科学通报 2025 年 第 70 卷 第 26 期: 4501 ~ 4511

离子液体在能源、环境和材料中的应用专题 进 展

《中国科学》杂志社
SCIENCE CHINA PRESS

离子液体在电催化合成氨中的应用

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2024-08-13 收稿, 2024-09-15 修回, 2024-10-21 接受, 2024-10-25 网络版发表
石油化工分子转化与反应工程全国重点实验室资助科研项目、中国科学院过程工程研究所前沿基础研究项目(QYJC-2023-03)、介科学与工程全国重点实验室自主部署项目(MESO-23-A08)和国家自然科学基金(22278402)资助

摘要 氨是农业化肥及绝大多数含氮化学品的上游工业原料, 同时也是优良的氢能载体, 因而备受关注. 与工业合成氨相比, 电催化合成氨反应条件温和且更易于利用可再生能源实现分散式氨生产. 然而, 由于氮气(N_2)强的化学惰性难活化、在水溶液中极低的溶解性、电化学反应析氢竞争性等, 造成氨的产率和法拉第效率较低, 其规模化氨生产仍存在着巨大挑战. 离子液体因具有结构可设计、功能可调控等特性, 在电化学领域已经实现了广泛应用. 本文综述了离子液体在电化学合成氨中的应用, 重点包括N_2在离子液体中的溶解性能, 离子液体对氨合成微环境调控, 以及离子液体作为电解质强化电催化合成氨性能, 同时阐述了离子液体的作用机制与机理, 并展望了离子液体在电催化合成氨体系中的发展趋势.

关键词 离子液体, 电催化, 合成氨, 界面修饰

氨(NH_3)是一种重要的农业、医药及化工原料, 更是无碳能源载体之一, 随着氨需求量的与日俱增, 预计2050年全球氨年产量可达2.04亿吨[1~5]. 目前, 合成氨的主流工艺为哈伯法, 但因氮气高度的化学稳定性($N\equiv N$, 941.69 kJ mol^{-1}), 该工艺需要高温(300~500℃)、高压(200~300 bar, 1 bar=10^5 Pa), 能耗高; 且原料氢气(H_2)生产75%采用化石资源, 碳排高[6~8]. “双碳”背景下, 各类低碳、零碳甚至负碳技术稳步推进, 其中, 通过绿H_2替代或水(H_2O)为质子源, 以及研发温和条件下合成绿氨新工艺是当前实现合成氨行业深度脱碳的关键[6,9~12].

除哈伯法外, 目前绿色合成氨工艺主要有生物催化、光催化和电催化三种[13~15](图1(a)). 其中, 电催化合成氨因具有更高的能源效率、与可再生能源(如太阳能、风能和热能)驱动的过程匹配性好、且在小型工艺设备即可操作的特点引发了众多关注[16]. 硝酸根/亚硝酸根电催化还原反应与N_2直接电催化还原反应是电化学合成氨的主要方法[17,18](图1(b)). 一方面, 由于在电催化反应过程中析氢反应($H^++e^- \rightarrow 1/2H_2$, E_0 = 0 V vs.可逆氢电极(RHE))比N_2还原反应($1/2N_2+3e^-+3H^+ \rightarrow NH_3$, E_0 = −0.148 V vs. RHE)在动力学上更有优势, 使得在合成氨过程中析氢反应较N_2还原反应更易发生[19]; 另一方面, N_2在水中的溶解度十分有限, 常温常压下仅有0.0006 mol L^{-1} [13], 反应过程中还存在杂质氮源污染等因素限制了电催化合成氨的发展[20]. 综上所述, 如何提升反应过程中原料气的溶解度, 增强N_2的活化性能, 降低析氢反应发生率是目前电催化合成氨中亟须解决的关键难题[5,21].

引用格式: 成曦, 韩丽君, 张聪, 等. 离子液体在电催化合成氨中的应用. 科学通报, 2025, 70: 4501–4511
Cheng X, Han L, Zhang C, et al. The application of ionic liquids in the electrocatalytic synthesis of ammonia (in Chinese). Chin Sci Bull, 2025, 70: 4501–4511, doi: 10.1360/TB-2024-0858

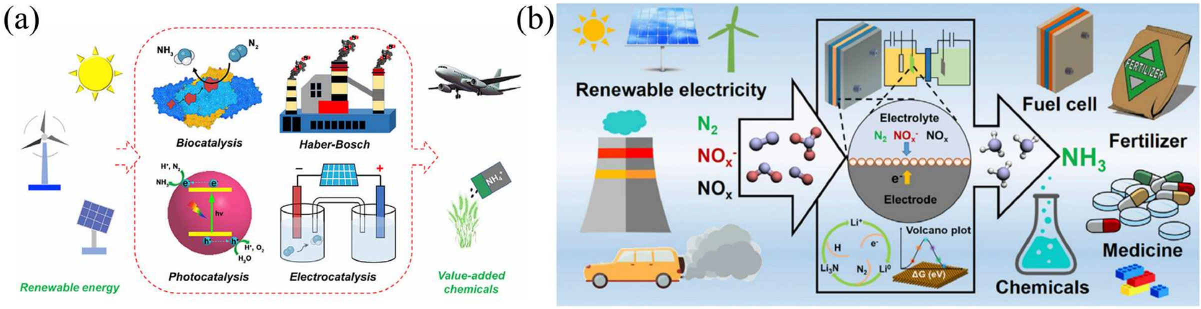

图 1　(网络版彩色)合成氨的主流技术路径. (a) 绿氨合成的主要方法[13]; (b) 硝酸根/亚硝酸根电催化还原和直接N_2电催化还原合成氨示意图[22]
Figure 1　(Color online) Mainstream technology path for ammonia synthesis. (a) Mainstream methods of green ammonia synthesis[13]; (b) schematic diagram of ammonia production by nitrate/nitrite and direct nitrogen electrocatalytic reduction[22]

