

# 质子交换膜燃料电池催化剂纳米铂材料研究进展

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**摘 要:** 提高活性、降低贵金属担载量是质子交换膜燃料电池(PEMFC)催化剂的重点研究内容, 纳米铂材料是提高阴极氧还原反应(ORR)活性的核心研究方向之一。基于对 104 篇文献的分析, 综述了纳米铂颗粒的粒径、晶面和形貌对催化剂的活性和寿命的影响, 以及纳米铂合金的成分和核-壳结构等因素对催化性能的影响。分析现有方法技术的优点和不足, 提出催化剂有序化结构和优化 ORR 反应过程的研究方向。

**关键词:** 质子交换膜燃料电池; 阴极催化剂; 氧还原反应; 纳米铂; 活性; 寿命

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## Research Progress on Pt-based Nanomaterials for ORR Electrocatalysts of PEMFC

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**Abstract:** Improving the activity and reducing the amount of supported precious metals play an important role in the research of electrocatalysts for proton exchange membrane fuel cells (PEMFCs). Platinum (Pt) based nanomaterials are one of the key parts of enhancing the activity of the cathode catalysts on oxygen reduction reaction (ORR). Based on the analysis of 104 published papers, the influences of particle size, crystal facets and morphologies of the Pt-based nanoparticles (NPs) on the activity and stability of catalysts, as well as the alloy compositions and the core-shell structure on the catalytic performance, are discussed. By analyzing the advantages and shortcomings of the existing methods and technologies, and the research directions of designing catalysts with ordered nanostructure and optimizing the ORR process are proposed.

**Key words:** PEMFC; cathode catalysts; ORR; Pt-based nanomaterials; activity; stability

氧还原反应(ORR)作为质子交换膜燃料电池(PEMFC)的首选阴极反应, 包含多个反应基元, 涉及多种中间态粒子, 历程异常复杂<sup>[1-3]</sup>。且由于 ORR 的高度不可逆性, 氧电极反应总是伴随着过高的超电势(>0.25 V), 存在阳极燃料渗透、阳极燃料与氧

竞争催化活性位点, 导致混合电位及催化剂中毒问题<sup>[4]</sup>。因此, 开展高活性、长寿命电极材料的研究对理解电催化材料 ORR 机理、调控催化反应过程有着重要作用<sup>[5]</sup>。以各种金属为催化剂所开展的研究表明, 金属类材料的氧还原活性与氧原子的吸附

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能之间呈现火山型关系<sup>[6]</sup>。金属铂具有优良分子吸附和离解行为, 催化活性高, 是目前 ORR 电极催化剂的主要材料<sup>[7-8]</sup>。但由于铂资源稀缺, 价格昂贵, 因此提高铂利用率、降低铂担载量(从目前 0.5 g/kW 的水平降低到 0.2 g/kW 以下)、开发高比质量活性的铂催化剂, 一直是 PEMFC 领域的重点研究课题之一<sup>[9]</sup>。

铂基负载型催化剂是最常用的 PEMFC 阴极催化剂, 早期研究主要以提升催化剂活性位点数量为主, 采用碳纳米球<sup>[10]</sup>、碳纤维<sup>[11]</sup>、碳纳米管<sup>[12]</sup>、石墨烯<sup>[13]</sup>等具有超高比表面积的碳材料为载体。随着纳米技术发展, 除载体外, 纳米铂颗粒的 ORR 催化活性和寿命的提升也日益受到关注<sup>[14]</sup>, 立足于粒径、形貌、组分等结构设计, 降低铂担载量的同时兼顾活性位点数量及提升耐久性<sup>[15]</sup>。本文对 PEMFC 阴极纳米铂催化剂颗粒的研究进展进行综述, 为相关研究的开展提供参考。

