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Hans汉斯

燃料电池Fe/N/C氧还原催化剂近十年研究进展

谢　敏，晁自胜

长沙理工大学，湖南　长沙
Email: 1225028838@qq.com

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摘　要

燃料电池阴极贵金属铂(Pt)基催化剂的高成本阻碍了其大规模商业化应用。铁和氮共掺杂的碳材料(Fe/N/C)在酸性条件下具有较高的活性和四电子选择性，使其成为最有可能替代铂的催化，近年来已经成为研究热点。为提高Fe/N/C催化剂的活性，创新策略被不断提出，金属有机框架(MOFs)和单原子催化剂(SACs)开始运用于催化剂的探究，Fe/N/C催化剂展现出更加优异的性能。由于氧还原过程的复杂以及热解产物的成分不确定性，Fe/N/C的催化机理和活性位点一直存在争议。近年来随着科技的进步，各种原位和非原位技术的运用，Fe/N/C的催化机理和活性位点逐渐清晰化。本文视角独特，详尽地介绍Fe/N/C近十年来研究进展，并且指出存在的主要问题，希望能为该类催化剂的优化设计指明方向。

关键词

燃料电池，氧还原催化剂，Fe/N/C，金属有机框架，单原子催化剂

Research Progress of Fe/N/C Oxygen Reduction Reaction Catalyst for Fuel Cell in Past Decade

Min Xie, Zisheng Chao

Changsha University of Science and Technology, Changsha Hunan
Email: 1225028838@qq.com

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Abstract

The expensive Pt-based catalyst for fuel cell cathode hinders its large-scale commercial applica-

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tion. Due to their high activity and four electron selectivity, iron and nitrogen Co-doped carbon materials (Fe/N/C) have been considered as the most likely catalyst to replace platinum. In recent years, it has become a research hot-spot. In order to improve the activity of Fe/N/C catalyst, innovative strategies have been put forward constantly. Metal organic framework (MOFs) and single atom catalyst (SACS) have been used in the exploration of catalyst research. Fe/N/C catalyst shows more excellent performance. The catalytic mechanism and active sites structure of Fe/N/C have been controversial for a long time because of the complex ORR path and uncertainty of pyrolysis products composition. In recent years, with the development of science and technology, the catalytic mechanism and active sites of Fe/N/C are becoming much clearer. This paper has a unique perspective. We introduce the research progress of Fe/N/C in past decade in detail, and the main problems are pointed out, hoping to point out the direction for the optimal design of this kind of catalyst.

Keywords

Fuel Cell, Oxygen Reduction Catalyst, Fe/N/C, Metal Organic Framework, Single Atom Catalysis

1. 引言

能源危机和全球变暖引起了人们对清洁可再生能源的探索，寻找可代替化石能源的新型能源装置是现在全球关注的焦点问题之一[1] [2] [3] [4] [5]。质子交换膜燃料电池(PEMFCs)因具有高效率、零排放、可在室温快速启动等优点，是目前唯一有希望用于商用汽车的燃料电池，引起了广发的研究兴趣[6] [7] [8] [9] [10]。该装置采用全氟磺酸型质子交换膜为电解质，氢气作为燃料，空气或纯氧为氧化剂，是最成熟的燃料电池类型。与阳极氢气快速的氧化反应相比，阴极氧气还原(ORR)是一个缓慢的动力学过程，目前商用的在 PEMFC 中，阴极氧还原催化剂为 Pt/C 或 PtRu/C [11] [12]。铂的储量稀缺，价格昂贵，根据调查显示，铂的成本约占整个燃料电池装置的 56% [13] [14]；此外铂基催化剂稳定性差，铂纳米粒子在高温高湿的腐蚀性环境下会发生溶解和部分团聚现象，从而导致活性位点减少和比表面积降低，氧还原活性降低[14] [15] [16]；同时，接触一氧化碳(CO)会让铂基催化剂中毒，研究表明，即便是很少量的 CO (10~20 ppm)也会造成铂基催化剂活性大幅下降[17] [18]。这些问题阻碍了质子交换膜燃料电池的规模化应用，研究者们把目光转向非贵金属催化剂领域，为探索高性能、低成本、材料来源广泛的催化剂做出了巨大的努力。非贵金属催化剂有很多种，如过渡金属氮碳(M/N/C，M = Fe，Co，Ni，Cu，Mn 等)、杂原子掺杂碳、缺陷碳、过渡金属氧化物、氮化物和/或碳化物、过渡金属硫族化合物等[19]。其中，铁和氮共掺杂的碳材料(Fe/N/C)因为在酸性和碱性条件下均具有较高的活性和四电子选择性，被视为最有前景的可替代铂的催化剂[12] [20] [21]。图 1 [22]为 Fe/N/C 催化剂作为质子交换膜燃料电池阴极催化剂的应用以及可能的活性位点示意图。

从 1964 年金属大环化合物的发现到今天的单原子催化剂，经过五十多年的努力，Fe/N/C 催化剂的活性有了大步提升。Fe/N/C 可以通过将具有 Fe-N4 配位的螯合物[23] [24] [25] [26]或者简单铁盐[27] [28]、含氮聚合物[29]-[34]或其他富氮小分子[35] [36]的简单前驱体在碳载体上高温热解获得。近年来，活性提升策略不断推陈出新，创新方法层出不穷。有的研究另辟蹊径，通过将含氮和碳的生物质材料比如棉花

[37]、内酯豆腐[38]、壳聚糖[39]等活化后再和金属铁盐热解的方法，制备出具有氧还原电催化性能的催化剂。球磨法、模板法、掺杂第四种元素法被不断用于 Fe/N/C 的制备。一种通过高温热处理金属有机框架(MOFs)的方法获得的 Fe/N/C 氧还原催化剂[40]-[46]，因其具有高的含氮量以及比表面积，具有良好的催化活性。同时，随着科学技术的进步，催化剂的尺度从纳米级进一步降至原子级，单原子 Fe/N/C 催化剂因其展现出超高的催化活性[25] [47] [48] [49]，具有良好的应用前景。到目前为止，Fe/N/C 催化剂在碱性条件下，展现出优于铂基催化活性[24] [50] [51] [52]，在酸性条件下与铂基催化剂也具有可比性[53]-[59]。其中，文献中报导的活性最高 Fe/N/C 催化剂是使用几种创新方法的结合制备的，其在电压 0.88 V，阻抗补偿(0.88 $V_{iR\text{-}free}$)情况下的电流密度可达 47 $mA\cdot cm^{-2}$，该催化剂 0.9 $V_{iR\text{-}free}$ 下的电流密度可达 22 $mA\cdot cm^{-2}$，实测极限功率可达 1.18 $W\cdot cm^{-2}$，均为目前报道的最高值[60]，具体工作后面将会详细介绍。