离子液体是一类非常规绿色介质, 由阴离子和阳离子组成, 具有酸碱可调、氢键-静电-离子簇耦合等特点, 可形成不同于经典水系或有机系的“离子微环境”, 使其在化工分离、材料合成、化学反应等领域展现出广泛的应用潜力[23,24]. 在离子液体强化电催化氨合成的过程中, 其作用重点总结为以下三个方面: (1) 离子液体因阴阳离子结构可调, 可筛选设计出优异N_2溶解度的离子液体种类, 其溶解度可达同体积下水的20倍, 使反应过程中有更加充足的原料气, 为实现高效氨生产创造了有利条件[25,26]; (2) 采用离子液体修饰催化剂, 可构筑催化微环境, 从而大幅提升合成氨的反应性能[27]; (3) 两亲性离子液体作为电解质, 在强化传质的同时, 可抑制水的参与, 极大避免电解质中H_2的析出[28,29]. 因此, 本工作就上述三个方面, 对离子液体在电催化合成氨中的应用及机理机制进行了综述(图2).

1　N_2在离子液体中的溶解度

电催化N_2合成氨是一种绿色环保的生产方法. N_2除了极难活化以外, 在水性或者常规有机体系中超低的溶解度也是制约电催化合成氨性能的关键因素. 因此, 提高N_2在电解质中的溶解度是改善电催化合成氨性能的必要手段之一[30]. 目前, 离子液体在气体吸收领域已经取得重大进展, 研究人员探究了气体在离子液体中的溶解机制, 结合实验和模拟数据, 从而设计筛选出高N_2溶解度的离子液体, 有效改善N_2在电解质中溶解度低的问题[31~38].

气体在液体中溶解通常有两个途径: (1) 物理混合, 气体分子进入液体溶剂内部后穿插在溶剂分子间, 占用溶剂中未被占据的自由体积. (2) 分子间相互作用, 气体分子与溶剂分子产生相互作用力, 如范德华分子作用力等[25]. 液体对气体的溶解性通常用溶解度、摩尔分数或亨利常数来表示. 气体的溶解性越强, 溶解度或摩尔分数越大, 亨利常数越小. 表S1展示了N_2在23种不同结构的离子液体中的溶解性能.

不同结构的离子液体阴阳离子均影响N_2溶解度(图3), 当阳离子相同时, 阴离子摩尔体积越大: 四氟硼酸盐<三氟甲烷磺酸盐<双(三氟甲磺酰基)亚胺盐($[BF_4]^-$<$[TfO]^-$<$[TFSI]^-$), N_2溶解度越高. 随着阳离子烷基链的增长: 1-乙基-3-甲基咪唑<1-己基-3-甲基咪唑<1-癸基-3-甲基咪唑($[Emim]^+$<$[Hmim]^+$<$[Dmim]^+$)、三乙基(辛基)鏻<三己基(十四烷基)鏻($[P_{2228}]^+$<$[P_{666(14)}]^+$), N_2溶解度呈现显著上升趋势, 说明使用长烷基链有助

