

新型碳材料质子交换膜燃料电池 Pt 催化剂载体的研究进展

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摘 要: 质子交换膜燃料电池(PEMFC)具有能量转换效率高、功率密度大、室温启动快、噪音低和零污染等特点, 有望减少二氧化碳排放量, 缓解能源危机, 在轨道交通、航空航天等领域具有广阔的应用前景。催化剂是 PEMFC 的关键材料, Pt 催化氧还原反应活性和稳定性好, 是广泛使用且很难被取代的电催化剂。然而 Pt 储量低、价格昂贵, 导致 PEMFC 成本较高, 使用 Pt 载体可减少 PEMFC 的 Pt 负载量, 提高 Pt 利用率。碳材料具有成本低廉、比表面积大、孔结构丰富、电导率和表面性质可调等特性, 是广泛应用的 Pt 载体。商用的炭黑载体对 Pt 的利用效率低, 抗电化学腐蚀性较差。为了进一步提高 PEMFC 的性能和持续性, 需要研发能够均匀负载 Pt、高效利用 Pt、抗电化学腐蚀性强且导电性好的碳载体, 进而实现 PEMFC 的大规模应用。炭气凝胶、碳纳米管和石墨烯等新型碳载体具有独特的结构和性质, 可以提高 PEMFC 性能和寿命, 引起了研究者的广泛关注。本文对近年来 PEMFC 新型碳材料 Pt 载体的研究进展进行了较为详细的综述, 并对其发展趋势作出了适当评论。

关 键 词: 质子交换膜燃料电池; 炭气凝胶; 碳纳米管; 石墨烯; 综述

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Research Progress on Advanced Carbon Materials as Pt Support for Proton Exchange Membrane Fuel Cells

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Abstract: Proton Exchange Membrane Fuel Cell (PEMFC) has the characteristics of high energy conversion efficiency, high power density, fast start-up at room temperature, low noise and zero pollution, which is expected to alleviate the energy crisis and reduce carbon dioxide emissions. It has broad application prospects in rail transit, aerospace and other fields. Catalyst is one of the key materials of PEMFC. Moreover, Pt catalysts are widely used and considered difficult to be replaced because of their good activity and stability in oxygen reduction reaction. Pt is expensive because of its limited storage. However, Pt loading could be significantly lessened by Pt support to improve PEMFC utilization. Carbon materials are widely used as Pt supports because of their low cost, high specific surface area, pore structure, adjustable conductivity and surface properties, but commercial carbon black supports have low utilization efficiency and poor electrochemical corrosion resistance for Pt. For realizing the large-scale application of PEMFC, it is necessary to develop new carbon supports which can uniformly disperse Pt, efficiently utilize Pt, be resistant to electrochemical corrosion, and have good conductivity, thus the performance and sustainability of PEMFC are im-

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proved. Carbon aerogels, carbon nanotubes, graphene and other new carbon supports with unique structures and properties, which are expected to improve PEMFC performance and life, have attracted the attention of many researchers. In this paper, the research progress on new carbon material as Pt support for PEMFC in recent years is reviewed systematically, and the development trend is also commented appropriately.

Key words: Proton Exchange Membrane Fuel Cell; carbon aerogel; carbon nanotube; graphene; review

面对化石能源日益减少的现状,人类社会迫切需要开发绿色、环保和高效的新能源。质子交换膜燃料电池(PEMFC)具有能量转换效率高、功率密度大、室温启动快、噪音低和零污染等特点,在轨道交通、航空航天等领域具有广阔的应用前景^[1-4]。PEMFC系统的核心部件为膜电极,由气体扩散层、催化剂层和质子交换膜组成^[5-6],如图1所示。Pt催化氧化还原反应活性和稳定性好,是在PEMFC中被广泛使用且很难被取代的电催化剂。然而,Pt在地壳中的储量稀少,阻碍了PEMFC的大规模生产应用。催化剂载体能够降低PEMFC中Pt的用量^[7],是实现PEMFC商业化应用的途径之一。