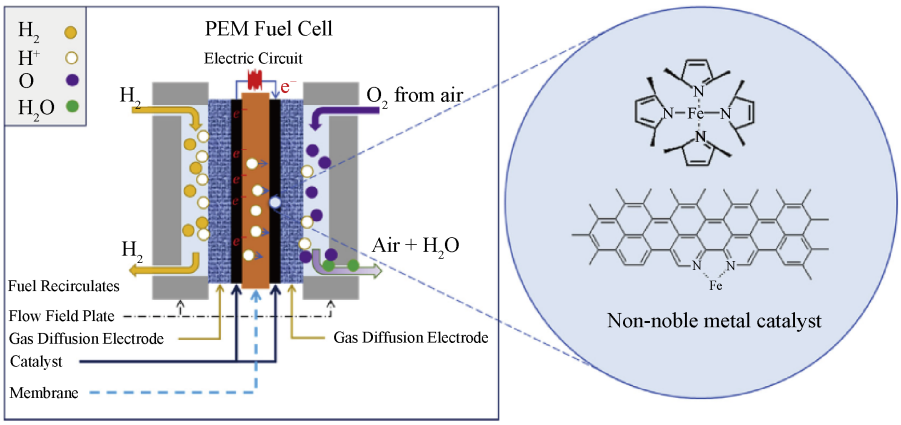


Figure 1. Application of Fe/N/C catalyst in PEMFC
图 1. Fe/N/C 催化剂在 PEMFC 中的应用

与此同时，由于催化机理对于研究高性能催化剂至关重要，研究者对于催化机理和活性位点的探索也从未停止。然而，Fe/N/C 经过热解后，原来的结构遭到破坏，并且同时存在有机、无机分子团以及大量杂原子复杂的电子结构，使得探索催化剂催化机理存在较大困难，催化机理和活性位点问题一直存在争议[54] [61]。近十年来，随着科学技术的进步，研究者们致力于发展各种原位和非原位技术，如 X 射线吸收光谱、飞行时间二次离子质谱(ToF-SIMS)、穆斯堡尔谱、和 X 射线光电子能谱(XPS)以及理论计算等，或设计明确结构的模型催化剂来进行结构表征和分析，对催化剂的催化机理和活性位点的确认展开大量探究工作[62] [63] [64] [65] [66]。虽尚未有明确证据和定论可以说明催化剂的具体催化过程，但是取得的进展还是值得关注[67] [68] [69]。

关于 Fe/N/C 催化剂较早期的研究进展已经有多篇优秀论文报道过[14] [16] [18] [21] [70] [71]，本文不再赘述，主要将重点放在最近的十年(2009~2020) Fe/N/C 催化剂的研究进展。目的是在分析已有突破的基础上，对 Fe/N/C 催化剂的研究，包括活性位点和催化机理、制备方法、稳定性和衰减机理进行全面的总结和论述，希望通过本文精心而系统的归纳，帮助人们快速了解 Fe/N/C 催化剂的研究现状，并为 Fe/N/C 的优化设计提供思路。

2. 活性提升创新策略

传统的 Fe/N/C 制备方法，一般包含五个关键步骤：制备前驱体→高温热解→酸刻蚀→高温热解→酸刻蚀，中间还有洗涤干燥等，最后收集催化剂粉末。近几年，研究者们在前人基础上不断探索和创新，金属有机框架(MOFs)、球磨法、模板法、掺杂第四种元素、单原子催化剂等策略被不断创新地用于 Fe/N/C

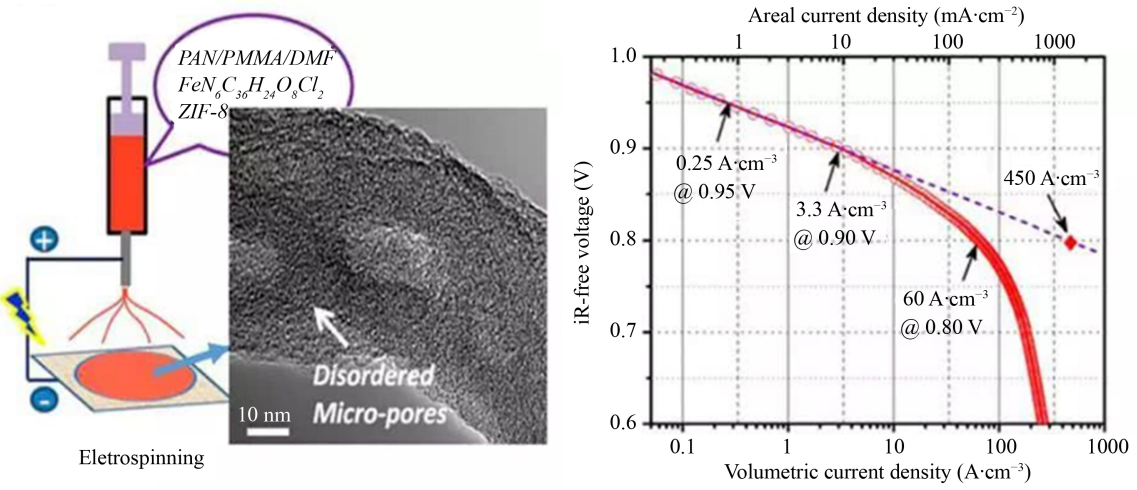
的合成，催化剂的活性不断提升。下面我将系统地论述近几年意义重大的创新突破策略。

2.1. 氮碳前驱体的丰富多样化

制备 Fe/N/C 的前驱体包括铁的前驱体、氮前驱体、碳前驱体(碳载体)，有的物质可以同时提供两种或两种以上所需元素，则为二者共同的前驱体。铁的前驱体最大的创新是发现可以用普通铁盐和氮和碳的前驱体共热制备 Fe/N/C 催化剂，而不仅限于价格较昂贵的金属大环化合物，这项工作于 1989 年由 Yeage 团队完成[72]。近几十年来，铁的前驱体上并没有较大改变。

意义重大的发现是 MOFs 开始用作氮碳前驱体。这项创新始于 2011 年，Dodelet's 团队[73]在《自然》上发表的一项突破性的结果，该报道通过乙酸铁、邻菲咯啉、沸石－咪唑酸盐骨架(ZIF-8)来制备 Fe/N/C 催化剂。ZIF-8 是一种金属有机框架材料(MOFs)，分子式为 $ZnN_4C_8H_{12}$，氮元素丰富。这种特殊的 MOF 拥有高氮含量和高微孔比表面积的特点，这两个因素对金属/N/C 催化剂的 ORR 活性都是至关重要的[74] [75]。事实证明，这是一种理想的氮碳前驱体材料。用该方法制备的电催化剂制成阴极，在 H_2-O_2 系统燃料电池中测试，在 0.8 V-free 的体积电流密度达到 230 A·cm^{-3}，这与美国能源部提出的 2020 年关于非贵金属催化剂的体积活性目标(300 A·cm^{-3})接近。这种前所未有的催化活性和功率密度，使 Fe/N/C 催化剂成为质子交换膜燃料电池铂基阴极催化剂的替代品展现出可能性，促进了更多基于 MOFs 的 Fe/N/C 催化剂的研究[44] [76] [77]。