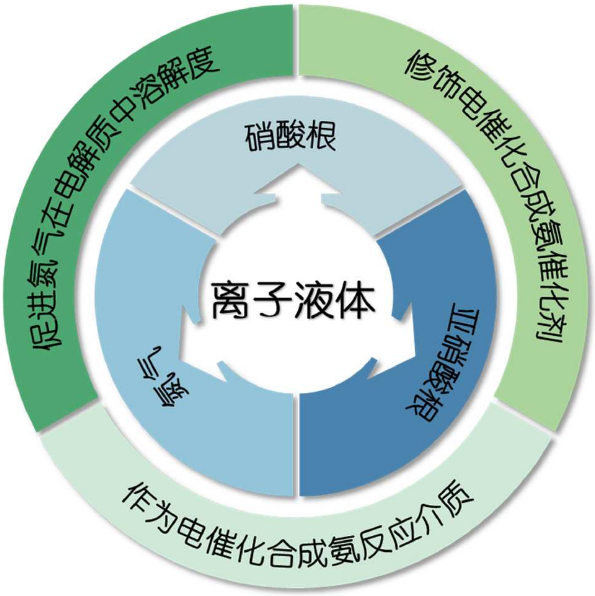

图 2　(网络版彩色)本工作的思路图
Figure 2　(Color online) Idea map for this work

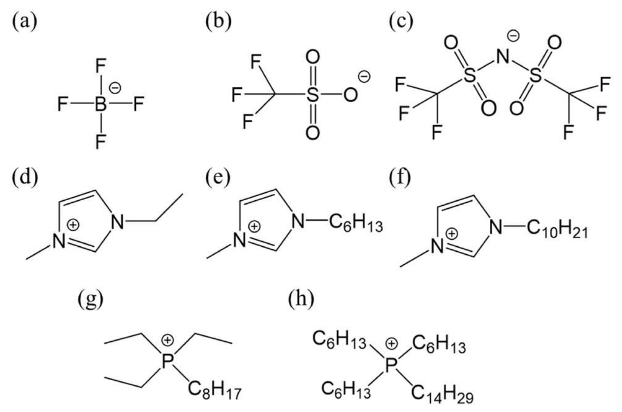

图 3 离子液体结构图. (a) $[BF_4]^-$; (b) $[TfO]^-$; (c) $[TFSI]^-$; (d) $[Emim]^+$; (e) $[Hmim]^+$; (f) $[Dmim]^+$; (g) $[P_{2228}]^+$; (h) $[P_{666(14)}]^+$. 根据文献[39]进行修改

Figure 3 Molecular structure diagram. (a) $[BF_4]^-$; (b) $[TfO]^-$; (c) $[TFSI]^-$; (d) $[Emim]^+$; (e) $[Hmim]^+$; (f) $[Dmim]^+$; (g) $[P_{2228}]^+$; (h) $[P_{666(14)}]^+$. Revised according to the Ref. [39]

于增强N_2溶解性[39]. Bentley等人[39]在压力为1.4×10^4 kPa下，采用重量法计算出N_2在12种离子液体中的溶解度，结果发现N_2的溶解度与离子液体的摩尔体积呈正相关性. 并且相同摩尔体积的离子液体中，具有环状结构的阳离子不利于提高N_2在其中的溶解度. Finotello等人[40]通过实验发现控制离子液体的摩尔体积可以提高对气体的溶解性，研究发现摩尔体积较小的咪唑基离子液体对N_2具有较高的气体溶解度，且N_2在咪唑基离子液体中的溶解度随温度升高而增加[41].

研究发现，使用氟化离子液体是一种提升N_2溶解度的有效方式. 离子液体阴离子上的氟原子可以与N_2发生相互作用，随着阴离子氟烷基链增长，N_2溶解度增加[25]. Zhou等人[32]合成了1-丁基-3-甲基咪唑七氟丁酸盐($[Bmim][CF_3CF_2CF_2COO]$)离子液体，计算发现气体在溶液中的溶解度可受到溶解熵的影响，溶解熵绝对值越大表明气体溶解度越大. 含氟离子液体有利于体系溶解熵向绝对值更大的方向移动，从而使N_2在$[Bmim][CF_3CF_2CF_2COO]$中的溶解度明显高于其他种类离子液体(1-丁基-3-甲基咪唑三氟乙酸盐($[Bmim][CF_3COO]$)、1-丁基-3-甲基咪唑三氟甲基磺酸盐($[Bmim][CF_3SO_3]$))，当N_2在303.15 K、4.24 MPa时，溶解度为0.98 mol kg^{-1}. Almantariotis等人[37]在研究中发现氟含量会影响N_2的溶解度，将咪唑基离子液体的阳离子进行一定程度的氟化，由1-辛基-3-甲基咪唑双(三氟甲磺酰基)亚胺盐([Omim][TFSI])氟化改性获得1-(3,3,4,4,5,5,6,6,7,7,8,8,8-十三氟辛基)-3-甲基咪唑双(三氟甲磺酰基)亚胺盐($[C_8H_4F_{13}mim][TFSI]$)离子液体，与未改性相比，N_2溶解度提升约1/3. 无论是通过氟化阳离子，还是增加阴离子的氟烷基链，都可以扩大体系中含氟结构区域，从而提升N_2的溶解度[38]. Kang等人[25]通过对比一系列不同氟化程度的离子液体证明了这个观点，同时发现在阴离子中加入含氟结构对提升N_2溶解度的作用要高于氟化阳离子的作用. 对比离子液体三丁基(辛基)鏻三(五氟乙基)三氟磷酸盐($[P_{4448}][eFAP]$)到三丁基-(3,3,4,4,5,5,6,6,7,7,8,8,8-十三氟辛基)-三(五氟乙基)三氟磷酸盐($[P_{444(8f)}][eFAP]$)，N_2的溶解度由摩尔分数0.0031提升到0.0038，而三己基十四烷基鏻壬氟丁烷磺酸盐($[P_{666(14)}][C_4F_9SO_3]$)到三己基十四烷基鏻十七氟辛烷磺酸盐($[P_{666(14)}][C_8F_{17}SO_3]$)使溶解度由0.0035提升到0.0052(图4(a)). Zhou等人[11]使用具有高N_2溶解度的特殊结构离子液体$[P_{666(14)}][eFAP]$，在常温常压下获得了高法拉第效率(Faradaic efficiency, FE)的合成氨电解质体系. 研究人员通过计算发现N_2与阴离子基团里的氟有强的相互作用，负电场越强与N_2的结合能力越强，其中$[eFAP]^-$上具有三个C_2F_5基团，进一步增强了与N_2的相互作用，在引入$[P_{666(14)}]^+$阳离子后，由于阴阳离子的协同作用，增大了N_2在$[P_{666(14)}][eFAP]$中的溶解度，FE达到60%(图4(b)~(e)). 此外，研究表明通过混合离子液体和氟化溶液发生协同作用，增加载流子，提高体系电导率，从而提高在电化学中的可用性[11,42]. Kang等人[42]研究发现在具有高N_2溶解度的1-丁基-1-甲基吡咯烷鎓三(五氟乙基)三氟磷酸盐($[C_4mpyr]$-[eFAP])离子液体的基础上添加一定量的氟化溶剂，因氟化溶剂中的相互作用氢键等效应，降低了溶液中具有极性作用基团的影响，强化了传质，进一步提升N_2在离子液体中的溶解度. 这些特性为提升电催化合成氨效率提供了潜在的可能性. 此外使用多孔结构增加N_2的溶解度是另一种具有潜力的方法，Avila等人[43]使用$[P_{666(14)}][TFSI]$制备稳定的金属有机骨架材料(metal-organic framework, MOF)悬浮液，这种悬浮液被称为多孔离子液体. 均匀分散的多孔MOF使体系中可吸附气体的自由体积增加，从而提升气体溶解度. 该团队进一步制备的多孔沸石咪唑框架-8(ZIF-8)低共熔离子液体悬浮液在不增加压力的条件下可以极大增加溶液对气体的吸附性[44]. 这种气体溶解度提升的方法为电催化合成氨保证充足的N_2源提供了新方案.

