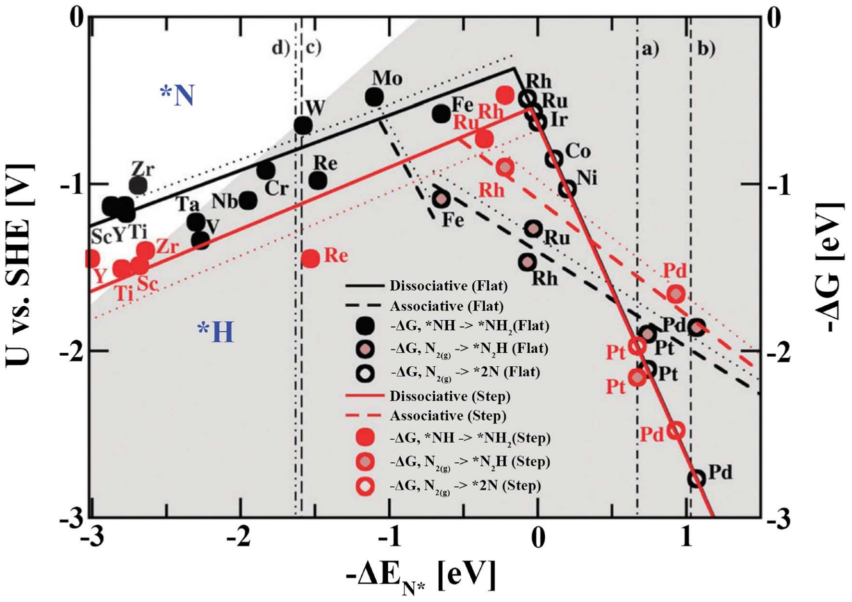

Figure 4. Volcano diagrams for electrocatalytic nitrogen reduction on different metals [108]
图 4. 不同金属电催化氮还原的火山图[108]

贵金属催化剂因其导电性好、活性高、稳定性好等诸多优点被广泛地应用于多种电催化反应如析氢反应(HER)、析氧反应(OER)、氧还原反应(ORR)等[75] [98]-[100]。在电催化 NRR 过程中，贵金属催化剂也表现出较好的性能。金(Au)被认为是电催化氮还原反应中最有潜力的贵金属催化剂之一。研究表明，发生在 Au 表面的电催化氮还原反应遵循缔合机制，N_2 三键的断裂和 N 原子的氢化同时发生。此外，由于 Au 表面的多晶面存在可用于 N_2 吸附和还原的各种活性位点，因此，与其他电催化剂相比，Au 表面的电催化氮还原速率更高[101]-[103]。El-Sayed 等人合成了一种中空 Au 纳米笼材料将其用于电催化氮还原反应[104]。与固体纳米颗粒相比，中空纳米催化剂的外表面和内表面均可发生催化反应，具有更大的活性比表面积。同时，部分反应物被限制在空腔中，有利于在催化反应的速率决定步骤中增加物种的稳态浓度，因此催化反应进行的速率更快。在室温下的 $LiClO_4$ 电解液中，获得了最高的氨产率($3.9\ \mu g \cdot cm^{-2} \cdot h^{-1}$)和法拉第效率(30.2%)。钌(Ru)是最先应用于电催化氮还原反应的催化剂，在 Haber-Bosch 法中表现出极佳的催化性能[105]。密度泛函理论(DFT)计算结果表明，Ru 具有适当的氮吸附能，在缔合和解离机制中的过电势也远低于其他贵金属如 Pt 和 Pd [106]。因此，也是一种较好的 NRR 催化剂。有研究表明，在 Ru 基催化剂中，电催化氮还原体系成功地合成了氨[107]。使用分布在氮掺杂碳上的 Ru 单原子作为 NRR 电催化剂，在−0.2 V 相对于可逆氢电极(vs. RHE)电位下，氨产率和法拉第效率分别达到了 $120.9\ \mu g \cdot mg^{-1} \cdot h^{-1}$ 和 29.6%。如图 4 所示，根据 Skúlason 团队构建的理论极限势与氮在不同金属表面上的吸附能火山图，铑(Rh)位于火山图的顶部，并具有最活跃的 NRR 表面，应当具有优异的 NRR 性能[108]。然而，迄今为

