低铂质子交换膜燃料电池氧还原催化剂的研究进展与展望

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2021-02-27 收稿, 2021-05-19 修回, 2021-05-21 接受, 2021-05-24 网络版发表

国家自然科学基金(21975157)和国家重点研发计划(2016YFB0101201)资助

摘要 Pt基催化剂是氧还原反应(oxygen reduction reaction, ORR)最有效的催化剂, 然而有限的Pt资源和高Pt载量严重制约了质子交换膜燃料电池(proton exchange membrane fuel cells, PEMFCs)的规模化应用. 开发同时具有低Pt含量、高活性的ORR催化剂是推动PEMFCs大规模商业化的有效途径. 本文从纯Pt催化ORR的机理出发, 对当前研究中具有优异性能的均匀Pt合金催化剂和核-壳结构Pt基催化剂的ORR催化机理进行了阐述, 并概述了其研究进展、研究策略和制备方法. 尽管目前的研究致力于对Pt基纳米颗粒的形貌、粒径、元素组成和晶面等进行精确设计和调控, 并在实验室层面实现了活性和耐久性的显著提升, 但是现有常用制备方法存在的问题使得其商业化生产无法取得突破进展. 最后对Pt基催化剂的规模化制备提出了见解, 并对其前景进行了展望.

关键词 低铂, 高性能, 氧还原反应, 质子交换膜燃料电池, 规模化制备策略

随着社会经济的飞速发展, 全球范围内的能源、环境问题日趋严重. 中国是能源和人口大国, 然而有限的储量使得能源进口依赖度持续提升, 近年来石油进口依存度已接近60%. 交通领域石油消费占比接近50%, 并且随着汽车保有量的飞速增加, 其中近80%被汽车消耗^[1]. 不仅如此, 汽车中内燃机排放的大量二氧化碳和氮氧化物等造成了严重的环境污染. 从可持续发展的趋势来看, 汽车产业必须解决能源问题和污染问题, 因此低碳、低污染、高效能的新能源汽车的发展势在必行^[1,2]. 《中国制造2025》提出“节能与新能源汽车”作为重点发展领域, 并制定了2025年“和传统汽车、电动汽车相比具有一定的市场竞争力, 实现批量生产和市场化推广”的发展目标^[1]. 2016年, 《节能

与新能源汽车技术路线图》提出, 2025年我国燃料电池电动汽车(fuel cell electrical vehicle, FCEV)的发展规模要达到5万辆, 2030年要达到百万辆^[3].

氢气不仅具有高热值(其热值是石油的2~3倍), 而且能量输出稳定、来源广泛、产物清洁零污染(仅有水)^[4], 是一种稳定清洁的能源载体. 燃料电池是一种将燃料的化学能直接转化为电能的装置, 由于不受卡诺循环限制, 具有比内燃机更高的能量转化效率(高达60%~80%). 质子交换膜燃料电池(proton exchange membrane fuel cells, PEMFCs)具有启动快、工作温度低等优点, 通过其实现氢能高效利用是氢能经济的重要一环. 交通运输领域氢燃料电池汽车是氢能战略中的重要方面^[2,3,5]. 国际知名汽车企业的氢燃料电池汽车

引用格式: 赵路甜, 程晓静, 罗柳轩, 等. 低铂质子交换膜燃料电池氧还原催化剂的研究进展与展望. 科学通报, 2022, 67: 2212–2225

Zhao L T, Cheng X J, Luo L X, et al. Progress and prospects of low platinum oxygen reduction catalysts for proton exchange membrane fuel cells (in Chinese). Chin Sci Bull, 2022, 67: 2212–2225, doi: 10.1360/TB-2021-0221

产业已初具产业化,如丰田(Mirai)、现代(ix35)、本田(Clarity)等。近10年,氢燃料电池汽车在功率密度、效率和低温启动等性能方面已取得了重要突破,行驶里程和功率都达到了乘用车的要求^[6]。然而,截至目前,燃料电池电堆的成本和耐久性依旧面临挑战^[7]。由于贵金属Pt不仅昂贵且储量有限,燃料电池中接近一半的成本来源于催化剂中的Pt^[6,8~10]。阴极氧还原反应缓慢的动力学,导致阴极催化剂Pt的用量高达阳极用量的4倍。并且,相关数据统计表明,伴随燃料电池电堆系统出货量的增加,催化剂的成本将会成为单一成本占比最大的成本^[7,11,12]。因此,开发低铂用量、高催化性能和耐久性的氧还原催化剂,探索其规模化生产策略是燃料电池长期发展和规模化应用的重点。

在降低燃料电池Pt用量方面,过去的20年取得了显著成效。2000~2003年,技术需要的Pt用量约为 1 g kW^{-1} ;2007~2008年,Pt用量降低到 $0.6\sim 0.8 \text{ g kW}^{-1}$;2015年,技术实现Pt用量约为 0.5 g kW^{-1} 。目前,用于示范运行的燃料电池汽车Pt用量约为 0.35 g kW^{-1} ,距离最终具有与内燃机竞争的商业化水平的Pt载量 0.1 g kW^{-1} 的超低Pt水平仍具有较大差距。因此,进一步降低Pt的含量,提高催化剂中Pt的利用率,成为下一代催化剂研究中的关键问题。

尽管非贵金属催化剂能够完全不使用Pt,也具有良好的ORR催化性能,但是电池实际工况下严重的衰减和 O_2 不完全氧化带来的毒化问题无法规避,因此,目前Pt基催化剂仍是主要的研究方向^[13]。本文将结合纯Pt上ORR的催化机理,对近年来用于PEMFCs的阴极Pt基催化剂——均匀Pt-M(M=Fe、Co、Ni、Mn、Y和Sc等)合金催化剂、核-壳结构Pt基催化剂的性能提升机理、研究现状、主要研究进展、研究策略和制备方法等进行阐述,并分析现存问题和未来有前景的发展方向。本文论述主要内容概括如图1所示。

1 Pt基催化剂的催化机理

通过改进Pt基催化剂提高ORR催化性能,需要首先理解Pt表面上催化ORR的机理。通常认为,氧分子的还原主要经历四电子过程,即氧分子得到4个电子直接生成水。由于二电子反应过程生成的过氧化氢会使电池性能降低,因此四电子反应也是最理想的反应路径。四电子的反应路径通常被认为有如下两种^[14,15]。

路径1: $\frac{1}{2}\text{O}_2 \rightarrow * \text{O} \rightarrow * \text{OH} \rightarrow \text{H}_2\text{O}$

图1 用于PEMFCs的ORR催化剂研究进展和发展趋势分析

Figure 1 Research progress and development trend analysis of ORR catalysts for PEMFCs

路径2: $\text{O}_2 \xrightarrow{U_{L,1}} * \text{OOH} \xrightarrow{U_{L,2}} * \text{O} \xrightarrow{U_{L,3}} * \text{OH} \xrightarrow{U_{L,4}} \text{H}_2\text{O}$

Kulkarni等人^[15]和Nørskov等人^[16]提出,用密度泛函理论(density functional theory, DFT)来量化不同材料上ORR关键中间体的能量与催化活性趋势的关系,并以热力学极限电势(limiting potential, U_L)作为催化活性的量度。在完全催化反应的基元反应路径中,决速步骤的速率将决定整个反应的速率,所以最低极限电位就能够定义反应的总体极限电位。Kulkarni等人^[15]根据不同金属表面的氧吸附绘制“火山型”曲线。他们认为,第一步和最后一步是所有过渡金属上ORR的决速步骤,且以金属表面的氧吸附能作为氧还原性能的描述符:对于与*OH牢固结合的金属,*OH $\rightarrow$ H₂O是决速步骤,而对于氧结合能弱的金属, O_2 的活化步骤 $\text{O}_2 \rightarrow * \text{OOH}$ 是决速步骤。Pt(111)单晶的上述关系最接近“火山型”曲线的顶部,因此被认为是最优的ORR催化剂。这与实验观察到的趋势一致^[17]。