2015 年，Liu 课题组[78]用 ZIF-8 纳米颗粒与三-1,10-菲咯啉乙酸铁(II)通过电纺丝法合成了纤维状催化剂 Fe/N/CF。将前驱体共同包裹在聚丙烯腈/聚甲基丙烯酸甲酯聚合物(PAN/PMMA)纤维中，然后高温热解，得到微孔结构主导的碳纤维如图 2(a)所示。Fe/N/CF 纤维的密集的微孔有利于形成高密度的 Fe-Nx 位点，连续的碳纤维网络结构促进了电子沿碳纤维传输，碳纤维网络间的大孔有利于氧和水的传递，上述优点的组合赋予 Fe/N/CF 优异的 PEMFC 性能。图 2(b)显示了电池高压段 0.95 ViR-free、0.9 ViR-free、0.8 ViR-free 的体积电流密度分别为 0.25 A·cm^{-3}，3.3 A·cm^{-3}，60 A·cm^{-3}，转换为面积电流密度依次为 0.75 mA·cm^{-2}，10 mA·cm^{-2} 和 182 mA·cm^{-2}。0.8 ViR-free 外推体积电流密度最高达到 450 A·cm^{-3}。



(a) (b)

Figure 2. (a) The composite V of polymer, TPI salt and zif-8 nanoparticles was prepared by electrospinning. The Fe/N/CF schematic diagram was synthesized by pyrolysis; (b) the Tafel diagram of Fe/N/CF kinetic activity was tested by fuel cell

图 2. (a) 静电纺走丝制备聚合物、TPI 盐和 ZIF-8 纳米颗粒的复合物，经过热解合成 Fe/N/CF 示意图；(b) Fe/N/CF 动力学活性的 Tafel 图

随着原子分辨率表征技术和理论模型的发展，电催化剂的表征从纳米尺度降到原子尺度，单原子催化(SACs)已成为多相催化的前沿领域之一，许多科学家相继报导了关于 Fe/N/C 单原子催化剂的合成和研究工作[12] [79] [80]。目前报道的性能最好的催化剂，是单原子催化剂与 MOF 作为前驱体的创新的完美结合。2019 年，水江澜[60]课题组以 ZIF-8 为原料制备的凹面 Fe/N/C 单原子催化剂，其制备过程流程如图 3(a)所示：首先在 ZIF-8 的外表面包覆一层介孔 SiO_2，再通过中温(650˚C)预碳化处理，实现 ZIF-8 载体表面 Zeta 电位由正向负的转变，从而可以大量吸附和锚定正价铁离子，再经过高温热处理，得到高铁载量的 Fe-N-C 催化剂。而其中的介孔 SiO_2 包覆处理，可在预碳化过程中诱导 ZIF-8 菱面十二面体面和棱上的非均匀热应力分布，从而形成凹面结构，提高外比表面积，图 3(b)和图 3(c)分别为添加和未添加 SiO_2 包覆的对比图。在 PEMFC 条件下测试表明(图 3(d))，该催化剂达到了美国能源部(U.S. DOE)设定的非铂催化剂 2018 年活性目标(0.88 ViR-free 下 PEMFC 电流密度 44 mA·cm^{-2})。该催化剂 0.9 ViR-free 下的电流密度可达 22 mA·cm^{-2}，实测极限功率可达 1.18 W·cm^{-2}，为目前报道的最高值[60]。

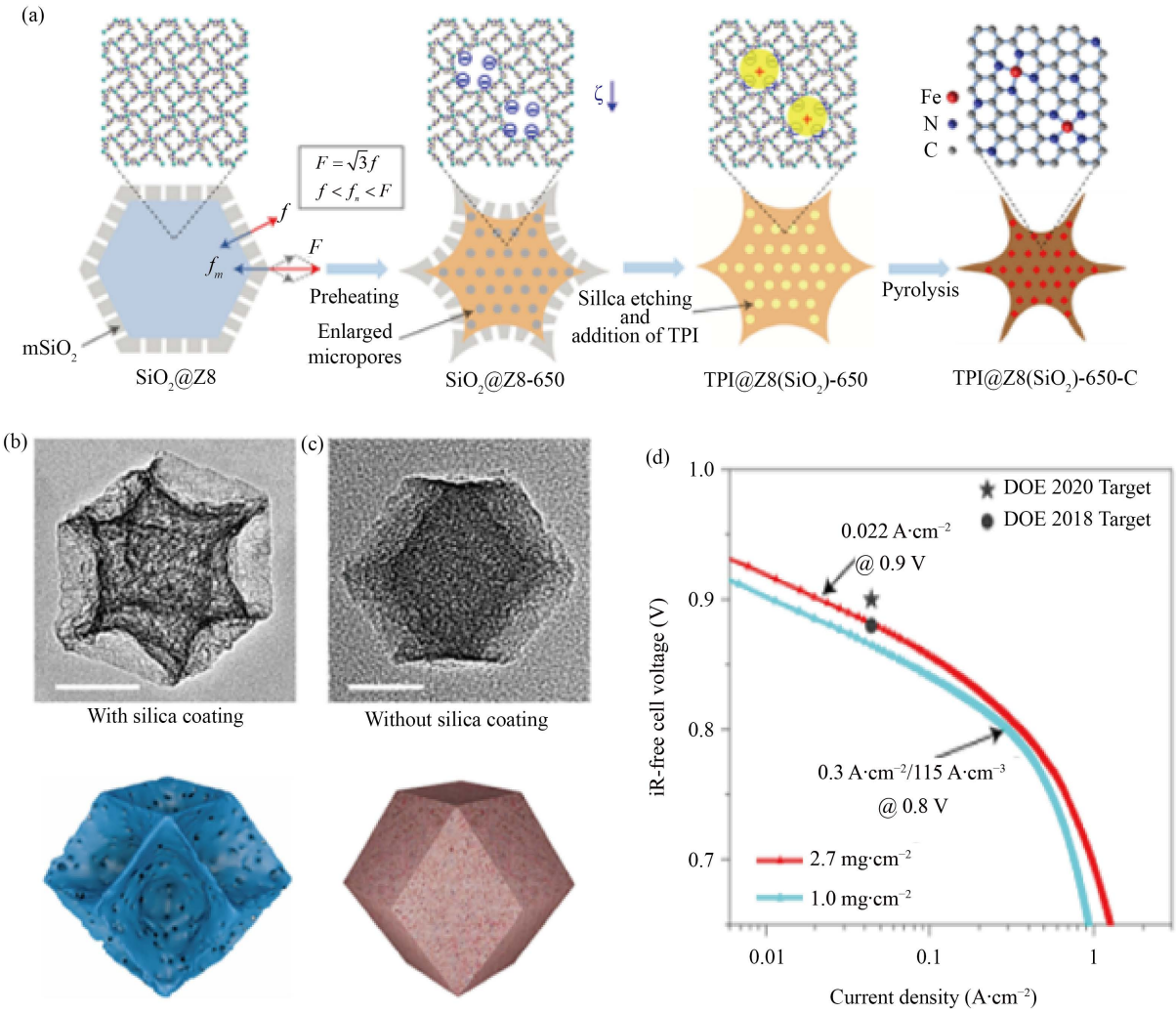


Figure 3. (a) Preparation process of concave Fe-n-C monoatomic catalyst; (b) morphology of planar catalyst; (c) morphology of concave catalyst; (d) Tafel diagram of mechanical activity of fuel cell test