止，关于 NRR 的 Rh 催化剂的报道很少，因此，用于 NRR 的 Rh 纳米结构的制备与研究十分重要与必要。Liu 等人制备出一种以无机聚合物 $RhCl_3$-$K_3Co(CN)_6$ 为前体的二维 Rh 纳米片自组装(Rh NNs)材料[109]。得益于合成的超薄 Rh 纳米片的高表面积、改性的电子结构、大量低配位缺陷原子以及独特的 3D 互联结构，Rh NNs 在 0.1 M KOH 碱性电解液中表现出优异的电催化活性、选择性和耐久性。在施加电压为−0.2 V vs. RHE 时，氨产率为 23.88 $\mu g \cdot mg^{-1} \cdot h^{-1}$。

近年来，由于非贵金属催化剂相较于贵金属催化剂在成本和资源储备等多方面的优势，引起了人们的重点关注。其中，过渡金属 d 带有接近费米能级的价电子，其 π 反馈效应促进 N_2 在催化剂表面的吸附并削弱 N≡N 三键，有利于 N_2 分子的活化[110] [111]。受生物固氮启发，学者们对固氮酶中 Fe、Mo、V 等重要的过渡金属元素进行了多元化的研究将其用于人工固氮催化剂中，在 NRR 应用中也表现出良好的活性。例如，在 0.5 $mol \cdot L^{-1}$ $LiClO_4$ 电解液中，氟掺杂的 β-FeOOH 在−0.6 V vs. RHE 电位下，氨产率达到 42.38 $\mu g \cdot h^{-1} \cdot mg^{-1}$，理论计算结果表明，Fe 有效降低了 NRR 的能垒[112]。作为豆科植物根瘤菌固氮过程中不可或缺的元素，钒(V)的化合物如钒氧化物、钒氮化物等在 NRR 中也表现出较好的活性。Yan 等人制备出高缺氧、多价的 VO_x 并将其应用于 0.1 M Na_2SO_4 电解液中测试其 NRR 性能。在−0.35 V vs. RHE 电位下，法拉第效率达到 16.97% [113]。如图 4，在 NRR 火山图中，钼基电催化剂位于所有金属首位，表明其具有很强的 NRR 活性，是实施电催化 NRR 的理想材料[108]。Sun 等人制备出一系列钼基催化剂包括硫化钼、氧化钼、碳化钼和氮化钼等用于 NRR。其中，由于 Mo 和 S 在固氮酶中发挥了关键作用，MoS_2 被认为是最具前途的 NRR 催化剂之一。Sun 等人的研究表明，Mo 上的正电荷在 MoS_2 表面对 N_2 的选择性吸附具有重要作用。同时，富含缺陷的 MoS_2 在各个方面都优于 MoS_2，在 0.1 M Na_2SO_4 电解液，−0.4 V vs. RHE 的电压下中，获得了 29.28 $\mu g \cdot h^{-1} \cdot mg^{-1}$ 的氨产率和 8.34%的法拉第效率[110] [114]。基于非金属材料经济环保的优势，材料表面对 H_2 的吸附相较于金属催化剂更弱，有利于抑制析氢反应。因此，非金属催化剂用于电催化氮还原的研究也在进行[115]。Lv 等人制备一种氮空位缺陷修饰的非金属氮化碳聚合物(PCN)作为电催化剂用于 NRR 过程中，环境条件下氨产率、法拉第效率分别达到 8.09 $\mu g \cdot h^{-1} \cdot mg^{-1}$ 和 11.59%。DFT 计算结果表明 PCN 中的氮空位能够构建吸附 N_2 的双核末端结合结构进行空间电子转移，使 N−N 键长显著增加，促进 N_2 活化[116]。Wang 等人在非金属基底中引入 Lewis 碱基团作为一种有效的电子供体制备了一种非金属 PNG 催化剂用于 NRR 过程中。DFT 计算表明 Lewis 碱基团不仅能为放热氮吸附过程提供能量，还能显著降低氮离解的活化势垒，与没有电子供体的纯底物相比，其极限电势几乎减半。同时，MD 模拟结果表明具有强 Lewis 碱基团的催化剂可以通过 vdW 相互作用极大地吸引 N_2 分子的进入，从而促进后续的氮吸附过程。后续通过实验验证了非金属 PNG 催化剂打破 N_2 离解的活化屏障、促进氮吸附的理论效果，在 0.1 M KOH 电解液中，−0.2 V vs. RHE 电压下，获得了 41.1 $\mu g \cdot h^{-1} \cdot mg^{-1}$ 的氨产率和 62.9%的法拉第效率，优于类似条件下已报道的大多数结果[117]。