2 Pt合金催化剂的研究进展和设计策略

2.1 Pt合金催化剂的研究进展

已有研究表明,Pt-M合金催化剂与纯Pt相比具有更高的ORR活性^[14,17~19],其中Pt₃M系列材料受到最广泛的关注。图2以实验测量的各种Pt₃M合金催化剂相对

图2 一系列 Pt_3M 合金催化剂的动力学“火山图”(基于微动力学模型, 虚线)、密度泛函理论得到的极限电势“火山图”(基于热力学分析, 实线), 以及实验测得的合金催化剂相对于纯铂的ORR电流密度之比(红色圆圈)与计算得到的*OH吸附能之间的关系^[15]

Figure 2 The kinetic volcano curves (based on micro-kinetic model, dashed line), limit potential volcano curves obtained by density functional theory (based on thermodynamic analysis, solid line) of a series of Pt_3M alloy catalysts, and the relation between the ORR current density ratio of Pt_3M alloy catalysts to pure Pt (red circles) and the calculated *OH adsorption energy^[15]

于Pt的ORR电流密度之比 j/j_{Pt} 作为DFT计算出的*OH结合能(相对于Pt)的函数, 绘制了ORR活性与*OH吸附能之间的关系散点图(图中红色圆圈所示)^[15]。基于微动力学模型计算得到的动力学“火山图”(虚线)和DFT计算的 U_L “火山图”(实线)与*OH结合能之间的关系也绘制在图2中, 与实验结果表现出相同的趋势, 即进一步适当地削弱*OH吸附能($\Delta G_{\text{OH}} \approx 0.1$ eV)可使热力学上的催化活性更接近顶点位置, 从而获得更优的催化性能^[15]。

Nørskov课题组^[15,20]和Morozan等人^[21]提出d带中心理论, 以d带中心作为催化剂电子性质的良好描述符。由于上述含氧中间反应物种在催化位点上的吸附是通过氧原子的2p电子与催化剂金属的d电子之间成键而实现的化学吸附, 在吸附物种与催化剂原子表面的相互作用过程中, 金属d轨道会分裂形成成键轨道和反键轨道。成键轨道上电子的占据会导致氧原子的吸附增强, 而反键轨道上电子的占据仅与其在费米能级上的位置有关: 随着d带中心远离费米能级, 氧吸附能减弱。通过在Pt催化剂的表面引入其他金属原子(通常是电负性更小的3d、4d过渡金属, 如Fe^[22]、Co^[23~25]、Ni^[26]、Cu^[27~29]、Ir^[26]、Y^[30]、Mn^[31]等), 能够使表面电子结构

发生改变: 一方面, 过渡金属原子的嵌入使Pt-Pt键的配位数降低; 另一方面, 由于其他过渡金属的原子半径小于Pt, 嵌入晶格后产生应力作用。收缩的Pt晶格使其d带展宽增加, d带中心的相应下移减弱了对上述含氧反应中间体的吸附强度^[32]。

通过配体效应和应力效应能够降低Pt的d带中心位置, 减弱*OH吸附能, 从而达到增强ORR性能的目的^[33]。当然, 氧吸附过强或过弱都不利于ORR活性: 氧吸附过强, 含氧物种的解吸变得困难, 使得催化表面被覆盖; 而吸附强度过弱, 则导致氧分子解离不易实现^[32,34]。从图2得知, 选择合适的合金元素使得Pt原子的d带中心下降, 从而导致ORR中间物的结合适当减弱, 将更利于增强ORR活性。

在Pt-M合金基础上添加第3种金属形成三元合金化合物, 对进一步调控催化剂的ORR活性具有一定的作用。Cao等人^[35]通过一种简便的乙二醇还原一锅法合成了碳负载PdPtNi三元合金催化剂, 得益于: (1) 具有丰富的孪晶边界、大量暴露的(111)晶面和催化活性位点的二十面体结构; (2) 略微收缩的fcc晶格产生的压缩应变效应; (3) Pd、Pt和Ni元素的电子相互作用(配体效应), 在0.9 V下的面积比活性(specific activity, SA)和质量比活性(mass activity, MA)分别约为商业Pt/C的9.59和5.40倍。尽管Pt-M合金大幅提升了ORR性能, 然而过渡金属M在长时间测试中的溶出导致了活性的损失, 其耐久性不佳。研究显示, 三元合金催化剂在提高耐久性方面也起到一定作用。Zhang等人^[36]通过固态化学法, 在 CO/H_2 气氛下还原得到了碳负载八面体 Pt_2CuNi 三元合金催化剂, 质量比活性 $2.35 \text{ A mg}_{\text{Pt}}^{-1} @ 0.90 \text{ V}$, 约为商业Pt/C催化剂的11倍。4000和10000圈加速衰减循环后, 活性仍保留81.3%和68.1%, 比同样条件下制备得到的Pt-Ni/C催化剂稳定性提升显著(分别保留活性52.9%和35.0%)。Liu等人^[37]通过微波辅助多元醇还原法合成了三元Pt-Au-Ni/C催化剂, 质量比活性和面积比活性均以Pt/C<Pt-Ni/C<Pt-Au-Ni/C的顺序增加。X射线光电子能谱(X-ray photoelectron spectroscopy, XPS)结果显示, Pt-Au-Ni/C中Pt 4f_{7/2}的结合能高于Pt/C, 但低于Pt-Ni/C, 表明Pt-Au-Ni/C表面的结合氧比Pt/C弱, 但比Pt-Ni/C略强, 可以更好地调节氧结合能。表面偏析的Au原子对催化剂稳定性具有积极影响, 富含Pt-Au的表面层可以有效防止Ni的溶解。Pt-Au-Ni/C在半电池和单电池加速降解试验中均表现出长期稳定性, 在5000圈加速衰减循环后活性仅损失了17.1%。

基于上述催化机理可知,影响Pt基催化剂活性的关键在于改变催化剂中Pt原子的电子结构.研究发现,除了在Pt晶格中嵌入不同种类金属原子能够实现Pt基催化剂ORR活性的增强^[38],通过调节Pt与过渡金属元素M的比例、合金催化剂颗粒的晶面种类、催化剂颗粒粒径等因素,均可以影响合金催化剂的电子结构.因此,Pt-M合金催化剂合成的精确调控对于提高催化活性和稳定性尤为重要^[15,39-41].

Pt-M合金催化剂的ORR性能受颗粒粒径的影响,并且当粒径处于合适的范围时,ORR性能可以实现最优值.评价Pt基催化剂ORR活性的重要指标——质量比活性由电化学比表面积(electrochemical specific area, ECSA)与面积比活性相乘得到.通常,为了增大活性比表面积,研究趋向于不断减小颗粒的尺寸.然而,Blanton等人^[42]发现,粒径为1.4 nm的Pt/C催化剂的面积比活性不及铂黑催化剂(粒径为10 nm)的1/20. Peuckert等人^[43]发现,Pt颗粒的粒径大于4 nm时,面积比活性没有明显增加,这是因为大颗粒内部的Pt原子无法直接参与ORR反应.而当粒径由3 nm降低到1 nm,面积比活性降低了20倍.研究认为,过小Pt颗粒的平均表面配位数更小,含氧中间物种在其上的吸附将增强,这将会阻碍后续氧分子在催化剂表面的反应^[44].研究表明,Pt合金催化剂也存在类似的粒径效应.Wang等人^[45]通过有机溶剂热法合成了尺寸控制在3~9 nm的单分散Pt₃Co纳米粒子.电化学研究表明,Pt₃Co纳米粒子的ORR催化活性与颗粒粒径有关,如图3所示.通过平衡电化学活性比表面积和面积比活性,能够实现最佳质量比活性的

最佳尺寸被确定为约4.5 nm.目前普遍认为,Pt颗粒粒径为3~4 nm时,ORR的质量比活性最佳^[8].同样地,当Pt合金纳米颗粒粒径减小时,表面Pt原子的平均配位数减少,导致*OH在晶面上的吸附增强,降低了ORR活性^[14,39].