结合实验研究，使用模拟计算对离子液体提升N_2溶解度的结果加以验证. Tian等人[45]基于类导体屏蔽

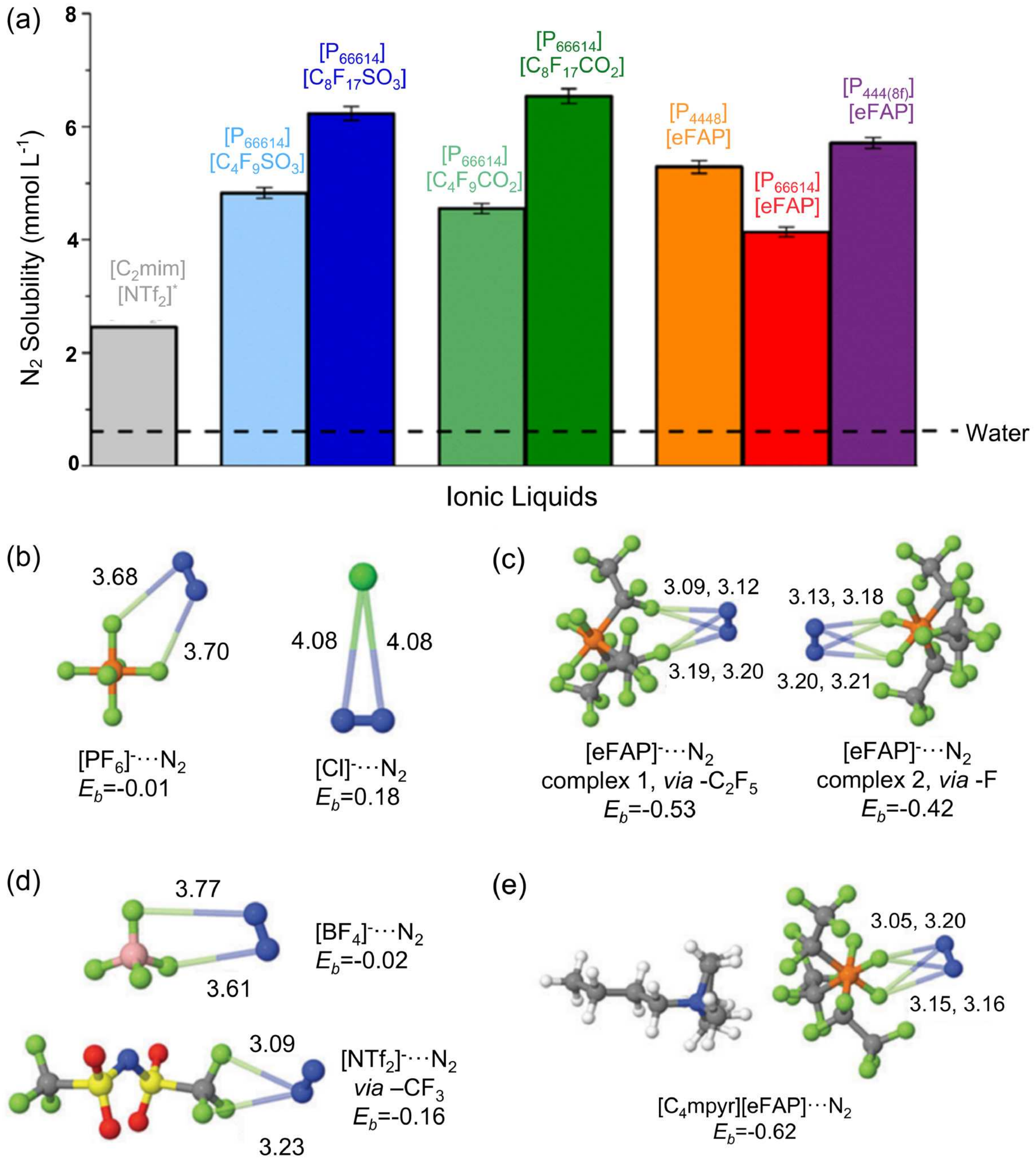

图 4 (网络版彩色)离子液体结构对N_2溶解度的影响. (a) N_2在不同离子液体中的溶解度[25]. (b)~(e) 离子液体与N_2相互作用示意图[11]