3.2. 电催化氮还原电解液研究进展

电解液作为电催化系统中的溶剂和质子源，通过与反应物、中间体甚至产物的相互作用，高度参与 NRR 过程中[50] [51]。因此，了解并掌握电解液的作用原理、合理选择适当的电解液对设计高效的 NRR 体系至关重要。根据目前的研究，常用的 NRR 电解液可分为两大类包括水系和非水系两种(如图 5 所示)，其中水系电解液可再细分为酸性、中性、碱性和高盐浓度(water-in-salt, WIS)电解液四种，非水系电解液可再细分为有机电解液及离子液体电解液两种[40] [118]。

常规水系电解液以水为溶剂，成本低，环境污染小，具有优异的导电性和较宽的电化学工作窗口，在 NRR 中应用广泛[119]。酸性电解液中虽然存在大量质子占据了较多催化剂表面的活性位点，但理论证明，一般情况下酸性溶液中氮气的溶解度较大，缓解了 NRR 过程中催化剂表面 N_2 供应不足的问题[50]。

Nørskov 等人发现，在酸性电解质中，一些不利于*H 吸附的催化剂(如 Au)上有更多质子，可以提高 NRR 的 PCET 过程速率，从而导致相对更多的表面位点可用于*N_2 吸附[120] [121]。类似地，Jiang 等人通过实验在 HCl 电解液(pH = 1)下测得较高的 NRR 活性。在−0.2 V vs. RHE 下实现了高 NH_3 产量(21.4 μg·h^{-1}·mg^{-1})、稳定的法拉第效率(8.11%)和良好的选择性[122]。中性电解液相较于酸性和碱性电解液更加温和，对反应器件的腐蚀较小。同时，电解液中可直接获得的质子活度大幅减少，来自 HER 的竞争得到抑制。Jiang 等人在不同电解液中观察到 Au 催化剂表面 NRR 活性不同的变化趋势[123]。酸性条件下，NRR 活性在−0.2 V vs. RHE 开始下降。而在中性电解液中，由于质子浓度较低，在−0.5 V vs. RHE 时才出现下降趋势。最终，在中性磷酸盐缓冲溶液(PBS)中，NRR 性能最为优异。碱性环境中有限的质子浓度使 HER 的 Volmer 步骤进行缓慢，进而使 HER 的反应速率降低，NRR 的选择性得到有效提高。Singh 等人发现 Cu (111)表面进行 NRR 的最佳 pH 为 13.5，当电解液 pH 从 13 增加到 13.5 时，NRR 可用的活性位点增加[76]。与此同时，*H 的结合能在该范围内增加，导致 HER 的电流密度较低，因而，NRR 的电流密度、法拉第效率有明显提升。当电解液的 pH 继续增加至大于 13.5 时，*H 的结合能也在持续变大，*H 的表面覆盖率变大的同时 NRR 的活性位点在减少，导致 NRR 的活性和法拉第效率降低。近年来，WIS 电解液引起了人们的关注[124]。与常规水系电解液相比，WIS 溶液中高浓度盐的强溶剂化效应将 H_2O 分子限制在一定范围内，限制了游离 H_2O 的供应，从而显著抑制 HER。并且，有研究证明，WIS 电解液可以将电化学稳定性窗口显著拓宽至 3.0 V 以上，对于 NRR 的后续研究极具吸引力。Wu 等人使用负载有 Au 纳米颗粒的富含氧空位的 TiO_2 作为 NRR 催化剂，在超浓 WIS 电解液(20 M LiTFSI)中成功合成 NH_3。在−0.4 V vs. RHE 下，获得了 37.2%的法拉第效率和 20.3 μg·h^{-1}·cm^{-2} 的 NH_3 产率[125]。理论计算验证了超浓 LiTFSI 盐溶液通过与 H_2O 的强离子相互作用有效阻止 H_2O 分子到达催化剂表面，并使 H_2O 分子失活，HER 的能垒增加。并且在该 WIS 电解液中 H_2O 扩散受到严重阻碍。因此，HER 的电流密度和起始电势经历了显著的衰减，表明 HER 过程被 WIS 电解液的独特效应强烈抑制。