对Pt合金的晶面控制和元素比例调控是提升ORR活性的重要方法.Vidal-Iglesias等人^[46]对比了Pt不同单晶晶面上的电化学曲线,结果表明,不同晶面对H吸脱附行为有显著的影响.Stamenkovic等人^[41]研究发现,Pt₃Ni(111)、Pt₃Ni(110)和Pt₃Ni(100)三种单晶电极对ORR催化活性按照Pt₃Ni(100)<Pt₃Ni(110)<<Pt₃Ni(111)的顺序增加,表明ORR对单晶表面的结构灵敏性.其中Pt₃Ni(111)晶面对ORR的活性比相应的Pt(111)晶面高10倍,并且比Pt/C催化剂高90倍.原位表面X射线散射(surface X-ray scattering, SXS)表征显示,在ORR测试工作条件下,其近表面层在最外层、第3层(富Pt)和第2原子层(富Ni)中表现出高度结构化的成分振荡.同时,他们利用理论计算研究了表面几何结构和表面电子结构对ORR的协同作用.结果表明,Pt表面原子与非反应性氧化物物种之间的弱相互作用增加了O₂吸附的活性位点,如图4所示.Oezaslan等人^[29]研究了Pt₃Cu、PtCu、PtCu₃三种Pt:Cu比例的合金结构、元素组成与ORR活性之间的“构-效关系”.结果显示,0.1 mol L⁻¹ HClO₄中质量比活性以Pt₃Cu<PtCu<PtCu₃的顺序增强,与纯Pt纳米粒子相比,PtCu₃的质量比活性增加了3~4倍,活性的提升是由于Cu原子的快速电化学溶解和富Pt外壳的形成.富Pt壳中产生的晶格应变导致Pt原子d带中心移动,

图3 颗粒粒径对Pt-M合金催化剂ORR性能的影响^[45]. (a) 不同粒径Pt₃Co/C催化剂的质量比活性变化; (b) 不同粒径Pt₃Co/C催化剂的面积比活性(0.9 V vs. RHE, 黑色)和电化学比表面积(红色)变化. 扫描速率为20 mV/s, 电极转速为1600 r/min

Figure 3 The effect of particle size on ORR performance of Pt-M alloy catalysts^[45]. (a) The mass activity changes of Pt₃Co/C catalysts with different particle sizes; (b) the specific activity (at 0.9 V vs. RHE, the black line) and the electrochemical specific area (the red line) changes of Pt₃Co/C catalysts with different particle sizes. The scanning rate is 20 mV/s and the electrode rotating velocity is 1600 r/min

图4 不同Pt₃Ni单晶的表面电子结构与ORR性能的关系^[41]. (a) 在0.1 mol L⁻¹ HClO₄中, 不同Pt₃Ni单晶与相应Pt单晶的循环伏安曲线对比; (b) 不同Pt₃Ni单晶与相应Pt单晶表面形貌和电子表面性质(以d带中心值表示)对ORR动力学(以在0.1 mol L⁻¹ HClO₄中, 1600 r/min的转速下, 旋转圆盘电极测试在0.9 V vs. RHE下电流密度 i_k 的值表示)的影响; (c) Pt₃Ni(111)单晶电极在0.1 mol L⁻¹ HClO₄中于循环伏安测试、旋转环盘电极测试中元素变化的原位表面X射线散射表征

Figure 4 The relation between the surface electronic structure and ORR properties of different Pt₃Ni single crystals^[41]. (a) The comparison of the cyclic voltammetry curves (CVs) of different Pt₃Ni single crystals and corresponding Pt single crystals in 0.1 mol L⁻¹ HClO₄; (b) the effects of surface morphology and electronic surface properties (denoted as values of d-band center positions) of different Pt₃Ni single crystals and corresponding Pt single crystals on ORR kinetics (i_k measured by rotating disk electrode at 0.9 V vs. RHE in 0.1 mol L⁻¹ HClO₄ at 1600 r/min); (c) *in situ* surface X-ray scattering characterizations of element changes during CV tests and rotating ring disk electrode (RRDE) tests of Pt₃Ni(111) single crystal electrodes in 0.1 mol L⁻¹ HClO₄

并削弱了活性氧的化学吸附,进而导致活性增强.对于PtCu催化剂,在 $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ 中,质量比活性比纯Pt的高2~3倍.

Tian等人^[47]以油胺作为溶剂和表面活性剂、油酸作为辅助表面活性剂和形貌控制剂、CO作为还原剂和晶面控制剂,使用热注射方法合成了富Pt核-富Ni中间层-富Pt壳“三明治”结构的高度均匀的 $\text{Pt}_{2.1}\text{Ni}$ 二十面体纳米晶体,如图5(a), (b)所示.具有(111)小面封闭的Pt壳和高度均匀的“三明治”结构共同改善了电催化性能,将面积比活性和质量比活度分别提高到 0.91 mA cm^{-2} 和 $0.32 \text{ A mg}_{\text{Pt}}^{-1}$ @ 0.9 V vs. RHE, 分别是商业Pt/C的4.1和2.5倍.得益于“三明治”结构良好的结构稳定性, $\text{Pt}_{2.1}\text{Ni}/\text{C}$ 在15000圈加速衰减循环后, ORR活性保持率在70%以上,表现出显著的催化稳定性,如图5所示.

高度有序的Pt-M合金催化剂在大大提升ORR性能和耐久性的突破方面,展现出进一步提升PEMFC性能方面应用的潜力^[18,19].研究发现,热退火方法在合金催化剂制备中能够促使Pt合金中元素重排,从而改变构型、活性和稳定性. Wang等人^[33]使用油胺油酸溶剂热法结合高温煅烧,合成了具有多层Pt-skin表面的Pt双金属催化剂,该催化剂显示出优异的电催化ORR性能.这种具有多层Pt-skin的Pt双金属催化剂与常规Pt催化剂相比,显示出超过1个数量级的活性增强,如图6所示.

Luo等人^[48]通过溶剂热法结合 H_2 气氛中热退火,得到了由NiO-Pt双壳包围的均相Pt-Ni合金核组成的催化剂.在轻轻去除NiO外壳后,脱合金的截角八面体 $\text{Pt}_{2.1}\text{Ni}$ 核-壳结构显示出大大增强的ORR活性,质量比活性较未退火样品提升达3.4倍,在经过30000圈加速衰减循环后,依旧能够保留45.4%.其膜电极(membrane electrode assembly, MEA)中的峰值功率密度达到 679.8 mW cm^{-2} ,相对于基于商业Pt/C的峰值功率密度增加了 138.4 mW cm^{-2} .

2.2 Pt合金催化剂的制备方法

最常用的Pt合金制备方法是溶剂热法.体系中稳定剂(或封端剂)是纳米颗粒合成中控制晶面生长和颗粒粒径的关键因素^[24,49-52].然而,其在进行大批量制备时将存在问题.一方面,这些长链有机物通常难以彻底清除,残余的有机物吸附在合金颗粒的表面,将会阻碍晶面与反应物的接触,造成催化剂性能下降^[53].另一方面,尽管溶剂热法具有颗粒生长均匀的优点,但是其工艺复杂,所使用的金属盐与有机物的成本和清洗成本都较高,造成了较大的制备成本和后处理成本,不利于商业化应用.因此,人们提出了其他的溶剂热体系(如多元醇^[54,55]、*N,N*-二甲基甲酰胺(*N,N*-dimethylformamide, DMF)体系^[56-62]),以及其他简化制备、降低成本的方法.

