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有序化膜电极研究进展

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摘要: 燃料电池的性能在近年来有很大提高, 但要实现商业化其成本和Pt用量需要进一步的降低. 大量的文献工作证明有序化膜电极有助于提高电极中催化剂的利用率、降低Pt的用量以及增加反应的三相界面, 特别是3M公司制备的纳米薄膜电极(NSTFs)是一种高活性, 高稳定性的薄膜状催化层, 从而电极稳定性也大幅提高. 此外, 也有不少工作使用导电性好的碳纳米管阵列以及稳定性高的金属氧化物阵列等作为这种3D结构催化层中催化剂的有序载体, 研究进一步提高Pt基催化剂的活性、降低Pt担载量及构效关系等一些基础性的工作. 但总体上看, 现有的有序化膜电极均需要进一步改进. 本文评述了目前国内外有序化膜电极的研究现状.

关键词: 质子交换膜燃料电池; 膜电极; 有序结构催化层

中图分类号: O646

文献标识码: A

燃料电池作为一种清洁且可持续的发电装置, 备受人们关注. 它是一种将燃料与氧化剂的化学能通过电化学反应直接转化成电能的环境友好型发电装置. 当前制约其大规模商业化的原因是其成本与寿命, 特别是做车用电源等动力系统大规模应用时, 这两者尤为突出. 美国能源部(DOE)对成本与寿命制定了目标: 2020年成本方面 $40 \$ \cdot \text{kW}^{-1}$, 寿命方面: 5000 h, PGM(Platinum-Group-Metals)担载量: $0.125 \text{ mg} \cdot \text{cm}^{-2}$ (电极). 单纯从催化剂的本征活性考虑, 如形成合金、核壳或Pt单原子层结构很难同时达到这些目标, 因为电池的性能不仅仅是由催化剂的本征活性决定, 更重要的是由催化剂构成的电极决定的.

有序化的理想模型是Middelmann等^[1]在2002年首次提出, 随后3M制备的NSTFs电极, 其性能及成本方面基本达到了2015年的DOE目标^[2]. 但低温启动的响应慢, 亲水的超薄电极容易导致水淹, 同时Pt的担载量还需要在保证性能的前提下进一步降低等问题, 需要进一步深入研究. 近年来出现了其他的有序化膜电极, 分别以碳纳米管/纳米线阵列^[3]、金属氧化物阵列^[4]、导电聚合物阵列为载体^[5]或者Pt纳米结构阵列直接作为电极^[6-8], 但现有的有序化

膜电极的性能均未超过3M公司的NETFs电极.

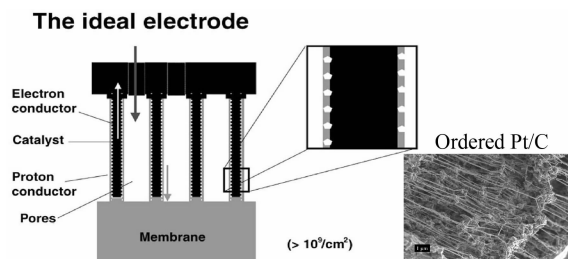
本文主要评述了国内外有序化膜电极的研究现状.

1 国内外有序化膜电极发展情况及相关问题

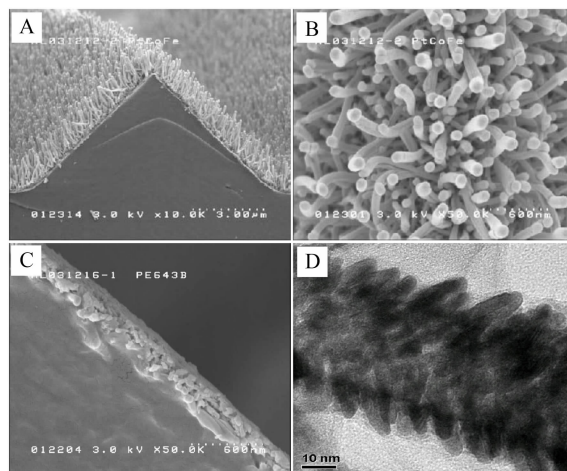
Middelmann^[1]在2002年通过可控自组装方法首次制备出有序结构膜电极, 他们在由碳颗粒组成的长链状定向结构表面均匀包覆分散的Pt颗粒, 然后在其表面制备一薄层质子导体, 其理想结构及SEM照片如图1所示. 同时, 模型计算表明, 当质子导体薄层的厚度小于10 nm时, 有利于气体扩散到三相界面以及排出产物水. 有序膜电极结构中Pt的利用率近100%, 使用传统Pt/C制备电极的20%的Pt担载量即可达到传统Pt/C电极的性能.