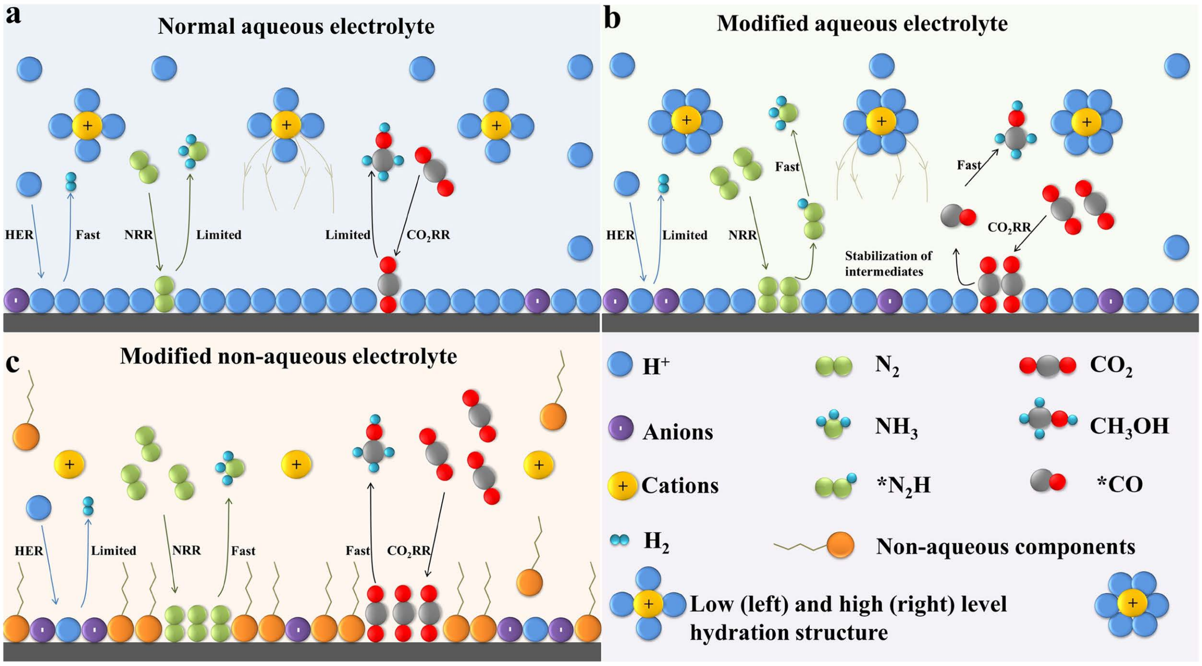

Figure 5. Schematic illustrations of (a) normal aqueous electrolyte, (b) modified aqueous electrolyte, and (c) modified non-aqueous electrolyte [40]

图 5. (a) 普通水系电解液，(b) 改性水系电解液，和(c) 改性非水系电解液体系的图示[40]

当水系电解液中大量质子不利于反应时，非水系电解液由于其含水量远低于水系电解液成为 NRR 电解液的理想候选者。此外，理论证明 N_2 在部分非水系电解液中的溶解度比在水系溶液中大很多[52]。因此，基于非水系电解液的 NRR 研究也在逐步进行。根据目前已发表的研究，可以将常见的非水系电解液分为有机电解液和离子液体电解液。