图5 $\text{Pt}_{2.1}\text{Ni}$ 二十面体的材料表征和形成机理示意图及ORR性能测试^[47]. (a) $\text{Pt}_{2.1}\text{Ni}$ 二十面体纳米颗粒的透射电子显微镜图、粒径分布、高分辨透射电子显微镜图和扫描透射电子显微镜-能量色散X射线光谱元素面扫描图; (b) $\text{Pt}_{2.1}\text{Ni}$ 纳米颗粒的“三明治”结构形成机理示意图; (c) $\text{Pt}_{2.1}\text{Ni}$ 与商业Pt/C催化剂的ORR性能对比

Figure 5 The material characterizations and the schematic illustration for synthetic mechanisms of $\text{Pt}_{2.1}\text{Ni}$ icosahedral nanoparticles and the ORR catalytic tests^[47]. (a) Transmission electron microscopy (TEM) images, particle size distribution, high resolution transmission electron microscopy (HRTEM) images and scanning TEM-energy dispersive X-ray spectroscopy (STEM-EDS) images of $\text{Pt}_{2.1}\text{Ni}$ icosahedral nanoparticles; (b) the schematic diagram of the formation mechanism of the sandwich-like structure of $\text{Pt}_{2.1}\text{Ni}$ nanoparticles; (c) the comparison of ORR performance between $\text{Pt}_{2.1}\text{Ni}$ and commercial Pt/C catalysts

图6 通过旋转圆盘电极对沉积在PtNi基底上的Pt层进行ORR催化的电化学研究^[33]。(a) 循环伏安图; (b) 极化曲线; (c) 各种Pt层的活性和相对于纯Pt表面相应的提升; (d) 不同厚度的Pt原子层退火前后的元素分布变化示意图

Figure 6 The electrochemical ORR catalytic study of Pt layers deposited on PtNi substrate by rotating disk electrode^[33]. (a) Cyclic voltammograms; (b) polarization curves; (c) the activity increases of various Pt layers relative to pure Pt surface; (d) schematic diagram of the element distribution changes before and after annealing of Pt atomic layers with different thicknesses

法(电化学沉积法、原子层沉积法、物理溅射沉积等)。

与其他需要封端剂(例如, 聚二甲基二烯丙基氯化铵(poly dimethyl diallyl ammonium chloride, PDDA)和聚乙烯吡咯烷酮(polyvinyl pyrrolidone, PVP))的方法不同, DMF体系不需要专用的表面活性剂来诱导晶体的形状选择生长^[52,59,62,63]。而且, DMF这种溶于水的小分子有机物也更易清洗掉, 有利于催化剂获得更加清洁的颗粒表面, 因此DMF体系被广泛应用到Pt合金制备中。Carpenter等人^[57]用DMF作为溶剂和还原剂, 合成了不同PtNi元素比例的合金纳米晶体。Pt₃Ni合金纳米颗粒催化剂的面积比活性大于1 mA cm⁻², PtNi合金催化剂的面积比活性接近3 mA cm⁻², 近15倍于商业Pt/C催化剂。Cui等人^[59]在DMF溶剂中制备了PtNi八面体合金, 面积比活性可达3.14 mA cm⁻², 基于Pt质量的质量比活性达1.45 A mg_{Pt}⁻¹, 比Pt/C电催化剂提高了10倍。他们在DMF体系中也制备得到了性能优异的八面体PtNi_{1.5}合金催化剂^[15]。

开发低Pt载量、高活性、耐久性的可扩展制备方法是燃料电池商业化的必由之路。用电化学沉积方法

或者物理溅射方法进行制备, 将Pt颗粒沉积到载体上^[64,65], 或者直接沉积到气体扩散层上^[66~71], 制备阴极催化层后组装电池进行测试。这种方法能够极大简化制备流程, 为单电池中催化层的规模化制备提供了新思路。

Shen等人^[72]提出一种简便的电沉积方法。他们在水溶液中加入一定量DMF溶液, 通过DMF分子与Pt前驱体离子的选择性配位拉近了Pt和Co之间的沉积电势差, 促进了合金催化剂的形成。电沉积过程形成了高度多孔富含Pt的表面, 得到的最佳Pt₄Co合金样品具有1.52 mA cm⁻²@0.9 V vs. RHE的面积比活性, 是商业Pt/C催化剂的7倍^[72]。他们还提出了一种在纯DMF溶剂中施行恒电位电沉积法制备Pt电催化剂的策略^[73]。试验结果表明, 随着沉积电位的负向移动, Pt催化剂会以渐进成核的方式从平面结构转变为树状和纳米棒状结构, 在-1.7 V vs. SCE处沉积的Pt催化剂表现出最高的面积比活性0.84 mA cm⁻²。该研究结合DFT计算表明, 支持电解质在沉积基底(此处为玻碳电极)上的过强吸附将对金属原子的沉积产生阻碍作用, 并提出以吸附

能作为电沉积体系中选择合适的支持电解质的重要因素^[73]。

Hsueh等人^[65]通过原子层沉积(atomic layer deposition, ALD)技术将Pt纳米颗粒沉积在氧等离子体处理的碳纳米管上,实现了尺寸为1.60~4.80 nm的非常均匀且分布均匀的Pt纳米颗粒的形成。Pt纳米粒子的生长速率可以通过ALD循环次数和氧等离子体处理时间来控制。这种制备方法的另一个显著优势在于,可以将Pt负载量控制在非常低的值,与用于质子交换膜燃料电池的商用E-Tek催化剂Pt/石墨(0.5 mg cm^{-2})相比,负载量可能低2~3个数量级。Cheng等人^[71]提出了一种通过区域选择性ALD稳定包裹在氧化锆纳米笼中的Pt催化剂的简便方法。封装在氧化锆纳米笼中的Pt纳米颗粒在酸性介质中显示出非常高的ORR活性和稳定性。活性增强主要是由于Pt颗粒的尺寸小以及Pt和 ZrO_2 的协同作用。稳定性显著改善归因于氧化锆纳米笼的存在,它可以防止Pt纳米颗粒迁移和在载体上发生团聚。Dhanasekaran等人^[67]通过单步电沉积方法将三维超细Pt纳米花直接沉积在碳包覆的气体扩散层电极上,伴随电沉积电流密度从 -1.6 mA cm^{-2} 增加到 -32 mA cm^{-2} ,Pt纳米球可转换为三维纳米花。纳米花型Pt催化剂在PEMFC中表现出 660 mW cm^{-2} 的高峰值功率密度。但是,用上述方法制备Pt合金却鲜有研究,也提出了更严苛的挑战。

3 核-壳结构Pt基催化剂

3.1 核-壳结构Pt基催化剂的研究进展

Pt-M合金催化剂具有优异的ORR活性,但是在旋转圆盘电极测试过程和全电池测试工况下,过渡金属M的溶出导致催化剂颗粒的形貌和表面无法完整地保持^[24]。Xin等人^[74]研究了酸性体系中电势循环前后Pt-Co合金颗粒内Pt、Co元素分布的变化,提出过渡金属溶出后Pt-Co颗粒的3个最外层是Pt,但壳层始终保持对Pt-Co核的应变。因此,其催化活性较纯Pt提升可能与表面上Pt原子的间距或排列有关,例如由于晶格参数的变化而引起的d带宽度的变化,而不是由于来源于直接耦合的Co原子。这也表明,在Pt-M合金、非Pt单金属或合金表面外包裹Pt壳的核-壳结构Pt基催化剂的设计策略对于减少Pt负载量是有必要的。该催化剂的优势在于:一方面,因为Pt原子都在表层,Pt原子的利用率将极大提升;另一方面,Pt表层与基底金属的晶格不匹配促使表面Pt层中产生晶格应力作用,从而改变其d带中心,进