## 1 纳米铂颗粒

### 1.1 尺寸优化

随着纳米铂颗粒尺寸减小, 催化剂颗粒表面铂原子配位数减少, 活性比表面积随之增大, 拥有的活性位点数量也将增多<sup>[16]</sup>。在纳米尺度上, 小尺寸效应将使催化剂活性比表面积增加至峰值<sup>[17]</sup>。由于 ORR 只发生在催化剂表面层, 内层原子的利用率很低。因此颗粒尺寸越小, 表面原子占比越高, 也越有利于提高铂的利用率<sup>[18]</sup>。然而, 纳米铂颗粒的稳定性随着尺寸减小将明显下降, 进而发生氧化失活; 此外, 过于微小的纳米铂颗粒会由于过高的 Pt-O 结合能而降低 ORR 活性。Wang 等<sup>[19]</sup>研究发现, 纳米铂粒径在 2~5 nm 时, 氧还原质量活性最高; 较窄的尺寸分布能够保证活性位点的均匀分布, 利于提升催化活性。Shao 等<sup>[20]</sup>系统研究了 1.3~4.65 nm 的纳米铂催化剂, 发现纳米铂尺寸为 2.2 nm 左右时具有最好的质量活性。

王鸿辉等<sup>[21]</sup>指出, 质量活性的变化规律与粒径变化时晶面变化有关; 而耐久性的变化规律则与粒子的热力学稳定性有关, 粒径越大, 粒子的表面吉布斯自由能越低, 越趋于稳定。近年来开发的纳米铂催化剂制备技术, 包括化学气相沉积、气体冷凝、电化学沉积、溶胶法、溶胶-凝胶技术、浸渍技术等方法<sup>[22]</sup>, 其粒径大小主导因素为稳定剂、热处理温度和 pH 值<sup>[19, 23]</sup>。

在还原后的铂颗粒经历成核、进化的过程中, 稳定剂附着于颗粒表面, 使得颗粒之间存在一定排斥力, 以确保颗粒不会过量团聚, 从而形成间隔一定的均匀、分散的空间分布。稳定剂分为两大类: 一类是离子型稳定剂<sup>[24]</sup>, 如醋酸钠(SA)<sup>[25]</sup>、四辛基溴化铵(TOAB)<sup>[26]</sup>、柠檬酸(CA)<sup>[27]</sup>、十六碳烷基三甲基溴化铵(CTAB)<sup>[28]</sup>、油酸胺(OAM)<sup>[29]</sup>等; 另外一类是非离子表面活性剂或高分子聚合物, 包括: 聚乙烯吡咯酮(PVP)<sup>[30]</sup>、聚二乙烯丙基二甲基氯化铵(PDDA)<sup>[31]</sup>、四氢呋喃(THF)<sup>[32]</sup>等。

热处理温度也是影响铂催化剂颗粒大小的因素之一<sup>[33]</sup>。在还原法生长纳米铂颗粒的过程中, 为预防催化剂颗粒出现大规模的团聚、活性表面积下降以及尺寸分布范围扩大等问题<sup>[34]</sup>, 需采取适中的温度范围。为了确保颗粒尺寸在 5 nm 以下, 通常选取的催化剂后处理温度范围在 700℃ 以内<sup>[19]</sup>。

pH 值在不同生长环境中对铂基纳米颗粒尺寸控制的敏感度不同<sup>[35]</sup>。Fang 等<sup>[36]</sup>开发了一种在碳载体上生长纳米铂颗粒的均匀沉积技术, 以缓慢增加生长体系的 pH 值实现小且均匀的颗粒尺寸。当调节初始前驱体 pH 的尿素用量逐渐增加时, 催化剂颗粒的尺寸将会因为氢氧根替换水分子或氯离子引起的空间收缩效应以及静电排斥作用而下降; Kim<sup>[37]</sup>用上述方法, 在 pH 为 9~10 的范围时获得了粒径最小的催化剂颗粒。Rusnaeni 等<sup>[38]</sup>运用多元醇辅助生长技术, 以不同浓度 NaOH 调节生长体系 pH(pH=7、10、12、13), 获得了火山式的催化剂尺寸演变过程。