Figure 4 (Color online) Influence of ionic liquids structure on N_2 solubility. (a) Solubility of N_2 in different ionic liquids[25]. (b)–(e) Schematic diagram of the interaction of ionic liquid with N_2[11]

模型(conductor-like screening model, COSMO), 发展了离子片模型耦合机器学习(随机森林、梯度提升回归)的筛选设计新方法, 精准预测了N_2在离子液体中的溶解度. Tian等人[45]收集了不同温度和压力下N_2在38种离子液体中的385个溶解度数据, 离子片-随机森林、离子片-梯度提升回归对训练集的判定系数分别为0.9983与0.9999, 同时使用[Hmim][eFAP]进行实验验证, 实验结果与模型预测高度吻合, 表明两种模型可以快速、准确地预测不同离子液体对N_2的溶解度.

2 离子液体修饰催化剂界面

离子液体除了在提升N_2溶解度方面有着促进作用, 同时在协同活化N_2、构筑催化微环境方面起着重要作用. 科研人员依据元素周期表, 研究了大多数元素用于

合成氨催化剂制备，发现Ⅷ族元素相比其他元素有更好的氨合成催化活性(图5)[46,47]. 因反应过程中析氢反应造成能量消耗，如何提升催化剂在电催化合成氨中的活性和选择性是众多科研人员研究的方向[48].

电催化硝酸根/亚硝酸根合成氨可以在温和条件下实现“变废为宝”，但电催化硝酸根/亚硝酸根合成氨目前最大的难点就在于催化剂选择性低、稳定性差等[49~54]. 因此, 诸多研究利用离子液体对催化剂进行修饰改性，通过调控催化剂表面电子结构和催化微环境，从而提升催化体系的选择性和稳定性. Qin等人[55]通过设计催化剂，使用*n*-丁基咪唑双(三氟甲磺酰基)亚胺盐修饰氧化钴(Co_3O_{4-x})，调节Co中心的酸度及电极表面微环境等，在增加N_2溶解度的同时抑制了析氢反应，成功将产氨速率由16 mg h^{-1} mg_{cat}^{-1}左右提升至30.23±4.97 mg h^{-1} mg_{cat}^{-1}，以及将FE由55%提升至84.74%±3.43%.

Becker等人[56]发现使用二氯化二茂钛(Cp_2TiCl_2)可以在室温环境下将N_2还原为NH_3，但该反应体系同样存在产氨率和电流效率过低的问题. Katayama等人[57]从Cp_2TiCl_2可以在–2.2 V电压下将N_2转化生成NH_3这一实验出发，用具有疏水性的离子液体1-丁基-1-甲基吡咯烷吡啶三(五氟乙基)三氟磷酸盐($[C_9H_{20}N]$-$[(C_2F_2)_3PF_3]$)修饰Cp_2TiCl_2，将其涂覆在工作电极表面，产氨率和电流效率分别提升27%和0.2%. $[C_9H_{20}N]$-$[(C_2F_2)_3PF_3]$离子液体的添加促进了Cp_2TiCl_2上氯离子的解离，生成的金属配合物二氮桥联双二钛三环戊二烯配合物($[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$)提升了电催化合成氨的性能，同时$[C_9H_{20}N][(C_2F_2)_3PF_3]$降低NRR反应活化能, 进一步促进合成氨反应.

由于钼基催化剂具有高的N_2吸附位点，近年研究人员对改性钼基催化剂在电催化合成氨中的应用进行了深入研究[58,59]. Mao等人[60]采用吡啶型离子液体功能化聚吡咯/氧化石墨烯复合物(pyridinium-ILs/PPy/GO)负载硫化钼(MoS_2). 研究发现吡啶中取代基的位置和种类可以影响电催化合成氨性能，当氨基在对位或者邻位时, pyridinium-ILs/PPy/GO可以促使结晶度更好的MoS_2合成，其中2-氨基-3-羟基吡啶合成的催化剂氨产率可达22.79 μg h^{-1} mg_{cat}^{-1}.

三维纳米结构具有高比表面积和更多的分子、离子传输通道，Chen等人[61]将离子液体用于三维铑(Rh)颗粒催化剂合成，甲酸正辛铵离子液体在反应中不仅可以作为溶剂, 同时可以有效促进Rh^{3+}还原. 与水体系相比，离子液体在三维Rh颗粒催化剂的制备过程中还可起到模板作用, 调控催化剂颗粒大小等. 电催化研究表明, 在0.1 mol L^{-1}氢氧化钾(KOH)电解质中三维Rh催化剂的产氨率高达35.58 μg h^{-1} mg_{cat}^{-1}，且远高于诸多贵金属催化剂的电化学稳定性和选择性.