而实现对Pt层活性和稳定性的调控^[75~77]。

催化剂表面电子状态对催化活性有重要影响,催化剂颗粒近表面调控引起的配体和应变效应对ORR活性有重要的作用^[49,59,62]。Kong等人^[78]提出了一种由超薄的富含Pt的壳(约两个原子层)和富含Pt的本体组成的 $\text{Pt}_{1.5}\text{Ni}$ 八面体,对ORR表现出优异的面积比活性和质量比活性(7.7 mA cm^{-2} , $1.9 \text{ A mg}_{\text{Pt}}^{-1}$ @0.9 V),分别约为商业Pt/C的20和10倍。此外,由于其可阻止表面Pt原子和内部Ni原子扩散和溶解,加速衰减测试(accelerated degradation test, ADT)后,质量比活性仅下降9.2%。

3.2 核-壳结构Pt基催化剂的制备方法

目前,核-壳结构Pt基催化剂主要通过胶体法、化学反应驱动的晶体重构和电化学方法制备。胶体法是在溶液相中,通过在现有纳米颗粒种子或核上进行异质成核而实现。Zhang等人^[79]在溶剂热法中,通过调控反应温度,制备得到了不同Pt壳厚度的Pd@Pt/C催化剂。随着Pt壳层厚度的增加,获得了 $-1.85\%\sim-0.18\%$ 的表面应变。Pd@Pt3.4L/C催化剂($0.95 \text{ A mg}_{\text{Pt}}^{-1}$)的最佳质量比活性较商业Pt/C催化剂的高5.3倍。对应变-活性关系的理论研究表明,Pd@Pt3.4L/C具有1.85%的表面压缩率和最佳的氧结合能(0.15 eV)。该催化剂也在8000圈加速衰减循环后表现出显著提升的稳定性。

化学反应驱动的晶体重构是由热诱导或吸附物诱导而引起的。Wang等人^[80]采用一种简单的制备方法,即先通过浸渍法合成Pt-Co合金,再通过 H_2 气氛煅烧诱导Pt原子和Co原子重排,形成了一种以有序 Pt_3Co 金属间化合物为核,由具有2~3个原子层厚的Pt外壳构成的核-壳结构催化剂。与无序的 Pt_3Co 合金纳米颗粒及Pt/C相比,这些纳米催化剂的质量比活性提高了200%以上,面积比活性提高了300%以上。5000圈加速电势循环后,活性损失最小,并且有序的核-壳结构保持了完整形貌。该催化剂的高活性和稳定性归因于富含Pt的壳和稳定的金属间化合物 Pt_3Co 核排列。

电化学方法制备核-壳结构催化剂分为电化学去合金方法和欠电位沉积方法。电化学去合金方法是指通过施加阳极电流,从合金金属表面选择性地溶解非Pt金属直到形成富Pt表面的过程,也可以通过电势循环来实现^[81,82]。欠电位沉积方法利用了平衡还原电位下Cu单层沉积在诸如Pt或Pd贵金属表面上的现象^[76,83,84]。Luo等人^[85]通过溶剂热法获得了高度均匀且成分渐变的 $\text{Pd}_x\text{Ni}_{1-x}$ 纳米颗粒,并在其上施行Cu欠电位

沉积和 Pt^{2+} 化学置换,将Pt单层或多层壳包覆到 $\text{Pd}_x\text{Ni}_{1-x}$ 核上,合成了粒径均匀的10 nm以下 $\text{Pd}_x\text{Ni}_{1-x}@\text{Pt}$ 纳米球,如图7所示.经过优化的 $\text{Pd}_{0.42}\text{Ni}_{0.58}@\text{Pt}/\text{C}$ 在0.9 V vs. RHE下显示出 0.61 mA cm^{-2} 、 $0.42 \text{ A mg}_{\text{Pd+Pt}}^{-1}$ 和 $1.45 \text{ A mg}_{\text{Pt}}^{-1}$ 的活性,分别是商业Pt/C的2.8、3.3和11.2倍.此外, $\text{Pd}_{0.42}\text{Ni}_{0.58}@\text{Pt}/\text{C}$ 还具有良好的电化学耐久性,在加速降解试验的12000圈电势循环后,保持了较高的ORR催化活性.之后,Luo等人^[86]进行了该方法的优化.首先,对具有组成渐变结构的碳负载的 Cu_1Pd_1 纳米球进行退火处理;接着,通过完全的Cu欠电位沉积和 Pt^{2+} 置换,得到覆盖Pt单层壳的催化剂.得益于Pt的结构效应和组成渐变的 Cu_1Pd_1 核对Pt单层的协同作用,该催化剂在碱性和酸性ORR催化中均表现出优异的活性和稳定性^[86].

值得注意的是,上述核-壳结构催化剂的核仍旧是贵金属,在实际应用中成本仍将是不可避免的问题,采用非贵金属作为核材料才能最终实现题中应有之义.在非贵金属(Fe、Co、Ni等)上进行欠电位沉积可控制Pt单层或多层核-壳结构催化剂的试验方案鲜有报道.在这些过渡金属上实现Pt单层可控沉积,要求首先

制备出过渡金属基底,而这些过渡金属由于电负性较小,极易被空气氧化,因此相应纳米颗粒的制备也少有研究.目前,非贵金属作核的核-壳结构催化剂的制备方法大多采用热合成法.Chen等人^[87]采用改性多元醇工艺,通过两步还原程序的溶剂热法合成并表征了具有多种Pt表面覆盖率的碳载 $\text{Ni}@\text{Pt}$ 核壳纳米颗粒催化剂($\text{Ni}@\text{Pt}/\text{C}$).结果表明,在制备的催化剂中,Pt在Ni颗粒上形成了扩展层,并且除了核心金属的性质和成分外,还可以通过改变其表面覆盖率来调整核-壳纳米催化剂中贵金属壳的电催化性能.Zhang等人^[88]通过种子介导的生长及其随后的转化,合成了大小可控的单分散核-壳 $\text{Ni}@\text{FePt}$ 纳米颗粒.其中FePt壳厚度约为1 nm,核尺寸从4.2 nm调整为9 nm.值得注意的是,Ni的表面氧化对核-壳的形成至关重要,只有防止Ni的氧化,才能形成均匀的FePt涂层.经过后处理, $\text{Ni}@\text{FePt}$ 转化为 Ni/Pt ,从而形成ORR活性催化剂.通过调整颗粒的核心尺寸,可以进一步提高其ORR催化效率,面积比活性和质量比活性分别为 1.95 mA cm^{-2} 和 $490 \text{ mA mg}_{\text{Pt}}^{-1}$ @0.9 V vs. RHE.该种催化剂表现出能够显著降低催化剂成本的应用潜力.

图7 欠电位沉积制备的 $\text{PdNi}@\text{Pt}/\text{C}$ 核-壳结构催化剂^[85]. (a) 单个 $\text{Pd}_{0.69}\text{Ni}_{0.31}@\text{Pt}$ 纳米颗粒的元素分布表征; (b) 不同的 $\text{Pd}_x\text{Ni}_{1-x}$ 核引起的Pt单层原子晶格压缩示意图; (c) 系列 $\text{Pd}_x\text{Ni}_{1-x}@\text{Pt}/\text{C}$ 催化剂的ORR测试曲线

Figure 7 $\text{PdNi}@\text{Pt}/\text{C}$ core-shell catalysts prepared by underpotential deposition^[85]. (a) The elemental distribution characterizations of a single $\text{Pd}_{0.69}\text{Ni}_{0.31}@\text{Pt}$ nanoparticle; (b) the schematic diagram of Pt monolayer atomic lattice contraction caused by different $\text{Pd}_x\text{Ni}_{1-x}$ cores; (c) the ORR test curves of a series of $\text{Pd}_x\text{Ni}_{1-x}@\text{Pt}/\text{C}$ catalysts

4 总结与展望

随着“低碳”概念的普及和国家对发展新能源的战略要求, 清洁、零排放的燃料电池汽车具有良好的发展前景. 在氢燃料电池商业化的推进过程中, 其成本是迫切需要解决的问题. PEMFCs电堆中阴极Pt的高用量是造成燃料电池成本居高不下的主要原因, 因此开发低Pt、高催化活性的Pt基催化剂势在必行. 已有研究表明, 均匀Pt合金催化剂(包括双金属合金催化剂以及三金属合金催化剂)和核-壳结构Pt基催化剂能够有效地

降低Pt用量, 通过对合金晶体颗粒的元素比例、晶面、粒径等进行精确调控, 显著提升了Pt基催化剂的ORR活性和耐久性. 然而, 目前常用的制备方法由于原料成本与制备成本高昂和过程复杂, 大都难以适应规模化生产需求. 因此, 在低Pt催化剂研究的进程中, 从开发可以实用化的催化剂角度进行突破性研究, 发展既能在微观层面通过精确调控催化剂纳米颗粒的粒径、元素组成、晶面等达到改变本征ORR催化活性的要求, 又能在宏观层面实现批量制备低Pt催化剂的制备策略是有必要的.