### 1.2 晶面调控

为了减小表面能及总的过量自由能, 纳米铂颗粒生长完成后自发暴露的封端晶面为基础晶面(100)及(111)<sup>[39]</sup>。而当颗粒以至少一个密勒指数大于单位值的高指数晶面封端时, 如(hk0)(四六面体)、(hkk)和(hhk)(三八面体), 由于高指数晶面中的台阶、边缘、转折处高密度低配位铂原子的存在<sup>[40]</sup>, 催化活性将明显高于基础晶面<sup>[41]</sup>。Wang 等<sup>[42]</sup>制备了粒径约 8 nm 的铂立方体, 氧化原活性是商业铂催化剂活性的 2 倍, 进一步通过反应温度控制, 制备了多面体、立方体及截角立方体结构, 并测试了其 ORR 催化活性<sup>[43]</sup>。

对不同制备技术而言, 封端剂、还原剂、前驱体的种类与浓度, 生长时间, 温度调控均能实现纳米铂颗粒的构型控制, 其中以封端剂的研究最为广泛。封端剂分为有机封端剂和无机封端剂两类, 两

者封端原理相同:不同铂晶面电子结构以及原子排布不同,使铂晶面对封端剂吸附能力不同,进而造成各晶面生长速度不同;封端剂有选择性或有差异地吸附到了颗粒表面,纳米颗粒的封端晶面便能够被控制<sup>[44]</sup>。常用的有机封端剂包括有机胺类、环氧乙烯-丙烯-聚氧乙烯共聚物等<sup>[45]</sup>,无机封端剂主要包括卤素离子以及小分子等<sup>[46]</sup>。Tian 等<sup>[47]</sup>通过化学还原法,在酸性条件下以抗坏血酸(AA)为封端剂,制备并研究了包含(730)、(210)、(520)三类高指数晶面的 24 面体,认为氢氧基元对铂核表面的吸附是获得该复杂结构的关键因素;Ma 等<sup>[48]</sup>等运用多元醇辅助生长技术,以 HCl 为封端剂,获得了三足、四足、六足以及八足的纳米铂颗粒构型,通过不同浓度 HCl 的氧化刻蚀作用可控制获得不同分支数的多足颗粒,由于分支间存在的高密度晶面台阶以及高指数晶面构造,该纳米铂催化剂在催化氧化过程中,表现出了超越商用 Pt/C 催化剂 10 倍以上的活性。

这些研究调控不同晶面上原子的生长速率,选择性地促进某些特定面的形成,从而改变了材料的催化性能。但由于设计的封端面或结构的表面能及自由能较高,容易在反应过程中产生颗粒团聚或形状变化<sup>[49]</sup>,耐久性不佳。对于催化活性研究,关于高指数纳米粒子改善耐久性的报道很少,Xia 等<sup>[50]</sup>通过化学法制备了具有(740)高指数晶面的内凹纳米铂粒子,经过 5000 圈的扫描后,活性面积几乎无衰减。

### 1.3 形貌调控

除制备高指数晶面纳米铂颗粒外,一些特殊的制备方法及技术,能构造出满足低铂担载量及高催化活性的特殊纳米颗粒结构。如模板辅助法也可以实现纳米铂颗粒构型控制,为催化剂生长提供限域效应或者功能化辅助结构<sup>[51]</sup>。Sui 等<sup>[52]</sup>以三氧化二铝(AAO)为模板,通过电化学沉积技术,获得了铂基纳米管结构;Cheng 等<sup>[53]</sup>在聚苯乙烯-聚甲基丙烯酸上用化学还原法直接沉积铂前驱体,获得了网状的催化剂结构。此外,Koh 等<sup>[54]</sup>采用三嵌段的高分子共聚物在有机溶液-水相中自组装了纳米铂颗粒生长的模板,该球形纳米模板的中间层为可负载铂前驱体的聚乙烯基吡啶,还原前驱体后,得到了空心的纳米铂颗粒;Chen 等<sup>[55]</sup>对 PtNi<sub>3</sub> 纳米多面体颗粒进行了选择性地腐蚀,得到了挖空式框架结构的 3D 纳米催化剂颗粒,通过热处理,该结构框架上包裹了以 Pt(111)面封端的铂单晶层。由于极高的铂利用率,该结构最后展示出超过商业 Pt/C 催化剂 22