Qiu 等人开发了一种新型的有机溶剂混合少量水的电解液体系，以调节电极–电解液界面处的质子浓度和微环境[126]。选择甲醇作为主要电解液限制了质子的量，从而抑制了 HER；加入微量水防止质子供应不足，不利于 NRR 过程。最终，使用 FeOOH/CNTs 催化剂，甲醇电解液呈现出创纪录的 75.9% ± 4.1%的法拉第效率和 262.5 ± 7.3 $\mu g \cdot h^{-1} \cdot mg^{-1}$ 的 NH_3 产率，与传统水性电解液相比提高了约 8 倍。离子液体由有机阳离子和无机或有机阴离子组成，在低于 100℃的温度下是液体[127]。由于其极低的蒸气压、高热稳定性、高离子电导率、可调节的溶解能力和宽的电化学稳定性窗口，它们被认为是一种新型的绿色溶剂，能够取代传统的水系和有机溶剂[128]。MacFarlane 等人证明离子液体中氟含量越高，N_2 的溶解度越大[129]。在此基础上，他们还比较了几种不同离子液体中合成 NH_3 的法拉第效率，发现其与 N_2 的溶解度有关。当使用[P_{6614}] [eFAP]作为电解液时，环境条件下，在纳米结构的铁催化剂上获得高达 60%的法拉第效率，而在[Hmim] [NTf_2]这一 N_2 溶解度较低的离子液体中，法拉第效率仅为 0.64%。DFT 计算结果表明，N_2 和离子液体阴离子之间相互作用强度不同导致 N_2 溶解度的差异[130]。N_2 和$[eFAP]^-$之间较强的相互作用是 N_2 溶解度较高的原因，因此合成 NH_3 的法拉第效率较高。非质子特性还决定了离子液体中质子的可用性比在水系电解液中要有限得多，从而极大程度抑制了竞争性 HER，提高了 NRR 的活性和选择性[131]。

3.3. 电催化氮还原工作电极研究进展

在目前广泛应用三电极体系中，电极本身结构、组成及表面状态对电催化反应也有一定的影响。利用一些材料独特的物理化学性质还可以通过对工作电极表面进行改性实现合理控制质子可及性和反应物传质的效果，从而提高 NRR 的性能。为促进原料气的溶解及传质过程，有研究设计采用气体扩散电极，电极材料一般采用碳纤维骨架，在非水系电解液中，有学者将其替换为不锈钢网促进反应三相界面的形成(如图 6 所示) [132]。同样是针对电极结构设计，有研究对阴极结构进行优化，构建亲气–亲水异质结构电极，有效强化了电催化 NRR 过程[83]。

对于电极组成和表面状态，为降低工作电极附近的电子或质子浓度，提高电催化氮还原的选择性，在电极表面包裹一层非质子疏水保护层，在允许 N_2 通过的同时减缓质子向电极表面的扩散过程，从而降低电极附近质子的浓度，提升反应选择性。由于电极与外电路直接相连，因而对于电子的控制难度较大。但有学者构建了“金属绝缘体–催化剂”形式的电极，控制电子从电极穿过绝缘体到达催化剂金属层的隧穿，减缓电子生成、转移的速率。当电催化氮还原反应中电子的生成及转移过程为决速步骤时，NRR 的选择性有望实现新的突破[133]。Yan 等人在 0.1 M HCl 酸性电解液中利用质子过滤共价有机骨架控制反应物的扩散，该策略成功实现了抑制质子供应、增强氮气通量的效果，有效调节了 NRR 在酸性介质中的传质。在使用传统的碳基催化剂的情况下，获得了优异的电化学合成氨性能(NH_3 产率为 287.2 ± 10.0 $\mu g\ h^{-1} \cdot mg^{-1}$，法拉第效率为 54.5 ± 1.1%) [134]。类似地，通过在工作电极表面修饰一层疏水层如 PTFE 等阻碍水吸附并在电极表面吸引 N_2 来调节反应物质子和 N_2 的浓度，在抑制竞争性 HER 的同时促进 N_2 还原为 NH_3。在 NRR 中，PTFE 处理的 Au 纳米颗粒产氨的法拉第效率比未处理显著增加了四倍。通过对 NRR 反应机理的深入研究，可依据机理对电极的组成、表面状态进行合理优化，进而改善电子、质子的传递途径，从而提高 NRR 反应的活性及选择性。