参考文献

- 1 The State Council of the People's Republic of China. Made in China 2025 (in Chinese). Technical Report, 2015 [中华人民共和国国务院. 中国制造2025. 科技报告, 2015]
- 2 National Development and Reform Commission of the People's Republic of China. Judgment on the Situation of Strategic Emerging Industries and Suggestions for the Development of the 14th Five-Year Plan (Part 1) (in Chinese). Technical Report, 2021 [中华人民共和国国家发展和改革委员会. 战略性新兴产业形势判断及“十四五”发展建议(上篇). 科技报告, 2021]
- 3 Shao Z G, Yi B L. Developing trend and present status of hydrogen energy and fuel cell development (in Chinese). *Bull Chin Acad Sci*, 2019, 34: 469–477 [邵志刚, 衣宝廉. 氢能与燃料电池发展现状及展望. 中国科学院院刊, 2019, 34: 469–477]
- 4 Pivovar B. Catalysts for fuel cell transportation and hydrogen related uses. *Nat Catal*, 2019, 2: 562–565
- 5 The State Council of the People's Republic of China. The Guideline on Emerging Sectors of Strategic Importance During the 13th Five-Year Plan Period (in Chinese). Technical Report, 2016 [中华人民共和国国务院. “十三五”国家战略性新兴产业发展规划. 科技报告, 2016]
- 6 Wang Y, Diaz D F R, Chen K S, et al. Materials, technological status, and fundamentals of PEM fuel cells—A review. *Mater Today*, 2020, 32: 178–203
- 7 Papageorgopoulos D. Fuel Cell R&D Overview. In: 2019 Annual Merit Review and Peer Evaluation Meeting, U. S. Department of Energy. Technical Report, 2019
- 8 Wang X X, Swihart M T, Wu G. Achievements, challenges and perspectives on cathode catalysts in proton exchange membrane fuel cells for transportation. *Nat Catal*, 2019, 2: 578–589
- 9 Wang J, Ding W, Wei Z D. Review: Performance of polymer electrolyte membrane fuel cells at ultra-low platinum loadings (in Chinese). *Acta Phys-Chim Sin*, 2021, 37: 2009094 [王健, 丁炜, 魏子栋. 超低铂用量质子交换膜燃料电池. 物理化学学报, 2021, 37: 2009094]
- 10 Yu H M, Yi B L. Current status of vehicle fuel cells and electrocatalysis (in Chinese). *Sci Sin-Chim*, 2012, 42: 480–494 [俞红梅, 衣宝廉. 车用燃料电池现状与电催化. 中国科学: 化学, 2012, 42: 480–494]
- 11 Papageorgopoulos D. Fuel Cell R&D Overview. In: 2018 Annual Merit Review and Peer Evaluation Meeting, U. S. Department of Energy. Technical Report, 2018
- 12 Kodama K, Nagai T, Kuwaki A, et al. Challenges in applying highly active Pt-based nanostructured catalysts for oxygen reduction reactions to fuel cell vehicles. *Nat Nanotechnol*, 2021, 16: 140–147
- 13 Li J, Feng X, Wei Z D. Recent progress in Pt-based catalysts for oxygen reduction reaction (in Chinese). *J Electrochem*, 2018, 24: 589–601 [李静, 冯欣, 魏子栋. 铂基燃料电池氧还原反应催化剂研究进展. 电化学, 2018, 24: 589–601]
- 14 Ma Z, Cano Z P, Yu A, et al. Enhancing oxygen reduction activity of Pt-based electrocatalysts: From theoretical mechanisms to practical methods. *Angew Chem Int Edit*, 2020, 59: 18334–18348
- 15 Kulkarni A, Siahrostami S, Patel A, et al. Understanding catalytic activity trends in the oxygen reduction reaction. *Chem Rev*, 2018, 118: 2302–2312
- 16 Nørskov J K, Rossmeisl J, Logadottir A, et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J Phys Chem B*, 2004, 108: 17886–17892
- 17 Nie Y, Li L, Wei Z. Recent advancements in Pt and Pt-free catalysts for oxygen reduction reaction. *Chem Soc Rev*, 2015, 44: 2168–2201
- 18 Ren X, Lü Q, Liu L, et al. Current progress of Pt and Pt-based electrocatalysts used for fuel cells. *Sustain Energy Fuels*, 2020, 4: 15–30
- 19 Tian X, Lu X F, Xia B Y, et al. Advanced electrocatalysts for the oxygen reduction reaction in energy conversion technologies. *Joule*, 2020, 4: 45–68