倍的 ORR 活性。

## 2 纳米铂合金材料

### 2.1 合金化

利用非铂金属与铂混合制备合金催化剂,是目前实现低担载量且高活性方面较成功的设计,并且获得了广泛而全面的研究<sup>[56]</sup>。合金化不仅可以减少铂用量、降低催化剂成本(通常占电池总成本的 30%至 40%)<sup>[19]</sup>,甚至能获得 2 到 4 倍于纯铂的催化活性<sup>[57]</sup>。以非贵金属与铂结合研究占主导,非贵金属相的混合方式、种类选择、含量配比等要素是合金化设计的关键。合金化中,金属原子主要有 3 种混合方式:随机式、团簇式、有序式,而以有序式更能优化铂催化性能<sup>[58]</sup>。合金的非贵金属相的选择一般有钴<sup>[59]</sup>、镍<sup>[60-61]</sup>、铁<sup>[62]</sup>、钯<sup>[63]</sup>、铬<sup>[64]</sup>、钼<sup>[65]</sup>、锰<sup>[66]</sup>、铝<sup>[67-68]</sup>等,其中以钴、镍、铁混合的合金催化剂活性最高<sup>[55]</sup>。研究表明,合金化提升催化活性有以下几种因素:较短的 Pt-Pt 原子结合距离导致的压缩应变<sup>[69]</sup>;过渡金属分解导致的高粗糙铂表面<sup>[70]</sup>;多相金属间应力或配体效应导致的铂原子 d 带中心下移<sup>[71]</sup>或 d 带空缺变化<sup>[72]</sup>;非贵金属原子表面掺杂导致的 ORR 中间产物吸附排斥等<sup>[73]</sup>。这些因素或是优化 Pt-O 结合能,或是增加铂活性位点数量,或是抑制铂中毒,进而提升性能。也有部分关于贵金属与 Pt 合金研究,如 Wang 等<sup>[74]</sup>研究了 PtM/Pd(111) (M=金、钌)表面层的活性位,发现不同活性位点在氧还原过程中会按不同的氧还原机理进行,改变合金表面杂原子的浓度可以使铂原子受到配位效应影响进而使 ORR 基元反应能垒相近,从而调控掺杂元素配比可以实现催化活性的提升。

铂催化剂合金化制备中最常用的方法是溶胶法,侧重于除尺寸、形状控制之外的组分控制。铂原子与其他金属原子在溶液中按设计比例同时还原成核并生长。溶胶法需要可热分解的金属前驱体以完成还原过程,同时需要较强的还原剂,如 NaBH<sub>4</sub>、肼、氢气等<sup>[39,75]</sup>,以确保合金比例前后一致,实现各金属前驱体以合适速率同时还原。Liu 等<sup>[76]</sup>用铂与钴的乙酰丙酮化物,热分解得到了合金比例按设计的 Pt<sub>70</sub>Co<sub>30</sub> 催化剂;Lee 等<sup>[77]</sup>以铂及钌的乙酰丙酮化物为前驱体,十六烷二醇为还原剂,油酸为稳定剂,通过二醇的长链与稳定剂耦合控制合金组分的成核生长,获得了 PtRu 合金。此外,溶胶法还能制备铂的金属间化合物,从而获得有序式原子混

合金<sup>[78]</sup>, 实现合金类型中最适合优化铂催化活性的设计。Wang 等<sup>[79]</sup>以  $\text{H}_2\text{PtCl}_6\cdot\text{H}_2\text{O}$ 、 $\text{CoCl}_2\cdot\text{H}_2\text{O}$  为前驱体, 通过溶胶法获得了有序的  $\text{Pt}_3\text{Co}$  金属间化合物纳米颗粒。以溶胶法制备并研究该种成分明确、结构有序的金属间相, 被认为是实现可控效应, 包括结构、几何及电子效应的有力途径<sup>[80-81]</sup>。