图 3. (a) 凹面 Fe-N-C 单原子催化剂的制备流程；(b) 平面催化剂的形貌；(c) 凹面催化剂形貌；(d) 动力学活性的 Tafel 图

无数的实验数据证明，MOFs 是一种比较理想的氮碳前驱体原料。除 MOFs 外，氮的前驱体还包括三聚氰胺[81]、聚苯胺[82]、聚苯二胺[83]、聚吡咯等含氮聚合物[84]。同时，碳载体的形式也呈现出多样化，用于 Fe/N/C 催化剂的碳载体还包括炭黑[85]、石墨烯[86] [87]、碳纤维[78]、碳纳米管[88] [89]、MXene (一种新型二维碳化钛材料) [90]，导电炭黑 Vulcan XC-72 [91] [92]等。这些工作中有许多取得优秀成绩，如 2013 年，《自然》报导的 Chung 的团队[93]制备的 N-Fe-CNT/CNP 催化剂，以乙酸铁为铁前驱体，氰胺为氮和碳纳米管的前驱体，采用简单、可扩展、单步的方法制备了一种新型氮掺杂碳纳米管/纳米粒子复合氧还原反应电催化剂。该复合材料在碱性介质中的氧还原反应活性是所有非贵金属催化剂中最高的。当在足够高的负载下使用时，该催化剂的性能甚至优于铂基催化剂。在高分辨率透射电镜下观察催化剂的形貌如图 4(a)所示，碳纳米管外径约为 20~30 纳米，长度约为 10 毫米，均匀地分布在碳纳米颗粒中。因为同时存在碳纳米管和碳纳米颗粒相，该催化剂标记为 N-Fe-CNT/CNP。图 4(b)显示的是碳纳米管的顶端，铁被包裹在碳的石墨烯纳米层里，形成了大量的氧还原活性位点。图 4(c)为在 0.1 M NaOH 条件进行旋转圆盘测试的极化曲线，其起始电位(E_{onset})和半波电位($E_{1/2}$)均高于铂基催化剂，说明氧还原催化能力能力非常强。作者还对其进行了稳态测试，稳态曲线如图 4(d)所示，在 10000 圈循环后，其半波电位没有减小，反而右移，稳定性良好，这可能是因为碳纳米管的包裹阻止了铁的流失。但遗憾的是，该项工作并没有报导催化剂在 PEMFC 环境下的测试数据。

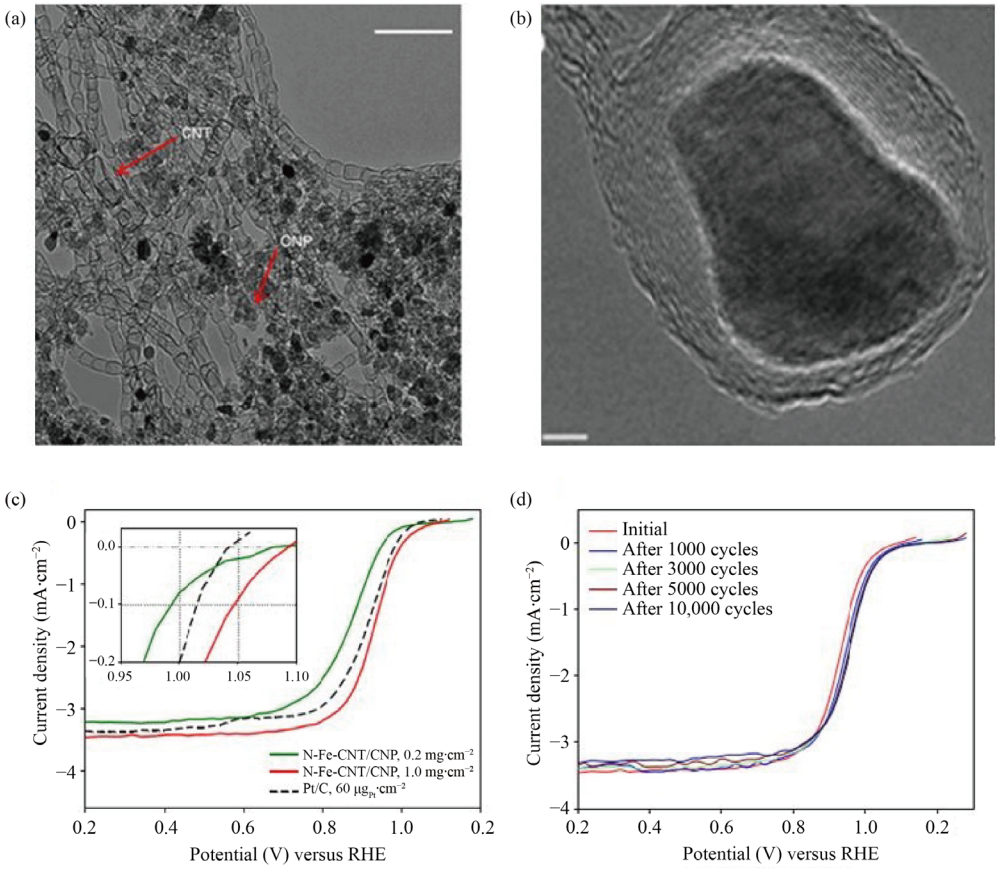


Figure 4. (a) Morphology of N-Fe-CNT/CNP under transmission electron microscope; (b) Fe encapsulated in graphene shell; (c) polarization curve; (d) cyclic stability test of N-Fe-CNT/CNP

图 4. (a) 透射电镜下的 N-Fe-CNT/CNP 形貌；(b) 铁被包裹在石墨烯壳层中；(c) N-Fe-CNT/CNP 的极化曲线；(d) 循环稳定性测试

2.2. 制备过程创新

催化剂合成设计上也推陈出新，一些新的方法，如模板法、多种元素共掺杂法、非热解法等。下面我将一一介绍。

1) 模板法。热解铁氮碳前驱体的过程是一个复杂的反应过程，通常热解产物的形貌和结构比较难得到控制，通过传统的热解方法获得具有合理孔径分布的产物显得比较困难，模板法被认为能较好地解决该问题。该方法采用具有一定机械强度(如二氧化硅)物质作为模板，然后将铁氮碳前驱体与模板混合，使前驱体充分填入模板，之后高温处理得到热解中间产物，最后通过强酸刻蚀或者加热等方法除去模板就可以得到具有规则孔结构的 Fe/N/C 催化剂。Zhang 的团队[28]以 Fe 掺杂的 ZIF-8 为前驱体，采用模板法(如图 5)合成了纳米杂化 FeNC-900 催化剂，具有由自生长碳纳米管交联的 Fe/N 共掺杂碳空心球的超结构。碳空心球和交联碳纳米管的微观结构不仅使电催化活性中心的表面积大，而且有利于电子和电解质离子的输运和纳米复合材料微观结构的稳定性。经电化学性能测试，在酸性和碱性条件下半波电位 $E_{1/2}$ 分别为 0.85 和 0.71 V 和商业铂基催化剂参数(分别为 0.85 V、0.79 V)相当，文献中没有报导该催化剂在真实 PEMFC 测试数据。