- 20 Hansen H A, Viswanathan V, Nørskov J K. Unifying kinetic and thermodynamic analysis of 2 e⁻ and 4 e⁻ reduction of oxygen on metal surfaces. *J Phys Chem C*, 2014, 118: 6706–6718
- 21 Morozan A, Jousselm B, Palacin S. Low-platinum and platinum-free catalysts for the oxygen reduction reaction at fuel cell cathodes. *Energy Environ Sci*, 2011, 4: 1238–1254
- 22 Wang N, Li Y, Guo Z, et al. Minute quantities of hexagonal nanoplates PtFe alloy with facile operating conditions enhanced electrocatalytic activity and durability for oxygen reduction reaction. *J Alloys Compd*, 2018, 752: 23–31
- 23 Zalitis C, Kucernak A, Lin X, et al. Electrochemical measurement of intrinsic oxygen reduction reaction activity at high current densities as a function of particle size for Pt_{4-x}Co_x/C (x = 0, 1, 3) catalysts. *ACS Catal*, 2020, 10: 4361–4376
- 24 Choi J, Cho J, Roh C W, et al. Au-doped PtCo/C catalyst preventing Co leaching for proton exchange membrane fuel cells. *Appl Catal B-Environ*, 2019, 247: 142–149
- 25 Li Z, Niu W, Yang Z, et al. Stabilizing atomic Pt with trapped interstitial F in alloyed PtCo nanosheets for high-performance zinc-air batteries. *Energy Environ Sci*, 2020, 13: 884–895
- 26 Lu S, Eid K, Deng Y, et al. One-pot synthesis of PtIr tripods with a dendritic surface as an efficient catalyst for the oxygen reduction reaction. *J Mater Chem A*, 2017, 5: 9107–9112
- 27 Kim H Y, Kwon T, Ha Y, et al. Intermetallic PtCu nanoframes as efficient oxygen reduction electrocatalysts. *Nano Lett*, 2020, 20: 7413–7421
- 28 Li C, Liu T, He T, et al. Composition-driven shape evolution to Cu-rich PtCu octahedral alloy nanocrystals as superior bifunctional catalysts for methanol oxidation and oxygen reduction reaction. *Nanoscale*, 2018, 10: 4670–4674
- 29 Oezaslan M, Hasché F, Strasser P. PtCu₃, PtCu and Pt₃Cu alloy nanoparticle electrocatalysts for oxygen reduction reaction in alkaline and acidic media. *J Electrochem Soc*, 2012, 159: B444–B454
- 30 Jeon M K, McGinn P J. Carbon supported Pt-Y electrocatalysts for the oxygen reduction reaction. *J Power Sources*, 2011, 196: 1127–1131
- 31 Liu S, Liu P. Optimized Pt-based catalysts for oxygen reduction reaction in alkaline solution: A first principle study. *J Electrochem Soc*, 2018, 165: J3090–J3094
- 32 Hammer B, Nørskov J K. Theoretical surface science and catalysis—Calculations and concepts. *Adv Catal*, 2000, 45: 71–129
- 33 Wang C, Chi M, Li D, et al. Design and synthesis of bimetallic electrocatalyst with multilayered Pt-skin surfaces. *J Am Chem Soc*, 2011, 133: 14396–14403
- 34 Nilsson A, Pettersson L G M, Hammer B, et al. The electronic structure effect in heterogeneous catalysis. *Catal Lett*, 2005, 100: 111–114
- 35 Cao F, Liu T, Si W, et al. One-pot synthesis of icosahedral PdPtNi/C twin crystal catalyst with high activity toward oxygen reduction reaction. *Adv Mater Interfaces*, 2018, 5: 1800783
- 36 Zhang C, Sandorf W, Peng Z. Octahedral Pt₂CuNi uniform alloy nanoparticle catalyst with high activity and promising stability for oxygen reduction reaction. *ACS Catal*, 2015, 5: 2296–2300
- 37 Liu F, Sun K, Rui Z, et al. Highly durable and active ternary Pt-Au-Ni electrocatalyst for oxygen reduction reaction. *ChemCatChem*, 2018, 10: 3049–3056
- 38 Zhao Z, Chen C, Liu Z, et al. Pt-based nanocrystal for electrocatalytic oxygen reduction. *Adv Mater*, 2019, 31: e1808115
- 39 Wang C, Markovic N M, Stamenkovic V R. Advanced platinum alloy electrocatalysts for the oxygen reduction reaction. *ACS Catal*, 2012, 2: 891–898
- 40 Wu D, Shen X, Pan Y, et al. Platinum alloy catalysts for oxygen reduction reaction: Advances, challenges and perspectives. *ChemNanoMat*, 2019, 6: 32–41
- 41 Stamenkovic V R, Fowler B, Mun B S, et al. Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. *Science*, 2007, 315: 493–497
- 42 Blurton K F, Greenberg P, Oswin H G, et al. The electrochemical activity of dispersed platinum. *J Electrochem Soc*, 1972, 119: 559
- 43 Peuckert M, Yoneda T, Betta D, et al. Oxygen reduction on small supported platinum particles. *Cheminform*, 1986, 17: 944–947
- 44 Han B C, Miranda C R, Ce Der G. Effect of particle size and surface structure on adsorption of O and OH on platinum nanoparticles: A first-principles study. *Phys Rev B Condens Matter*, 2008, 77: 439–446
- 45 Wang C, Dennis V, Chang K C, et al. Monodisperse Pt₃Co nanoparticles as a catalyst for the oxygen reduction reaction: Size-dependent activity. *J Phys Chem C*, 2009, 113: 19365–19368
- 46 Vidal-Iglesias F J, Arán-Ais R M, Solla-Gullón J, et al. Electrochemical characterization of shape-controlled Pt nanoparticles in different supporting electrolytes. *ACS Catal*, 2012, 2: 901–910
- 47 Tian R, Shen S, Zhu F, et al. Icosahedral Pt-Ni nanocrystalline electrocatalyst: Growth mechanism and oxygen reduction activity. *ChemSusChem*, 2018, 11: 1015–1019
- 48 Luo X, Guo Y, Zhou H, et al. Thermal annealing synthesis of double-shell truncated octahedral Pt-Ni alloys for oxygen reduction reaction of polymer electrolyte membrane fuel cells. *Front Energy*, 2020, 14: 767–777

- 49 Coutanceau C, Urchaga P, Brimaud S, et al. Colloidal syntheses of shape- and size-controlled Pt nanoparticles for electrocatalysis. [Electrocatalysis](#), 2012, 3: 75–87
- 50 Moglianetti M, Solla-Gullón J, Donati P, et al. Citrate-coated, size-tunable octahedral platinum nanocrystals: A novel route for advanced electrocatalysts. [ACS Appl Mater Interfaces](#), 2018, 10: 41608–41617
- 51 Chang Q, Xu Y, Duan Z, et al. Structural evolution of sub-10 nm octahedral platinum-nickel bimetallic nanocrystals. [Nano Lett](#), 2017, 17: 3926–3931
- 52 Huang X, Zhu E, Chen Y, et al. A facile strategy to Pt₃Ni nanocrystals with highly porous features as an enhanced oxygen reduction reaction catalyst. [Adv Mater](#), 2013, 25: 2974–2979
- 53 Zhao Q, Li H, Zhang X, et al. Platinum *in-situ* catalytic oleylamine combustion removal process for carbon supported platinum nanoparticles. [J Energy Chem](#), 2020, 41: 120–125
- 54 Chen Y, Wang J, Liu H, et al. Enhanced stability of Pt electrocatalysts by nitrogen doping in CNTs for PEM fuel cells. [Electrochem Commun](#), 2009, 11: 2071–2076
- 55 Fang D, Wan L, Jiang Q, et al. Wavy PtCu alloy nanowire networks with abundant surface defects enhanced oxygen reduction reaction. [Nano Res](#), 2019, 12: 2766–2773
- 56 Arán-Ais R M, Dionigi F, Merzdorf T, et al. Elemental anisotropic growth and atomic-scale structure of shape-controlled octahedral Pt-Ni-Co alloy nanocatalysts. [Nano Lett](#), 2015, 15: 7473–7480
- 57 Carpenter M K, Moylan T E, Kukreja R S, et al. Solvothermal synthesis of platinum alloy nanoparticles for oxygen reduction electrocatalysis. [J Am Chem Soc](#), 2012, 134: 8535–8542
- 58 Lu Y, Thia L, Fisher A, et al. Octahedral PtNi nanoparticles with controlled surface structure and composition for oxygen reduction reaction. [Sci China Mater](#), 2017, 60: 1109–1120
- 59 Cui C, Gan L, Li H H, et al. Octahedral PtNi nanoparticle catalysts: Exceptional oxygen reduction activity by tuning the alloy particle surface composition. [Nano Lett](#), 2012, 12: 5885–5889
- 60 Dong A, Ye X, Chen J, et al. A generalized ligand-exchange strategy enabling sequential surface functionalization of colloidal nanocrystals. [J Am Chem Soc](#), 2011, 133: 998–1006
- 61 Gan L, Heggen M, Cui C, et al. Thermal facet healing of concave octahedral Pt-Ni nanoparticles imaged *in situ* at the atomic scale: Implications for the rational synthesis of durable high-performance ORR electrocatalysts. [ACS Catal](#), 2015, 6: 692–695
- 62 Gumezi C, Marathe A, Behrens R L, et al. Solvothermal synthesis and electrochemical characterization of shape-controlled Pt nanocrystals. [J Phys Chem C](#), 2014, 118: 14433–14440
- 63 Zhang N, Tsao K C, Pan Y T, et al. Control of the composition of Pt-Ni electrocatalysts in surfactant-free synthesis using neat N-formylpiperidine. [Nanoscale](#), 2016, 8: 2548–2553
- 64 Martín A J, Chaparro A M, Folgado M A, et al. Electrodeposition of platinum on carbon black for fuel cell application. [ECS Trans](#), 2008, 13: 13–18
- 65 Hsueh Y C, Wang C C, Liu C, et al. Deposition of platinum on oxygen plasma treated carbon nanotubes by atomic layer deposition. [Nanotechnology](#), 2012, 23: 405603
- 66 Taylor E J, Anderson E B, Vilambi N R K. Preparation of high-platinum-utilization gas diffusion electrodes for proton-exchange-membrane fuel cells. [J Electrochem Soc](#), 1992, 139: L45–L46
- 67 Dhanasekaran P, Lokesh K, Ojha P K, et al. Electrochemical deposition of three-dimensional platinum nanoflowers for high-performance polymer electrolyte fuel cells. [J Colloid Interface Sci](#), 2020, 572: 198–206
- 68 Ruengkit C, Tantavichet N. Influence of gas diffusion layer on Pt catalyst prepared by electrodeposition for proton exchange membrane fuel cells. [Thin Solid Films](#), 2017, 636: 116–126
- 69 Sievers G, Vidakovic-Koch T, Walter C, et al. Ultra-low loading Pt-sputtered gas diffusion electrodes for oxygen reduction reaction. [J Appl Electrochem](#), 2018, 48: 221–232
- 70 Cheng N, Shao Y, Liu J, et al. Electrocatalysts by atomic layer deposition for fuel cell applications. [Nano Energy](#), 2016, 29: 220–242
- 71 Cheng N, Banis M N, Liu J, et al. Extremely stable platinum nanoparticles encapsulated in a zirconia nanocage by area-selective atomic layer deposition for the oxygen reduction reaction. [Adv Mater](#), 2015, 27: 277–281
- 72 Shen S, Li F, Luo L, et al. DMF-coordination assisted electrodeposition of highly active PtCo alloy catalysts for the oxygen reduction reaction. [J Electrochem Soc](#), 2018, 165: D43–D49
- 73 Shen S, Li F, Zhao L, et al. Communication—An organic solvent system-assisted electrodeposition of highly active Pt for the oxygen reduction reaction. [J Electrochem Soc](#), 2018, 165: J3392–J3394
- 74 Xin H L, Mundy J A, Liu Z, et al. Atomic-resolution spectroscopic imaging of ensembles of nanocatalyst particles across the life of a fuel cell. [Nano Lett](#), 2012, 12: 490–497
- 75 Adzic R R, Zhang J, Sasaki K, et al. Platinum monolayer fuel cell electrocatalysts. [Top Catal](#), 2007, 46: 249–262