## 2.2 核壳结构

核壳化是合金化的进一步发展, 二元  $\text{PtM}_x$  (如  $\text{PtNi}_x$ 、 $\text{PtCo}_x$ 、 $\text{PtCu}_x$  等) 类材料作为催化剂, 在燃料电池阴极反应一定时间, 或以此类材料为前驱体, 除去表层的活泼金属元素后, 在适当温度下进行退火, 形成的大多数是铂包覆层( $\text{Pt-monolayer}$ 、 $\text{Pt-skin}$  或  $\text{Pt-skeleton}$ ) 的核-壳( $\text{Core-Shell}$ ) 结构<sup>[82]</sup>。以过渡金属等为核构造的纳米铂催化剂在保证活性面积的同时有效减少了铂担载量, 并通过核材料与铂壳层间的协同作用优化了表层铂对氢氧基元( $\text{OH}_{\text{ad}}$ ) 的吸附<sup>[83]</sup>。Zhang 等<sup>[84]</sup>提出, ORR 可简单理解成一个氧气分子吸附在催化剂表面后  $\text{O-O}$  键断裂和  $\text{O-H}$  键生成的过程, 铂原子的  $d$  轨道态密度中心位置与吸附物种的吸附能密切相关。高的中心位置将存在更多  $d$  带空穴, 进而倾向于更强的吸附作用, 反之则减弱吸附<sup>[73]</sup>。由此, 可通过核材料调控壳层铂的  $d$  轨道态密度中心位置来优化其催化活性。

利用引入金属与铂的电子结构效应或协同作用等, 提高核-壳类纳米铂材料的反应活性和耐久性, 是目前 ORR 催化剂研究的重点领域, 其主要关注点是铂壳层。Stamenkovic 等<sup>[85]</sup>对  $\text{PtNi}$  框架式合金结构研究后指出, ORR 动力学依赖于铂在催化剂表面的分布, 均匀的铂壳层展示出最高的催化活性。不断减少载铂量、提高铂利用率并强化两相界面各效应对  $\text{Pt-O}$  吸附能调控力度, 研究方向从组装均匀的纳米级厚度铂壳层结构发展到目前的生长单原子层铂或可控原子层铂, 并趋向于开发超薄壳层的核-壳结构。Shao 等<sup>[86]</sup>利用铜欠电位沉积技术在 3 nm 的金纳米颗粒的特定晶面上沉积了铂单层薄膜, 打破了通常金核对铂壳层产生拉伸应变的规律, 所得催化剂 ORR 活性是同尺寸钯为核时的 1.6 倍。Xie 等<sup>[87]</sup>通过动力学方法制备了 1~6 个原子层可控的  $\text{Pd-Pt}$  立方体核-壳结构, 其中铂原子层数为 1 时质量比活性( $\text{mass activity}$ ) 最高, 为 2 或 3 时面积比活性( $\text{specific activity}$ ) 最高。Vukmirovic 等<sup>[88]</sup>研究发现, 在铂壳层表面掺入其他金属能一定程度上抑制  $\text{OH}$  物种吸附, 防止铂中毒。Adzic 等<sup>[89]</sup>将金、钯、铑、铱、钼等掺入单层铂壳中抑制铂中毒, 所

得的  $\text{Pd-PtRe}$  催化剂的催化活性是商用  $\text{Pt/C}$  的 4~4.5 倍。核-壳结构催化剂由于金属间协同作用<sup>[90]</sup>, 展现出了超越单金属纳米材料的催化性能。并且由于不同组分的催化剂在整个反应过程中具有特定反应机理<sup>[91]</sup>, 使双/多金属纳米材料具有多种功能, 可以实现单金属催化剂前所未有的化学转化从而提高选择性。