酞菁铁(FePc)是一种铁掺杂的过渡金属化合物催化剂, 通常具有重叠层状结构, 这种结构相对阻碍了层间的活性位点参与反应. Li等人[62]利用1-丁基-3-甲基咪唑氯盐([Bmim][Cl])和[Bmim][TFSI]混合液打破FePc层间π键，使催化剂暴露出更多活性位点，所获得

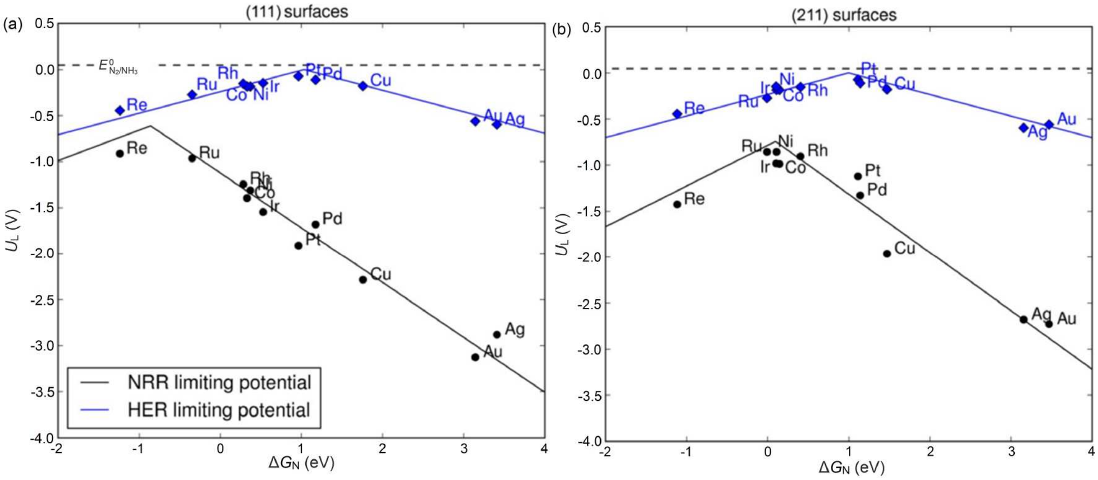

图 5 (网络版彩色)催化剂差异对合成氨催化活性的影响对比. 析氢反应(蓝色)和N_2电催化还原反应(黑色)在金属(111)表面(a)和(211)表面(b)上的火山图[46]

Figure 5 (Color online) Comparison of the effect of catalyst differences on the catalytic activity of ammonia synthesis. Volcano of hydrogen evolution reaction (blue) and nitrogen reduction (black) reactions on metal (111) surface (a) and (211) surface (b)[46]

的FE和氨合成速率为30.59%和24.25 μg h^{-1} $mg_{cat}{}^{-1}$. 近年来，离子液体不仅在修饰金属基催化剂方面初见成效，同时在非金属基催化剂方面的应用也逐渐被人们所重视[63~67]. Zhang等人[68]以[Bmim][BF_4]作为原料，合成含有硼、氮、氟的三元掺杂碳. 三元掺杂碳中引入的B、F原子可以干扰催化剂中的析氢活性位点，降低合成氨决速步的反应能垒，B、F原子为N_2的吸附提供路易斯酸位点，共同提高电催化合成氨性能，氨产率可达41 μg h^{-1} $mg_{cat}{}^{-1}$.

3 离子液体作为电解质

离子液体具有较宽的电化学窗口、高离子电导率等特性为电催化合成氨提供更加有利的环境. 如含氟化基团$[eFAP]^-$的离子液体可以在提高N_2溶解度的同时避免析氢反应[69]，或使用$[P_{666(14)}]^+$作为质子梭，与乙醇相比，其在阳极被破坏的程度更小，可提升系统的稳定性[10]. Pappenfus等人[70]使用*N*-丁基-*N*-甲基吡咯烷双(三氟甲烷磺酰)亚胺盐(Pyr14-TFSI)作为溶剂，添加氮化锂(Li_3N)进行电化学评价，平均氨产率达到42.8%，使用咪唑类离子液体为溶剂，锂盐种类为高氯酸锂($LiClO_4$)时氨的生产效率约5.1%. Suryanto等人[69]使用一定比例的疏水高氟化离子液体[C_4mpyr][eFAP]，利用离子液体拓宽体系电化学窗口的同时抑制了竞争性析氢反应，使电解质电导率达1.95 mS cm^{-1}，电化学窗口为3.40 V, 更适合电化学还原氮气, 在此体系下，产氨量为2.35×10^{-11} mol s^{-1} $cm_{GSA}{}^{-1}$, FE为32%(图6(a)). Sansiñe-