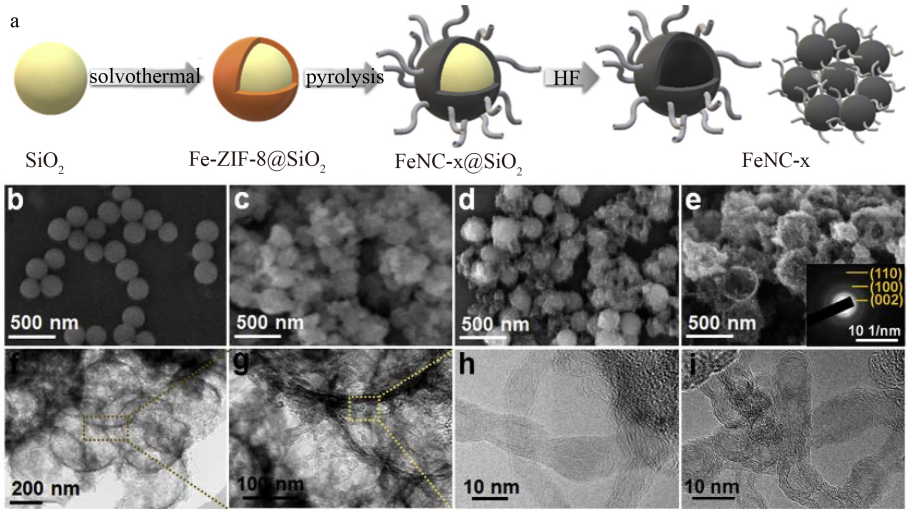


Figure 5. Schematic diagram of FeNC-900 synthesis process and SEM
图 5. FeNC-900 合成过程示意图及相应物质的扫描电镜图像

2) 球磨法。球磨可以给碳载体引入足够多的缺陷点，并通过小球之间碰撞产生的能量，利用物理方法有效地将金属和氮的前驱体结合到碳的微孔中[94] [95]。2009 年，Dodelet 团队[96]将球磨法引入 Fe/N/C 催化剂前驱体的制备。实验中，将碳载体、邻菲罗啉(充当孔的填充剂)和醋酸亚铁的混合物用球磨机进行球磨，然后先后在氩气和氨气中热处理，制备出的催化剂活性有了大幅提升。其电流密度在电池电压大于 0.9 V 时与每平方厘米负载 0.4 mg 铂的铂基阴极的电流密度相当，团队认为球磨引入了更多的微孔组织，而前驱体充分混合分散，活性位点密度增加。这项堪称里程碑式的研究发表于《科学》杂志上。

2018 年，Bao 的团队[97]，利用高能球磨实现了 Fe/N/C 单原子催化剂的制备。其机制如图 6 所示，球磨破坏了酞菁铁(FePc)的结构和 FeN_4 中心的悬挂键，使其连接到石墨烯晶格的缺陷点，从而形成活性中心。该催化剂具有很高的 ORR 活性，几乎达到工业 40% Pt/C 催化剂的活性，且稳定性良好。实验进一步证实，该反应在单原子铁活性位点上可以通过四电子转移路径很容易地进行。优异的稳定性可能来源于石墨烯基体通过 4N 原子的独特约束。该实验方法和理论研究将为进一步了解 Fe/N/C 催化剂的性质

提供依据，也为设计高效的电催化催化剂提供参考。

3) 非热解法。仿生催化剂是通过非热解法制备 Fe/N/C 催化剂的代表。由于铁的聚集主要发生在高温热解过程中，非热解方法可以从根本上防止铁的聚集。因此不经热处理直接将 FeNx 加入导电碳基体中是非常理想但非常具有挑战性的[98] [99] [100]。2014 年，Liu 的团队[101]报道了一种仿生 Fe/N/C 催化剂，他们从酶的过程中得到灵感，通过将铁卟啉共价接枝到多壁碳纳米管(MWCNTs)上，模拟含血红素的氧活化酶的活性位点(图 7)。经旋转环盘电极测试，这种未热解催化剂显示出与商用铂/碳相当 ORR 活性，更高的稳定性和优异的甲醇耐受性酸和碱催化剂，显示出该类催化剂的前景。

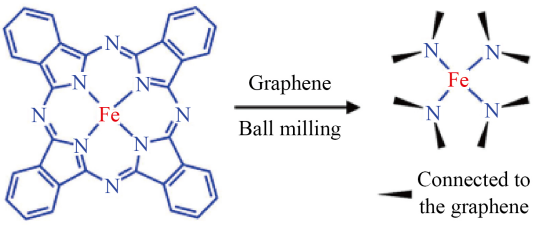


Figure 6. FeN_4 schematic diagram formed by ball milling method

图 6. 利用球磨法形成 FeN_4 示意图

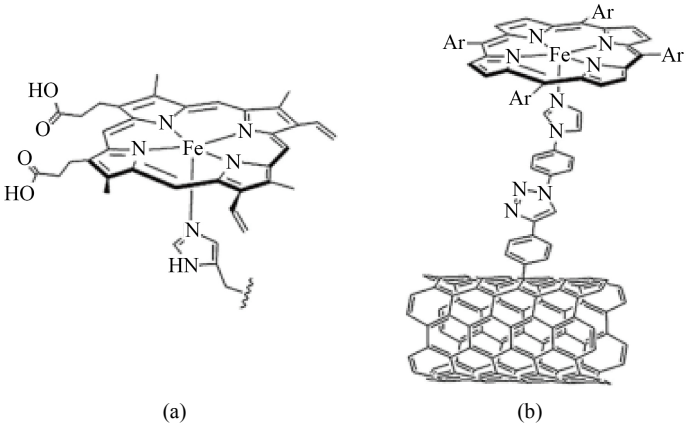


Figure 7. (a) Iron porphyrin structure; (b) Iron porphyrin is covalently grafted onto multi-walled carbon nanotubes

图 7. (a) 卟啉铁结构；(b) 将铁卟啉共价接枝到多壁碳纳米管上

2.3. 掺杂第四种元素

Fe-N-C 催化剂是一种铁和氮共掺杂的碳材料，研究者发现在制备的过程中，掺入第四种元素能够提升催化剂的性能。比如铁钴(Co)双金属氮碳催化剂，Guo 的团队[102]发现，作者认为是铁、钴双金属活化对氮掺杂石墨碳层、丰富的孔结构和均匀分散的掺杂剂的协同作用，可以提高 ORR 的性能。再如硼(B)元素掺杂的 Fe-N-C 催化剂[103]，实验数据表明，在 Fe/N/C 中加入硼可显著提高催化剂的比表面积，并能调节催化剂的表面极性和电子性质，为提高催化 ORR 性能提供更多的活性中心，从而使催化剂性能得到提高。除钴元素和硼元素，磷(P) [104]、硫(S) [9] [105] [106]等也被发现和铁共掺杂到碳氮材料对催化性能的有提升作用。

近日，shui 的团队[107]报道了一种掺杂 Pt 元素制备的催化剂，该方法将 Pt 原子通过氧分子以“单原子到单原子”桥接的方法，精确地嫁接到 Fe 原子上，形成 Pt_1-O_2-Fe_1-N_4 的活性部分，其结构如图 8(a)

所示[107]所示。由于 Pt 原子的保护，Fe-N_4 活性中心在催化过程中避免了被有害成份攻击，改善 Fe/N/C 催化剂的稳定性，使电池稳定性提升一倍，如图 8(b)所示，在酸性介质中的 ORR 稳定性显著提高。此外，它同时对析氧反应(OER)和析氢反应(HER)显示出非常高的催化活性。密度泛函理论计算表明新活性部分的协同作用，促进了质子的吸附和还原动力学。这项研究为提高Fe/N/C催化剂的稳定性提供了一种思路。