相对于壳层控制整个结构的介质适应性、分散性、稳定性、选择性、有序识别等, 核层成分主要提供催化剂颗粒的支撑, 并降低铂消耗。也有研究将核成分单核材料拓展到二元合金核材料, 用比单质金属更加多样性的电子及晶体结构, 以进一步拓宽两相界面各效应对  $\text{Pt-O}$  吸附能的调控范围<sup>[89]</sup>。目前报道过的核壳结构催化剂合金核多以钯合金为主, 制备方式多为欠电位沉积技术及脱合金技术, 如  $\text{PdCo}$ <sup>[92]</sup>、 $\text{PdNi}$ <sup>[93]</sup>、 $\text{PdFe}$ <sup>[94]</sup>、 $\text{PdCu}$ <sup>[95]</sup>、 $\text{PdIr}$ <sup>[96]</sup>、 $\text{PdAu}$ <sup>[97]</sup> 等。Xia 等<sup>[98]</sup>制备的碳纳米管负载的  $\text{Pd@Pt}$  核壳催化剂, 质量比活性比商业  $\text{Pt/C}$  催化剂高 7~9 倍, 过氧化氢产率仅为 0.148% (相比于商业  $\text{Pt/C}$  催化剂降低了 85.9%); Shao 等<sup>[93, 95]</sup>制备的  $\text{PdCu@Pt}$  催化剂得到相当于  $\text{Pt/C}$  催化剂 14 倍的 ORR 活性。

## 3 结语及展望

综上, 目前纳米铂颗粒催化剂在调控手段方面的研究, 旨在降低铂使用量, 最大限度提升铂利用率和活性。从尺寸、晶型及形貌等主控因素来看, 制备尺寸、晶型及形貌可控的催化剂, 研究表面原子排布、微观形貌结构、晶型等与催化剂活性间的构效关系, 研究催化剂的组分、形貌及结构在 ORR 过程中的变化规律, 以提高铂基催化剂的 ORR 活性和利用率<sup>[99]</sup>; 从设计方法来看, 核壳化是目前铂基纳米催化剂制备中比较成功的一类, 因为电极反应一般发生在纳米催化剂表面层, 以非贵金属为核替代部分铂元素, 不仅可以大幅度降低铂的使用量、提高铂利用率, 还可以通过非贵金属与铂之间的协同作用, 优化铂元素对氢氧基元的吸附, 提高铂基纳米催化剂的反应催化活性; 但由于非贵金属种类繁多, 物理化学性质有较大差异, 尤其是在酸性环境中, 一些非贵金属元素(如铁、铜、镍等) 耐腐蚀性不佳, 因此非贵金属核壳类铂基纳米催化剂在质子交换膜燃料电池应用方面仍面临较大的挑战。

此外, 以上所述调控手段更倾向于铂基纳米催化剂单一颗粒纳米性质(如小尺寸效应、表面效应)

及催化活性。而从催化剂在质子交换膜阴极的应用来看<sup>[100]</sup>,笔者认为同时也应考虑到纳米催化剂颗粒总体分布及宏观性活性的提升,由低维度(如纳米点、线、载体等)提升至高维度,使铂基纳米催化剂宏观性有序分布,构筑有序结构三相界面,以解决催化剂颗粒之间、或催化剂颗粒和电解质之间阻挡质量传递和电子传递的迁移阻挡物存在;在催化剂反应动力学上,氧还原反应讨论更多的是反应途径,仍需优化反应过程,进一步降低中间体如氧基元( $O_{ad}$ )、氢氧基元( $OH_{ad}$ )等在催化剂表面活性位上的吸附,探明铂催化剂表面结构对 ORR 速率的影响。

作者研究组近期将嵌段共聚物自组装用于纳米铂催化剂设计中<sup>[101]</sup>,控制组装过程的开始、结束或逆向进行<sup>[102]</sup>,可形成多种尺度的纳米铂结构。近期通过二次自组装制备了金属/聚合物杂化二维六角网状结构<sup>[103]</sup>,在此基础上探索了有序纳米铂颗粒阵列在尺寸、间距、形状上的控制<sup>[17]</sup>,进一步测试了铂有序阵列催化剂在 PEMFC 电池中的 ORR 电催化性能,研究了自组装参数、催化剂阵列形貌参数以及燃料电池性能三者间的关系<sup>[104]</sup>。结果表明,有序阵列铂催化剂在 PEMFC 应用中有着独特优势,构造出的功能性铂自组装有序结构有明确的形貌结构参数,为进行 ORR 机理研究提供了独一无二的条件。有序化可作为开发高活性、高稳定性、低担载量铂催化剂的未来途径,在燃料电池催化剂制备中具有极高的研究价值及应用价值。

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