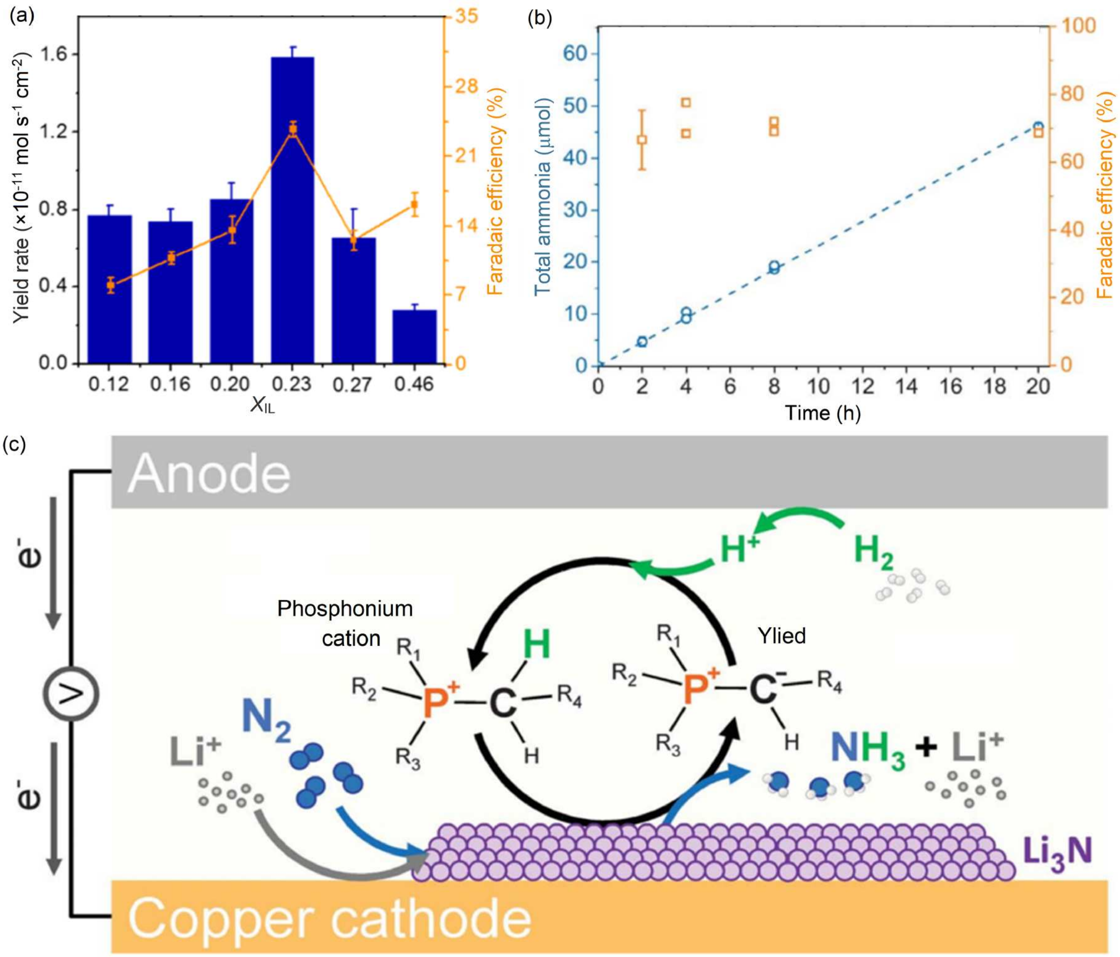

图 6 (网络版彩色)离子液体优化电化学反应介质. (a) 离子液体添加比例与氨产率和法拉第效率的关系[69]; (b) 含0.1 mol $L^{-1}$$[P_{666(14)}]$[eFAP]的电解质中氨产率和法拉第效率的关系[73]; (c) 离子液体在电催化合成氨过程中作用示意图[73]

Figure 6 (Color online) Optimisation of electrochemical reaction media by ionic liquids. (a) Relationship between ionic liquid addition ratio and ammonia yield rate and Faradaic efficiency[69]; (b) Relationship between ammonia yield rate and faradaic efficiency in an electrolyte containing 0.1 mol L^{-1} $[P_{666(14)}]$[eFAP][73]; (c) Schematic diagram of the role of ionic liquids in the ammonia synthesis process[73] na等人[71]设计并表征了具有良好质子传导性和热稳定性的苯并咪唑类离子液体, 它可以在较宽的温度范围内进行电催化合成氨, 由于电解质具有疏水性, 避免了过多降低电子利用率的竞争性析氢反应. 同时该团队发现[72]在添加了离子液体的体系中, 系统压力范围可以达到0~20.7 kPa, 温度范围可以达到−30~400℃, 使反应具有更充足的尝试空间.

质子梭是一种在电解质中用于传输质子的载体, 以往研究中质子梭在反应生成NH_3的过程中被消耗[74]. Suryanto等人[10]认为, 在锂介导氮还原合成氨的系统中牺牲性质子梭是限制系统性能和寿命的一个重要因素. 在研究中发现[$P_{666(14)}$][eFAP]的阳离子可以作为可逆的质子梭, 同时还提供了额外的离子电导率, 使锂离子在系统中的还原速度比在乙醇为质子源的系统中快许多. 在此体系中, FE可提高至近70%且在20 h的实验中NH_3产率达到0.053 mol s^{-1} cm^{-2}(图6(b), (c))[73].