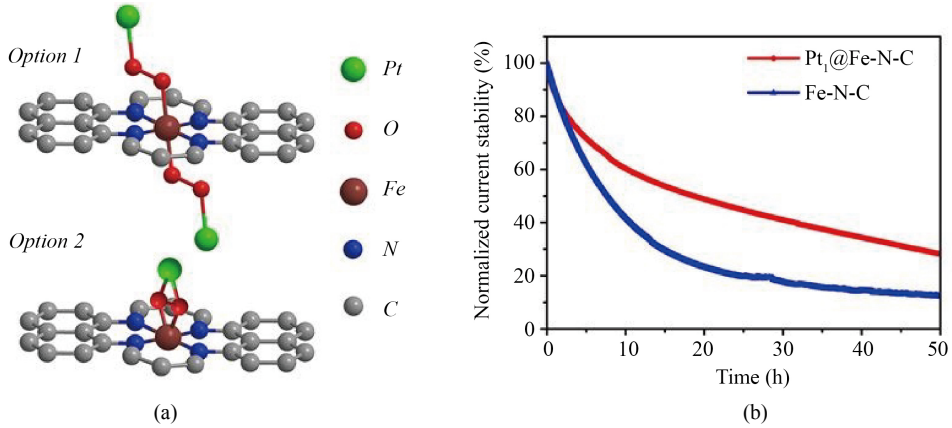


Figure 8. (a) Pt_1@Fe-N-C Diagram of active center; (b) Fe-N-C and Pt_1@Fe-N-C Current stability of catalyst at 0.5 V voltage

图 8. (a) Pt_1@Fe-N-C 活性中心示意图；(b) Fe-N-C 和 Pt_1@Fe-N-C 催化剂在 0.5 V 电压下电流稳定性

2.4. 小结

在许多已经发表的文献中，Fe/N/C 催化剂在旋转环盘电极技术下测试的各项指标数据都有许多良好的性能，但是文章中没有实际运用装置中的测试数据。在模拟燃料电池酸性电解质环境下表征催化剂的 ORR 活性有一定的参考价值，但真实 PEMFC 环境下，要考虑电池内传质阻力对催化剂的使用效果的影响。推陈出新的探索精神，值得赞扬和学习，但是也要综合考虑运用前景。一些创新的策略，比如第四种元素的掺杂，对 Fe/N/C 有提升作用，但是必然也会造成成本和加工程序的复杂化，成本的提升与性能提升需要同步量化考虑。

3. 催化机理和活性位点

一般来说，催化过程涉及到参与反应的分子和反应生成的中间产物等与活性位点的相互作用。一个氧气分子需要与四个电子和四个质子结合才能被完全还原生成水(酸性电解质)或氢氧根离子(碱性电解质)，所以氧气还原是一个复杂的多电子多步反应过程，并伴有不同的中间产物，比如 O_2^{2-}、O_2^-、HO_2^-、H_2O_2 等[43] [54] [108]。有可能的 ORR 路径如图 9(a) [109]所示，a 路径：O_2 在第一个活性位点处失去 $2e^-$ 还原成 H_2O_2，然后被第二个活性位点吸附再失去 $2e^-$进一步还原成 H_2O，所以这个路径也称为 2 * $2e^-$路径；b 路径被称为非直接的 $4e^-$，在一个活性位点上，O_2 相继被还原成 H_2O_2 和 H_2O，从电子转移角度，这个路径被称为 $2e^- + 2e^-$路径；最理想的路径为 c 路径：O_2 直接在一个活性位点上一步被还原成 H_2O，即直接 $4e^-$路径。由于多种类型的表面化学成分共存，很难阐明 Fe/N/C 上的 ORR 途径采取的是哪一种路径，很可能是多种路径同时共存，如图 9(b) [110]中所示。

目前尚缺少明确证据表明 Fe/N/C 催化剂活性位点的构成。比如关于铁的作用[111] [112] [113]争论在最近十年一直没有停止过。一些研究者认为，Fe/N/C 催化剂表面 Fe 含量非常有限(<0.1%)，而具有如此高的活性，可以排除 Fe 作为活性中心成分的可能性，铁可能只是起的促进活性位点形成作用[114]。然而，

Varnell 等[112]通过 CN^-等离子或小分子探针技术的应用发现 Fe 的作用非常重要，如果 Fe 被毒化，催化剂的活性将大幅下降，从而提出 Fe 是参与形成活性位点的观点。

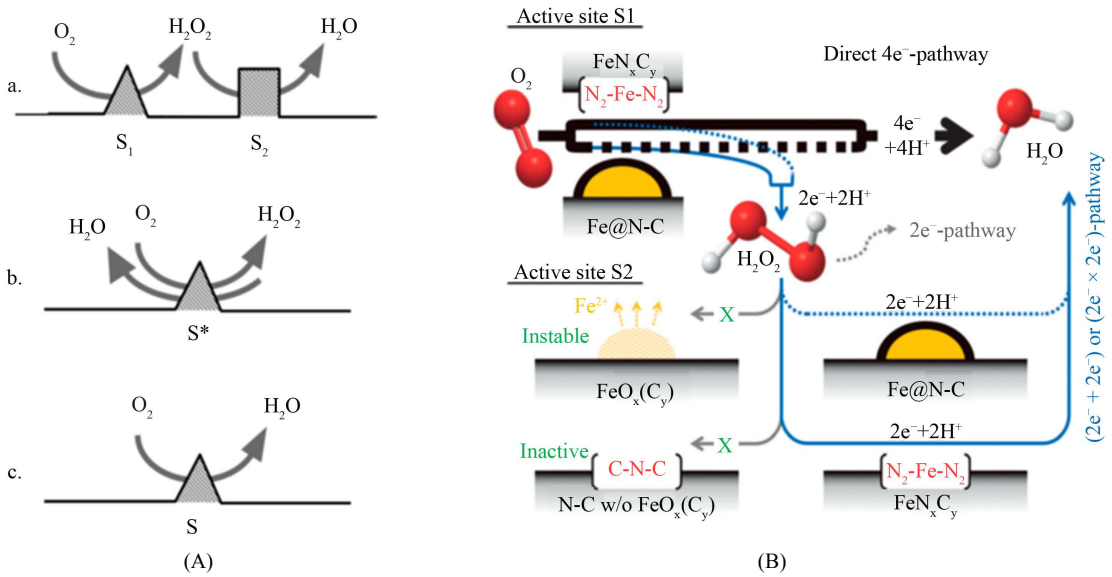


Figure 9. (A) The possible oxygen reduction pathways: a: 2 * 2e path; b: indirect $4e^-$ path; c: direct $4e^-$ path; (B) ORR mechanism of Fe/N/C catalyst in acidic medium

图 9. (A) 可能的氧还原路径 a：2 * $2e^-$路径；b：非直接的 $4e^-$路径；c：直接 $4e^-$路径[109]；(B) 酸性介质中 Fe/N/C 催化剂的 ORR 机理