1.1 3M公司的NSTFs电极

3M公司在近十五年来一直发展着NSTFs电极, 发表了大量的文章和综述^[2,9-16], 研究了载体和催化剂的制备、水管理及稳定性测试. 他们在MCTS(Microstructured Catalyst Transfer Substrate)基底上先溅射一层金属(Cu、Al等)热退火制备单层定向有机染料晶须(PR-149)作为催化剂载体, 并在晶须上通过物理气相沉积溅射Pt或者Pt合金

图1 理想的有序化膜电极的示意图及其SEM照片^[1]Fig. 1 Schematic illustration and the SEM image of an ideal electrode^[1]

薄层催化剂(10~15 nm),如图2A-2B所示. NSTFs电极的四大特征:1)载体的特征:板条状的晶须(长度0.5~2.0 μm),体心立方结构(有两面主要暴露(111)晶面),与基底成约90°生长^[10]. 2)催化剂性质:磁控溅射将催化剂沉积在有机纳米晶须上成柱状催化剂(如图2D所示),催化剂为元素Pt、双元素PtM(Ni、Fe、Co、Cr、Nb)、三元素PtCoMn^[17]等,通过中等温度(350 $^{\circ}\text{C}$ ~500 $^{\circ}\text{C}$)退火处理之后得到膜状催化剂^[13]. 膜状催化剂的质量比活性是传统的Pt/C的催化剂活性的5~10倍左右,制备二元合金或三元合金膜状催化剂后其质量比活性进一步提高.但是由于膜状催化剂的比表面积比较小(5~17 $\text{m}^2\cdot\text{g}^{-1}_{\text{Pt}}$ vs. Pt/C 50~70 $\text{m}^2\cdot\text{g}^{-1}_{\text{Pt}}$),因此,将MCTS做成锯齿状结构,增加整体的比表面积,从而提高催化剂的总活性,稳定性大幅提高.膜状的NSTFC和传统的Pt/C催化剂进行加速衰减实验(ADT),0.6 V~1.2 V(vs. RHE),NSTFC在5000周ADT中ECSA只衰减了33%,而传统的Pt/C催化剂在加速衰减2000周之后衰减90%,且在1.5 V(vs. RHE)恒电位条件下,NSTFC只是减少很少的一部分活性面积,而传统的Pt/C催化剂则在30 min之后基本完全消失^[18]. 3)电极性质:电极的厚度是传统的催化层厚度的1/30~1/20,其传质明显优于后者.催化层无需质子导体(Nafion等),质子可能是靠催化剂表面的水或是Pt-OH来传导.同时有机纳米晶须取代了碳载体后,稳定性测试过程中 H_2O_2 的产生的量明显比Pt/C电极少,因此F的释放速率较小,表明Nafion膜的降解速度明显比传统的Pt/C催化层作电极慢. 4)几何结构的意义:催化剂的电化学活性面积(ECSA)随着催化剂的负载量的降低变化没有Pt/C那么明显,同时氧气分子在阴极催化层中的扩散属于努森扩散,增加了氧分子与催化剂的碰撞次数,

图2 NSTF电极的SEM照片^[2]

A. 小倍率; B. 大倍率; C. 转印至膜上的电极的侧面照片; D. PtM-NSTF的STEM照片

Fig. 2 SEM images of NSTF electrode^[2]

A. Low magnification; B. High magnification; C. Cross-section of NSTF electrode after transferred to membrane; D. STEM image of the PtM-NSTF

Debe等对此进行了相应的模型计算^[19].