4 总结与展望

在温和条件下实现高效电催化合成氨是绿氨工业的关键, 本文综述了离子液体在电催化合成氨三个方面的应用进展: (1) 离子液体促进N_2在电解质中溶解度. (2) 离子液体修饰电催化合成氨催化剂. (3) 离子液体作为电催化合成氨反应介质. 研究表明离子液体的添加对提升合成氨性能有正向促进作用. 尽管电催化合成氨为实现可持续和分布式氨生产提供了一条前景广阔的途径, 但电催化合成氨大多数都停留在实验室阶段, 距离工业要求的电流密度、产氨量及FE仍有一定差距, 且尚有许多作用机理不明确, 工艺过程中设计的科学技术难题面临解决. 目前限制电催化合成氨的主要瓶颈是催化剂与电解质两部分, 未来可以通过深入探究以下方面来提升电化学合成氨的整体性能: (1) 设计合成具有特殊结构的氟化离子液体用于提高原料气的溶解度: 未来可以着眼于将分子模拟与实验相结合, 定向开发新型功能化离子液体, 研究不同结构对合成氨性能的影响. 对多孔离子液体提高N_2溶解度在电催化合成氨中的应用有待深入探索, 可以尝试结合氟化离子液体, 为合成氨提供良好的反应环境, 形成高效电催化体系. (2) 使用离子液体修饰催化剂并探究作用机制: 可以深入探究离子液体组成结构与催化剂相互作用的机理机制, 优化催化剂结构和体系微环境, 以显著提高氨的产率和法拉第效率. (3) 与其他方式协同作用: 同时将电催化与光催化、生物催化等作用方式交叉融合, 综合利用原位表征和模拟计算等多种手段, 进一步明晰离子液体在电催化合成氨体系中的作用机理与机制.

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补充材料

表S1　N_2在不同离子液体中的溶解性能

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Summary for “离子液体在电催化合成氨中的应用”

The application of ionic liquids in the electrocatalytic synthesis of ammonia

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Ammonia is a versatile compound that has recently attracted considerable interest as a green hydrogen energy carrier. The ability of ammonia to efficiently store and transport hydrogen, which is essential for the development of sustainable energy systems, makes ammonia’s potential in this field enormous. The conventional method of ammonia synthesis, namely the Haber-Bosch process, is energy intensive, relies on fossil fuels, and results in significant carbon emissions. In contrast, electrochemical ammonia synthesis offers a promising alternative that can utilize renewable energy sources, thereby reducing environmental impact and enabling decentralized production.

Electrochemical ammonia synthesis is based on the principle of using electricity to drive chemical reactions to synthesize ammonia from hydrogen and nitrogen or nitrate. This method offers the potential for significant energy savings and carbon emission reductions compared to the Haber-Bosch process. In addition, it can be combined with technologies such as thermal and photovoltaic, thereby facilitating a more sustainable and flexible ammonia production infrastructure. However, the electrochemical ammonia synthesis approach faces significant challenges that hinder its practical application and industrialization.

One of the main difficulties in the electrochemical synthesis of ammonia is the inherent inertness of the nitrogen molecule, which requires considerable energy to break its strong triple bonds. This property of nitrogen makes the electrochemical reduction process complex and inefficient. In addition, the electrochemical reduction process suffers from many side reactions that compete with the desired ammonia synthesis reaction. These side reactions not only cause unnecessary energy loss, but also reduce the overall efficiency and yield of ammonia production. Currently, the relatively low ammonia production rates and Faraday efficiencies achieved through electrochemical ammonia synthesis make the process inadequate for large-scale industrial applications. Addressing these issues is critical to advancing electrochemical ammonia synthesis as a viable alternative to traditional ammonia synthesis methods.

This review focuses on the role of ionic liquids (IL) in improving the efficiency of electrochemical ammonia synthesis. ILs have unique properties that can be used to enhance the performance of electrochemical ammonia synthesis, including high ionic conductivity, low volatility, and high nitrogen solubility. This review explores how different types of ionic liquids can improve the efficiency of ammonia synthesis through three primary mechanisms. Firstly, IL can increase the solubility of nitrogen in solution, providing more nitrogen for the reduction reaction. Secondly, they can modulate the behavior of the catalyst in the electrolyte system, optimizing the reaction environment and increasing catalytic activity. Finally, by utilizing IL to adjust the internal environment of the electrolyte system, researchers can achieve more efficient nitrogen reduction and higher ammonia yields.

In addition, the review suggests future research directions to overcome the limitations of current electrochemical ammonia synthesis. These directions include developing functionalized IL to enhance nitrogen solubility, studying new catalyst materials that work in concert with IL, and optimizing the electrolyte to maximize ammonia productivity and efficiency.

In summary, while electrochemical ammonia synthesis offers a promising pathway toward sustainable and decentralized ammonia production, significant challenges remain. The application of IL provides a potential pathway to address these challenges and improve the efficiency of the electrochemical ammonia synthesis process. Continued research in this area is essential to realize the potential of electrochemical ammonia synthesis and contribute to the development of a greener and more sustainable hydrogen economy.

ionic liquid, electrocatalysis, ammonia synthesis, interface modification

doi: 10.1360/TB-2024-0858