需要指出的是，Fe/N/C 催化剂的活性中心可能不是一个特定的结构，而是多个活性组分或结构中心共同作用来催化 ORR，在不同的电位下，活性位点可能发生变化，施加一定的电位会引起活性位点电子结构的重新分布[110] [115]。随着原位和非原位条件下先进光谱技术的发展，如扩展 X 射线吸附精细结构(EXAFS)和 Fe-Mo-ssbauer 光谱，通过模拟和 DFT 计算建立不同结构基序的构效关系，进一步了解了电子结构和催化机理。经过大量研究，逐渐表明 Fe/N/C 中的活性中心在不同的 pH 值范围内应该是相同的[20]。关于 Fe/N/C 催化剂的活性位点构成的探究，目前被广泛接受的观点可以概括为以下两大类：

1) Fe-Nx (x = 2, 3, 4, 2 + 2)活性位点。铁是否直接参与 ORR 的催化作用一直是争论的焦点，为了阐明 Fe 在 Fe/N/C 中的作用，人们进行了大量的研究工作，目前学术界支持的由 Fe 参与构成的活性位点构成如图 10 [116]所示，Fe-Nx-C 部分，有可能以 FeN_4、FeN_3、FeN_{2+2}、FeN_2 等形式同时存在于 Fe/N/C 催化剂中。Lefevre 等[117]用 ToF-SIMS 检测 Fe/N/C 催化剂的活性中心。结果表明，Fe-N_4-C 和 Fe-N_2-C 同时存在于催化剂中。通过将 ToF-SIMS 检测到的离子与催化活性关联，他们发现 Fe-N_2-C 比 Fe-N_4-C 更具有电催化活性，而 Fe-N_2-C 的含量与铁的前驱体和制备时的热解温度有关。尽管没有直接的实验证据支持 Fe/N/C 中存在 Fe-N_3-C，Kabir [118]等人基于 DFT 计算和 XPS，提出 Fe/N/C 催化剂至少在热解过程中存在 Fe-N_3-C 缺陷。根据形成能，缺陷丰度遵循以下顺序：Fe-N_4-C > Fe-N_3-C > Fe-N_2-C。他们指出，Fe-N_3-C 的几何结构比 Fe-N_2-C 的几何结构更稳定。尽管对其它 Fe-Nx-C 结构存在争议，但 Fe/N/C 催化剂中 Fe-N_4 型催化中心的高活性是无可争议的[119]。

2) N-Cx 活性位点。N 在 Fe/N/C 催化剂中的重要作用是已被研究者证明的[120]。除了形成上面提到的 Fe-Nx 型催化中心外，N 还可以在热解过程中原位掺杂到碳基体中。氮在元素周期表中仅次于碳，具有比碳更大的电负性(N 为 3.04，C 为 2.55)，因此，N 的引入可以使邻近的碳原子电子缺乏，并减少费米

能级和导带之间的间隙，从而使石墨烯晶格具有更高的电荷迁移率[121]。根据 DFT 计算，杂原子掺杂石墨烯的本征催化活性和 ORR 机理取决于含碳活性位的电荷、自旋密度和配位状态，自旋密度效应和电荷效应在调节碳活性位催化活性方面尤为重要[122] [123]。氮掺杂引起的碳原子电荷密度和自旋密度的重新分布对氧合物的吸附作用和 ORR 过程中的第一电子转移有重要影响[124] [125]。N 掺杂到石墨烯中主要形成三种不同的结构，如图 11 [126] [127]所示：石墨 N、吡啶 N 和吡咯 N，这些类型的 N 均与 ORR 催化活性密切相关。N 直接取代碳原子，形成六元环为石墨 N 和吡啶 N(边缘)，而形成五元环的则为吡咯 N。N-Cx 活性位点参与的 ORR 过程则可用图 B 表示。O_2 分子的吸附位点是靠近吡啶 N 的碳原子，氧还原通过间接 $4e^-$过程或直接 $4e^-$过程发生[128] [129]。

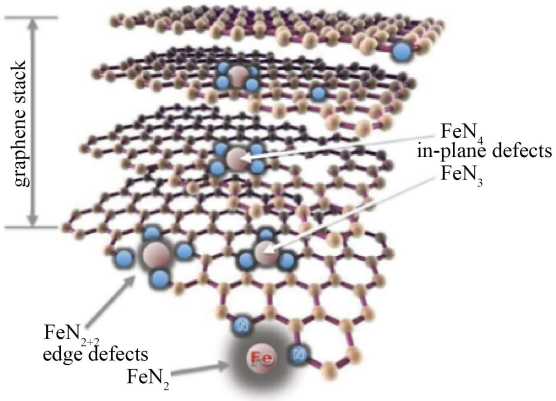


Figure 10. Active site structure of Fe-Nx
图 10. Fe-Nx 活性位点结构

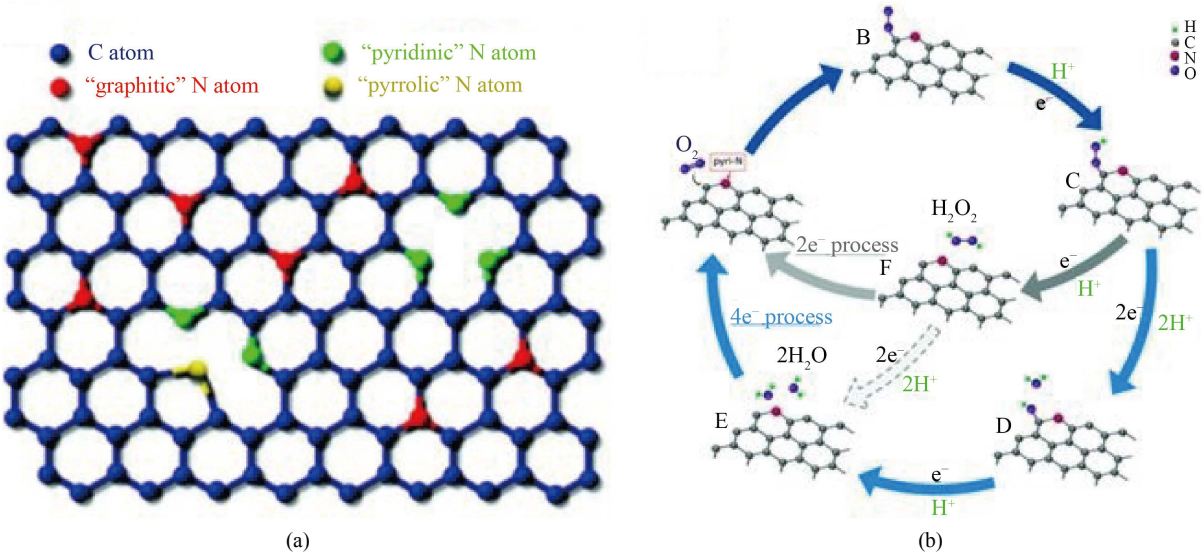


Figure 11. (a) N-Cx active site; (b) the ORR pathways on N-C
图 11. (a) N-Cx 活性位点结；(b) 发生在 N-C 上的氧还原路径

4. 在实际应用环境中的稳定性

Fe/N/C 催化剂的活性已经与铂基催化剂具有可比性，但其稳定性仍需进一步提高(特别是在最初的几个小时内，性能损失高达 50%)，这是在质子交换膜燃料电池等装置实际应用的另一个挑战性障碍[73] [130]