在水管理方面^[20-21],NSTFs电极由于其超薄的催化层,容水的空间比传统的催化层小且亲水性较强,使得该类电极容易发生水淹,特别是在低温启动和高电密时. 3M公司及其合作单位研究了很多种改进方式来缓解阴极的水淹,包括将阴极的水从阳极排出(使用薄膜,且 $P_{\text{O}_2} > P_{\text{H}_2}$),同时优化阳极的气体扩散层. 总体上看,3M公司制备的电极具有明显的优势.

1.2 碳纤维/纳米管/N掺杂碳纳米管阵列为载体有序膜电极

有序的碳纳米管/纳米线阵列作为一种Pt纳米颗粒的载体,能够提高Pt的利用率、降低Pt负载量. 以有序碳纳米管/纳米线阵列为载体的有序化电极的制备包括两部分内容:有序载体的制备和催化剂的负载.

大量文章以及综述^[22-29]讲述有序碳纳米管/纳米线的制备方法,同时在催化剂的负载方面,通常是磁控溅射沉积Pt颗粒,而磁控溅射的方法负载的Pt纳米颗粒催化剂会在阵列顶端堆积. 电沉积^[30]也被用作这种3D结构的电极的催化剂的沉积方式,但是也局限于导电的基底. Bonnefont等^[31]在碳纳米线阵列上通过抗坏血酸还原 H_2PtCl_6 溶液,反应前

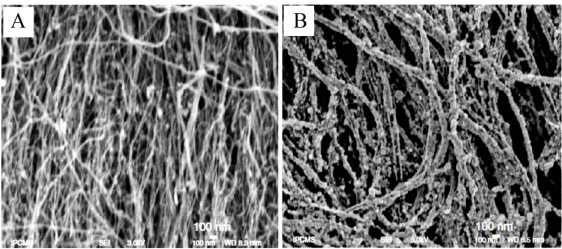


图3 在碳纳米线阵列上通过抗坏血酸原位还原 H_2PtCl_6 的SEM照片^[31]

A. 还原前;B. 还原后

Fig. 3 SEM images showing Pt deposition in VACNF arrays realized by *in-situ* reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with ascorbic acid before (A) and after (B) the reduction^[31]

后没有改变阵列形貌,同时催化剂均匀地包覆在碳纳米线表面,如图3所示.也有研究者通过碳纳米管阵列表面处理,如等离子体功能化^[32]以及N掺杂^[33]等,有效地提高Pt纳米颗粒的均匀沉积.

目前碳纳米管阵列有序膜电极的典型代表工作有两个.一个是Tian等在铝箔上制备有序碳纳米管阵列,磁控溅射负载Pt催化剂.通过调节两个影响因素:阵列的密度和Nafion的负载量,在Pt载量为 $35\text{ }\mu\text{g}\cdot\text{cm}^{-2}$ 和Nafion载量为 $10.8\text{ }\mu\text{g}\cdot\text{cm}^{-2}$ 时得到最佳的性能,与传统的Pt/C($0.4\text{ mg}\cdot\text{cm}^{-2}$)的性能相当(如图4A所示).另外一个Murata等^[34]制备的有序碳纳米管阵列,负载 $0.1\text{ mg}\cdot\text{cm}^{-2}$ 的Pt催化剂表现出良好的电化学性能, $2.6\text{ A}\cdot\text{cm}^{-2}$ 时仍有 0.6 V (如

图4B所示).

有序碳纳米管/纳米线阵列作为载体的膜电极的稳定性也有一些研究工作^[35-37],通过N掺杂和负载金属氧化物(NbO_2 ^[37]、 TiO_2 ^[38]等)来提高催化剂的稳定性,但是载体的稳定性没有涉及.

总的来说,碳纳米管/纳米线阵列作为有序的催化剂载体的明显优势在于其高机械强度、高电导率、足够大的比表面,但在强酸性、强氧化性及高电位的环境下需要考虑其稳定性.此外,碳基材料为有序载体时,电池运行过程容易产生中间产物 H_2O_2 ^[39],导致膜腐蚀及降解,从而使电池的稳定性受到影响.