载体是PEMFC中非常重要的组成部分,直接影响催化剂的粒径大小、分布、电化学活性比表面积、稳定性和利用率,最终影响PEMFC的性能和寿命^[8-9]。PEMFC中反应物、产物、电子以及质子传输效率和速度也与载体性质密切相关^[10-13],并且载体与催化剂协同效应能够提高催化剂性能^[14-15]。好的载体主要具备^[16-20]:(1)高的活性比表面积,能够均匀负载催化剂;(2)合适的孔结构,能提供高活性三相反应界面;(3)较强的稳定性,在高湿、高电压等苛刻条件下,长时间不发生严重电化学腐蚀;(4)高电导率。以上条件之间存在矛盾或依赖的关系:(1)比表面积与孔结构有关,电导率与结晶度有关;(2)高电导率载体的稳定性好;(3)中孔结构有利于负载催化剂,但大量中孔结构的载体,稳定性往往较差。理想载体能够搭建高效电催化反应界面、锚定催化剂纳米粒子、减缓催化剂失活,延长PEMFC寿命、提升性能、降低成本。

炭黑是商品PEMFC的主要载体。美国Cabot公司生产的Vulcan XC性能较好,BET比表面积约为 $250 \text{ m}^2 \cdot \text{g}^{-1}$,中孔和大孔达54%以上,电导率 2.77 S/cm ,基本满足电催化剂载体对比表面积和导电性的要求,是目前应用最为广泛的商品载体。

然而,炭黑的缺点之一是结构中微孔含量较高^[21]。Thommes等^[22]研究表明,导电高聚物无法进入微孔,陷入炭黑微孔中的Pt实际上没有参与电催化反应过程。因而,炭黑负载Pt利用率较低。同时,Maillar等^[23]研究发现,分散在炭黑表面的Pt虽能够参与反应,但在催化过程中容易发生溶解、团聚和位置转移等失活行为,如图2所示。炭黑抗电化学腐蚀性也较差^[24],炭黑的常温电化学腐蚀热力学电压(0.203 V vs. NHE)低于PEMFC的工作电压($>0.6 \text{ V vs. NHE}$)。提高炭黑的石墨化程度虽能够降低电化学腐蚀速率^[25],但很难在热力学上避免发生腐蚀。Tuaev等^[26]研究了碳载体孔结构对催化剂活性的影响,发现中孔结构有利于阻止Pt失活。炭黑的抗电化学腐蚀性和孔结构均存在一定的缺陷,较难满足理想电催化剂载体的条件。由图3可知炭黑在电化学腐蚀前后,结构发生了明显的改变^[27]。

近年来对碳载体的研究主要集中在新型碳载体的开发和利用上:炭气凝胶具有可控的孔结构,可

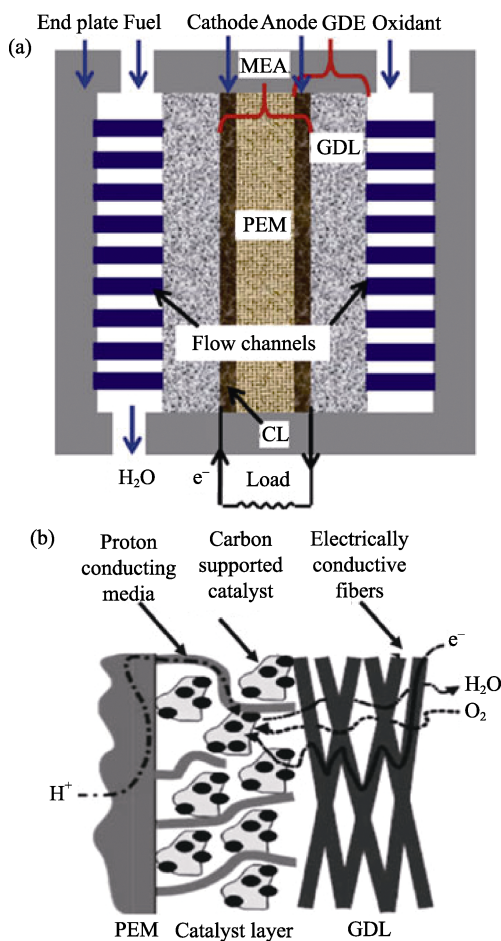


图1 PEMFC的组成结构示意图^[6]