[131]。以下是研究者普遍接受的几种稳定性衰减机制：

1) 燃料电池启动过程中发生的碳氧化。最初发现碳的侵蚀对催化剂稳定性的影响是在研究铂基催化剂作为 PEMFC 的阴极催化剂的工作中[132] [133]，与碳作为导电载体的 Pt/C 催化剂不同，Fe/N/C 材料中的碳基质不仅作为导电体，而且还直接参与活性位点的构成，所以影响更为显著[134]。研究表明，碳的氧化一方面会导致催化剂微观结构的崩溃，碳孔隙减少，破坏活性中心的结构，降低活性中心的密度，甚至阻断气体向催化中心的扩散和电极的排水的通道；另一方面则是催化剂层疏水性的降低，碳氧化会在碳表面引入一些亲水基[135]。

2) 中间产物 H_2O_2 对活性位点的攻击。前面已经提到，除了直接 $4e^-$ 的氧还原路径外，其它路径均会产生 H_2O_2，Choi 等[136]发现，H_2O_2 的 Fenton 反应是催化剂活性降低的一个因素。Dodelet 课题组[137]对此现象做了大量研究，将一系列 Fe/N/C 催化剂浸入不同浓度的 H_2O_2 溶液中，模拟催化剂附近释放的 H_2O_2，通过旋圆盘测试，发现催化剂的活性显著下降。通过 H_2O_2 和过渡金属之间的 Fenton 反应生成一种自由基：$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$；$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$，这种自由基对活性位点起破坏作用。所以，在 ORR 过程中，应当尽量减少中间产物 H_2O_2 的生成。Chen 等[3]制备了一种高性能 Fe-N-C 催化剂膜电解质组件，并对其降解机理进行了研究，燃料电池的初始峰值功率密度高达 1.1 $w \cdot cm^{-2}$，但仅在 20 小时内，在 0.4 v 时，其电流损耗为 52%。实验和 DFT 计算结果表明，催化剂活性中心的 Fe 受到 H_2O_2 分解的自由基的侵蚀，导致活性损失增加。催化剂层和膜的离聚物进一步受到铁离子的污染，导致膜电阻和阴极催化剂层质子传导电阻增大，对电池性能影响很大。

3) 催化剂微孔浸水。有研究表明，催化剂内微孔的浸水是导致活性衰减的重要原因[138] [139]。Yang 等[140]实验发现微孔比表面积占总 BET 比表面积的比例越高，电池性能衰减越快。假设微孔的浸水会阻碍氧气向微孔中的活性中心的迁移，并导致快速的性能损失。但是该观点有许多科学家提出质疑，Choi [141]等人对稳定性试验前后的现场微孔进行了系统的研究，结果不支持微孔浸水是导致不稳定的因素。

4) 热处理氛围。Pietro [142]等制备了两种催化剂，不同之处在于第二种催化剂在第一种催化剂基础上增加了碱性介质(NH_3)中的氨氛围热分解，实验表明，在负载循环模式下的电化学操作中，碱性热处理氛围的催化剂具有较高的 ORR 耐久性。

在质子交换膜燃料电池中，大多数 Fe/N/C 催化剂的稳定性衰减问题可能不是单独一种机制，而是上述几种或是其它尚未发现的机制的结合作用。这些降解途径可能相互影响。例如，碳氧化会降低催化剂表面的疏水性，从而进一步加剧微孔的浸水现象。

5. 结论与展望

本文从活性提升创新策略、催化机理和实际运用环境中的稳定性问题三个方面总结了近十年来 Fe/N/C 催化剂取得的研究进展。毫无疑问，其电催化性能较铂基催化剂性已经展现优势，但是挑战仍然存在，主要障碍是活性和稳定性。提高活性是非贵金属催化剂研究和开发的首要任务，在短期内，稳定性研究仅在活性能够实际接近目标水平时才有意义。从根本上讲，提高活动性和稳定性有赖于对活性位点和催化机理的进一步认识。目前，活性位点构成仍然是争议的焦点，阻碍了以活性位点和催化机理为导向的催化剂优化和设计。

传统的制备 Fe/N/C 催化剂的五个基本步骤：制备前驱体→热解→蚀刻→热解→刻蚀，热解和刻蚀条件因制备方法不一样而各异。活性提升创新策略都是围绕这个基础展开的。为了提高 Fe/N/C 催化剂的活性，过去的研究大多集中在通过优化合成条件来寻求本征活性的提高。MOFs 材料的应用和单原子催化剂的成功制备对催化剂的活性提高都有巨大的推动作用。传统的铁盐和碳氮的前驱体共热制备 Fe/N/C 催化剂的方式也在不断优化，取得的进步也不容忽视。究竟哪种方法才是 Fe/N/C 催化剂通向大规模制备成

功商业化应用大门的金钥匙？尚无定论。解决之一问题的关键在于明确 Fe/N/C 催化剂的催化机理和活性位点组成问题，对活性位点的进一步研究和加深了解，进而以原理为驱动区设计高活性位点密度、高稳定性的催化剂才是硬道理。但是有一点可以指出，通过热解昂贵的金属大环化合物酞菁铁等，不仅成本不亚于铂，综合性能不及现在商用铂基催化剂，这方面的研究对探索催化剂的活性位点构成有帮助，但是使得其作为非贵金属催化剂的研究价值减弱。

确定活性中心结构的困难在于催化剂表面的复杂性和多样性。催化剂活性位点目前普遍接受的观点是两大类：1) Fe-Nx (x = 2, 3, 4, 2 + 2)，氧还原是由 Fe^{2+}/Fe^{3+}氧化还原转变引起的，伴随着 Fe 远离或朝向 N4-C 平面的切换行为。因此，通过调节 Fe-Nx 电子结构和几何结构，有望进一步提高 Fe-Nx 的活性。2) N-C 活性位点，金属起促进特定氮活性中心的形成，如石墨氮、吡啶氮和吡咯氮，而不是承担活性位点的角色。创造更多的缺陷位的碳载体或许对提升活性有帮助。

除活性问题外，Fe/N/C 在质子交换膜燃料电池等实际应用装置上稳定性差，是阻碍 Fe/N/C 材料商业化的另一个问题。稳定性减弱可能是由于碳基质的氧化和活性中心的破坏、Fenton 反应以及微孔水浸引起的。因此，为了提高耐久性，应避免 H_2O_2 中间体的生产，减少碳氧化，多从催化剂和工程设计的角度提高耐久性。

最后，目前不同研究团队针对 Fe/N/C 催化剂的性能评估标准各有不同，测试条件有的单纯在碱性条件下，而诸如质子交换膜燃料电池等可用于汽车能源转换装置的氧还原催化剂均要求在酸性条件下工作。碱性条件下催化性能虽好，但是运用前景更受限制。不同的评估标准对不同团队之间报道的研究成果的横向比较造成障碍，也会阻碍 Fe/N/C 催化剂的发展。应建立一个统一的评估标准，比如以实际运用条件下的电流活性密度等为标准，这样可以更有效的使 Fe/N/C 催化剂向规模运用靠近。科研的意义在于为人类解决难题，促进社会的进步，使人类命运共同体持续良好发展，背离这个目标的工作都将黯然失色！

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