- 76 Lima F H B, Zhang J, Shao M H, et al. Pt monolayer electrocatalysts for O₂ reduction: PdCo/C substrate-induced activity in alkaline media. *J Solid State Electrochem*, 2007, 12: 399–407
- 77 Vukmirovic M B, Zhang J, Sasaki K, et al. Platinum monolayer electrocatalysts for oxygen reduction. *Electrochim Acta*, 2007, 52: 2257–2263
- 78 Kong F, Ren Z, Norouzi Banis M, et al. Active and stable Pt-Ni alloy octahedra catalyst for oxygen reduction via near-surface atomical engineering. *ACS Catal*, 2020, 10: 4205–4214
- 79 Zhang Y, Qin J, Leng D, et al. Tunable strain drives the activity enhancement for oxygen reduction reaction on Pd@Pt core-shell electrocatalysts. *J Power Sources*, 2021, 485: 229340
- 80 Wang D, Xin H L, Hovden R, et al. Structurally ordered intermetallic platinum-cobalt core-shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. *Nat Mater*, 2013, 12: 81–87
- 81 Strasser P, Koh S, Anniyev T, et al. Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. *Nat Chem*, 2010, 2: 454–460
- 82 Huang Y, Garcia M, Habib S, et al. Dealloyed PtCo hollow nanowires with ultrathin wall thicknesses and their catalytic durability for the oxygen reduction reaction. *J Mater Chem A*, 2014, 2: 16175–16180
- 83 Adzic R, Marinkovic N. *Platinum Monolayer Electrocatalysts*. Cham: Springer, 2020
- 84 Zhang J, Shen S. *Low Platinum Fuel Cell Technologies*. Berlin, Heidelberg: Springer, 2021
- 85 Luo L, Zhu F, Tian R, et al. Composition-graded Pd_xNi_{1-x} nanospheres with Pt monolayer shells as high-performance electrocatalysts for oxygen reduction reaction. *ACS Catal*, 2017, 7: 5420–5430
- 86 Luo L, Fu C, Shen S, et al. Probing structure-designed Cu-Pd nanospheres and their Pt-monolayer-shell derivatives as high-performance electrocatalysts for alkaline and acidic oxygen reduction reactions. *J Mater Chem A*, 2020, 8: 22389–22400
- 87 Chen Y, Liang Z, Yang F, et al. Ni-Pt core-shell nanoparticles as oxygen reduction electrocatalysts: Effect of Pt shell coverage. *J Phys Chem C*, 2011, 115: 24073–24079
- 88 Zhang S, Hao Y, Su D, et al. Monodisperse core/shell Ni/FePt nanoparticles and their conversion to Ni/Pt to catalyze oxygen reduction. *J Am Chem Soc*, 2014, 136: 15921–15924

Summary for “低铂质子交换膜燃料电池氧还原催化剂的研究进展与展望”

Progress and prospects of low platinum oxygen reduction catalysts for proton exchange membrane fuel cells

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In the past decades, wide attention has been attracted by Pt-based electrocatalysts due to the high catalytic activity towards oxygen reduction reaction (ORR) and the corresponding outstanding enhancement on the intrinsic sluggish kinetics at cathode of proton exchange membrane fuel cells (PEMFCs). However, the forthcoming large-scale application of PEMFCs would lead to a scarcity and price increase of Pt, which in turn restrict the further development and advance of PEMFCs. As a result, it is necessary to design and synthesize the ORR catalysts with low Pt loading, high performance as well as long lifetime.

It has been proved that the surface electronic structure can be regulated via optimizing the nanoparticle morphology, elemental composition, facet exposure as well as particle size, and thus improving ORR activity and stability of Pt-M (M = Ni, Co, Fe, Cu, Y, Sc, etc.) alloy catalysts. However, the conventional synthetic methods are complex and expensive, for which it is hard to transform from laboratory level to commercialization level. Therefore, there is an urgent need to explore strategies that could not only realize microscopic controllability on nanoparticles but also achieve large-scale preparation.

Another effective way to further reduce Pt loading is to construct core-shell structures where Pt exists as atomic layers on the surface of a non-Pt core. Meanwhile, the core-shell structure also benefits the ORR catalytic performance and durability via regulating the synergy effect between the core and the shell. But it is noticed that the core is composed of noble metal elements (such as Pd) in most of the research, whose price is equal or higher than that of Pt. Actually, a non-precious metal core could also alter the surface electronic structure of the nanoparticle crystals and increase the ORR activity. Nevertheless, the non-precious metal core is prone to dissolve when facing tough conditions whose key point lies on the catalyst durability as well as antioxidation during the synthetic process.

In this review, we elaborated the acknowledged theoretical ORR catalytic mechanism of Pt crystal catalysts, and deepened the understanding of performance enhancement benefiting from the Pt-based catalysts including Pt-M alloy and core-shell structure Pt-based catalysts. Subsequently, we summarized the representative studies on the progress and fabrication strategies of Pt-M alloy nanoparticles catalysts, including binary and ternary Pt alloy catalysts, as well as core-shell catalysts, including noble metal-Pt and non-noble metal-Pt core-shell catalysts, in recent years. It is believed that low-Pt ORR catalysts with precise control on shape, facet, elemental composition and particle size could boost the scientific and commercial development of PEMFCs and also need further exploration on suitable large-scale synthesis methods.

low platinum, high performance, oxygen reduction reaction, proton exchange membrane fuel cells, large-scale preparation strategy

doi: [10.1360/TB-2021-0221](https://doi.org/10.1360/TB-2021-0221)