1.3 金属氧化物阵列作为载体的有序膜电极

由于金属氧化物具有强的耐酸、耐氧化等特点,被认为可替换碳载体的一类材料,特别是 NbO_2 、 TiO_2 、 WO_3 等^[40-42],同时这些材料跟Pt基催化剂之间有很强的作用力,可以提高催化剂的活性与稳定性.在半电池测试中,金属氧化物为有序载体的电极表现出良好的稳定性和活性,但由于其较差的电导率而催化剂又未成膜,电极内阻大,因此在全电池测试中单纯的金属氧化物阵列电极,欧姆极化太大,从而没有理想的全电池性能报道.

Lim等^[43]通过磁控溅射技术在二氧化钛纳米管阵列上负载 20 nm 厚的Pt催化剂,在 $0\sim 1.2\text{ V}$ (vs. RHE)的电势范围内进行循环10000周后,其电化学生活性面积保留了原来的79.6%,表现出良好的稳定

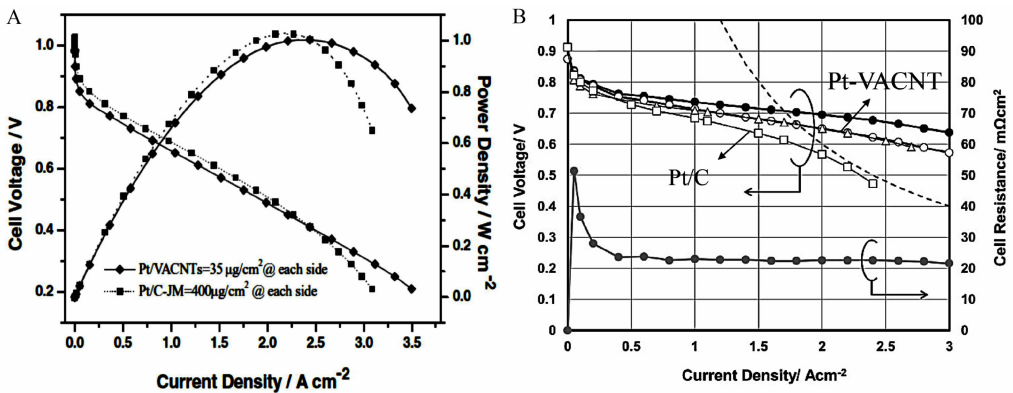


图4 Tian等^[3](A)和Murata等^[34](B)制备的碳纳米管阵列的单池性能与传统的Pt/C电极性能比较图(○:20 cm²碳纳米管阵列电极,●:20 cm²碳纳米管阵列电极*IR*校正,Δ:236 cm²碳纳米管阵列电极,□:236 cm²传统Pt/C电极,●:碳纳米管阵列电极的单池内阻,虚线:DOE目标 $0.125\text{ g}_{\text{PGM}}\cdot\text{kW}^{-1}$)

Fig. 4 The cell performance of CNT arrays based electrode prepared by (A) Tian et al.^[3] and (B) Murata et al.^[34] compared with that of the traditional Pt/C based electrode (○: VACNT electrodes (20 cm² cell), ●: VACNT electrodes *IR* corrected (20 cm² cell), Δ: VACNT electrodes (236 cm² cell), □: Conventional electrodes (236 cm² cell), ●: Cell resistance of VACNT electrodes. Dashed line: DOE target $0.125\text{ g}_{\text{PGM}}\cdot\text{kW}^{-1}$)