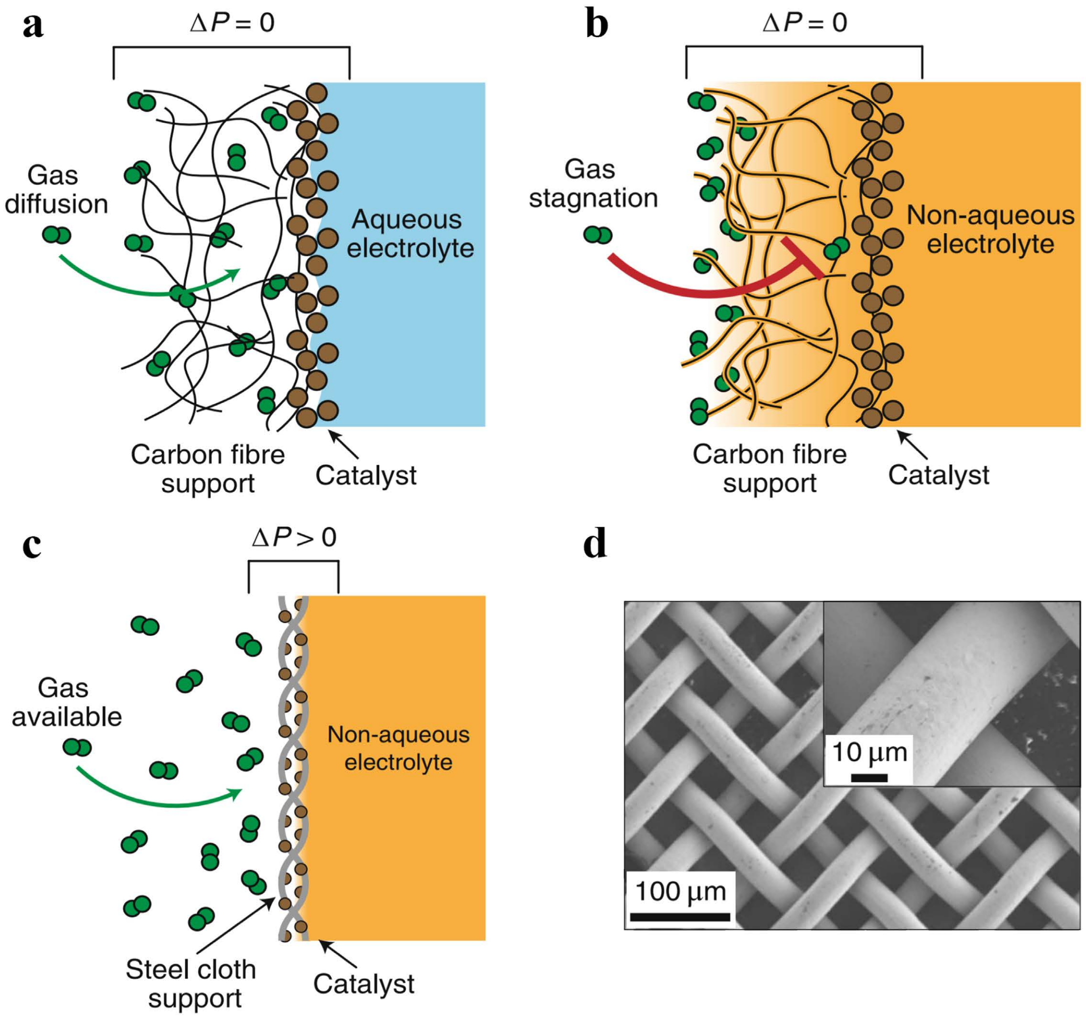

Figure 6. Structural design of the gas diffusion electrode for electrocatalytic nitrogen reduction [132]
图 6. 电催化氮还原气体扩散电极结构的设计[132]

4. 总结与展望

电催化氮还原将 N_2 转化为高附加值的化学品，为缓解全球变暖和化石燃料广泛燃烧造成的能源危机提供了一个极具研究前景的方向。然而，现阶段 NRR 研究所能达到的性能与美国能源部发表的指标要求之间还存在着较大的差距。由于 NRR 过程涉及较多的因素包括催化剂、电解液、反应界面等，任一方面都会对最终性能产生较大的影响，只将研究方向聚集在单一的方面难以实现电化学合成氨的实际工业应用及推广。在将 NRR 过程中研究方向向精细化、深入化推进的同时也需要关注整体体系的提高与优化。

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