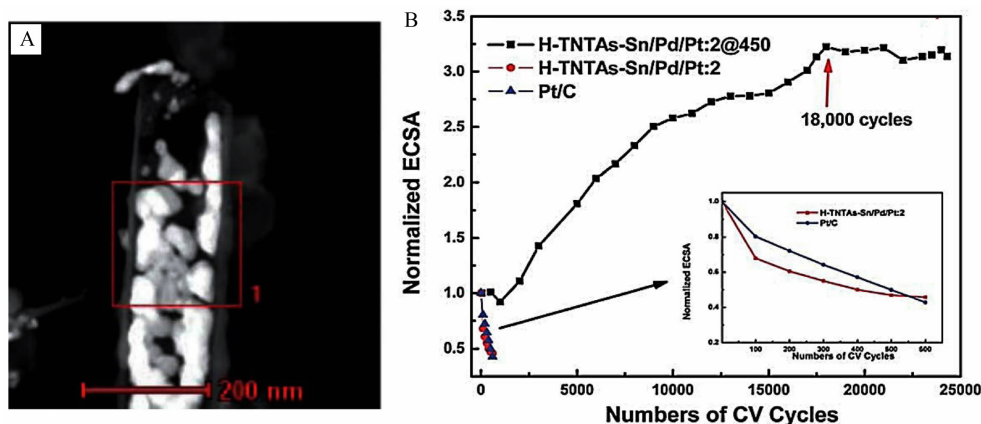


图5 A. PtPdSn-H-TNTs的STEM照片;B. ADT测试后,PtPdSn-H-TNTs与Pt/C的ECSA对其CV周数作图^[45]

Fig. 5 A. STEM image of PtPdSn-H-TNTs; B. Normalized ECSA as a function of the number of CV cycles for the commercial JM Pt/C and PtPdSn-H-TNTs after ADT^[45]

性. Bonakdarpour等^[40]采用掠射角沉积制备的NbO₂阵列,担载0.1 mg·cm⁻²的Pt催化剂后,其ORR活性在0.9 V(vs. NHE)超过1.0 mA·cm⁻². Zhang等^[44]采用阳极氧化法制备有序的二氧化钛纳米管阵列(TNTs),为调节TNTs电子电导率,通过高纯氢气退火处理TNTs(H-TNTs),H-TNTs的电子电导提高了1个数量级. 采用连续离子吸附和反应的方法(SIAR)得到Sn/Pd-H-TNTs,然后进行甲醇还原法将Pt催化剂在Sn/Pd周围还原,催化剂主要在纳米管的内部形成,同时通过热处理形成了PtPdSn三元合金催化剂,均匀分布在3 μm长的H-TNTs管内(图5A). 半电池测试表明催化剂的ECSA是商业化Pt/C的1.3倍,且0~1.2 V(vs. RHE)的电势范围内循环24300次后,电化学活性依然保持稳定(图5B),这远优于文献报道的Pt-TNT的稳定性^[43, 45]. 为进一步调节TiO₂载体的电导率,作者对其进行了NH₃处理,使得其转化成TiN阵列. 在TiN阵列表面制备Pt-PdCo三元合金催化剂,该电极的催化活性和稳定性优于商业化Pt/C电极.

这类有序超薄电极容易发生水淹,可以考虑通过调节催化层的亲疏水性来改善催化层的水淹问题. 具体来说就是将疏水物质(如PTFE)引入催化层,疏水物质可以是颗粒状或是网络状夹杂在催化剂之间.

2 结 语

目前来看,制备低Pt载量且高稳定性的催化剂目前有两条途径:1)将催化剂制备成致密的Pt薄膜的核壳结构,担载在碳载体上,喷制成电极;2)在

有序纳米阵列上直接制备薄膜催化剂,构成有序化膜电极. 后者优于前者,因为后者能够有效改善传质,且在催化层厚度低于1 μm时,可以不加质子导体(如Nafion等). 但要确保电极的表面积,就要做成阵列状或晶须状,催化层可以做成薄膜形式也可以做成核壳形式,但是要找到合适催化剂的固定方法和担体表面的亲疏水性的调整手段.

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Progress of Order-Structured Membrane Electrode Assembly

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Abstract: Performances of proton exchange membrane fuel cells (PEMFCs) have been recently improved. However, the cost and Pt loading must be further reduced for the commercialization of PEMFCs. Previous researches have proved that the order-structured electrode is beneficial to the effective utilization of Pt-based catalysts, decreasing the Pt loading and increasing the three-phase boundary for reaction. Especially, the nanostructure thin films (NSTFs) electrode, an ultra-thin catalytic layer developed by 3M Company, demonstrates high performance and durability. Besides, some other researchers have employed the high conductive carbon nanotube arrays or high stable metal oxide arrays as the order-structured catalyst supports for fundamental researches (such as, improving the Pt-specific activity, decreasing the catalysts loading or studying the essential relationships between electrode performance and structure). However, further improvement in the present advanced catalytic layer is required. This article reviews the recent developments of the order-structured catalytic layer.

Key words: proton exchange membrane fuel cells; membrane electrode assembly; order-structured catalytic layer