Fig. 1 Schematic diagram of PEMFC^[6]

PEM: Proton exchange membrane; MEA: Membrane electrode assembly; GDL: Gas diffusion layer; CL: Catalyst layer

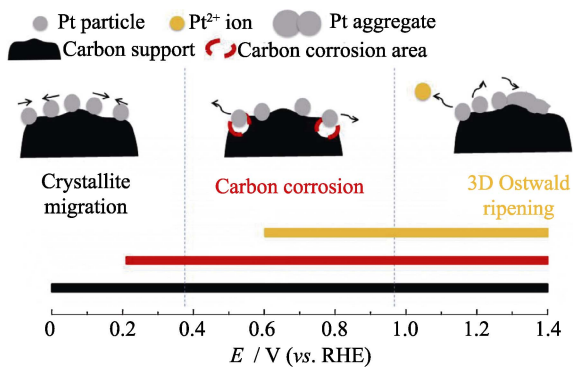
图2 Pt纳米粒子在炭黑载体上的失活示意图^[21]

Fig. 2 Degradation schematic diagram of Pt nanoparticles on carbon black^[21]

根据应用需要, 设计孔性质; 碳纳米管和石墨烯具有低阻抗、高导电性和高电化学稳定性等优异性质。新型碳载体有望克服炭黑的缺点, 是很有潜力的 PEMFC 载体材料。本文主要综述了近年来研究者在炭气凝胶、碳纳米管和石墨烯等新型碳载体上的研究进展。

1 炭气凝胶

炭气凝胶是一种非晶态碳材料, 其纳米多孔三维网络结构可控(图 4), 具有高比表面积($600\sim 1100\text{ m}^2\cdot\text{g}^{-1}$)、高孔隙率(80%~98%)和高稳定性^[28]的特点。载体孔结构对 PEMFC 非常重要, 合适的孔结构有利于传质和阻止 Pt 失活。通过调控炭气凝胶的孔结构有望制备出满足 PEMFC 要求的载体。

为研究孔结构对 PEMFC 性能的影响, Ouattara 等^[29]制备出具有不同孔径分布的炭气凝胶。由图 5 可知, 载体孔径在 25~30 nm 时, PEMFC 性能最佳; PEMFC 的传质阻力主要依赖于炭气凝胶孔结构, 孔径大于 40 nm 时, 导电高聚物易堵塞孔结构, 增大传质阻力。Smirnova 等^[30]研究表明, 炭气凝胶孔径由 16 nm 增大到 20 nm, 电池性能逐步增强; 孔径 20 nm 的炭气凝胶负载 $0.1\text{ mg}\cdot\text{cm}^{-2}$ Pt 时, 达到最大功率密度 $800\text{ mW}\cdot\text{cm}^{-2}$ 。合适的载体孔结构有利于

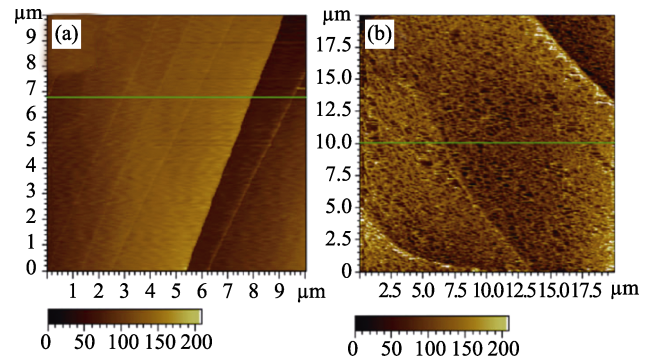
图3 炭黑电化学腐蚀前(a)后(b)的原子力显微镜照片^[27]

Fig. 3 AFM images of high oriented polyrotic graphite surface before (a) and after (b) electrochemical corrosion^[27]

减小传质过程导致的功率损失。Ouattara 等^[31]针对如何更好地调控膜电极的水, 设计了三维多孔炭气凝胶载体, 0.4 V 电压下电池功率提高了 40%。Wang 等^[32]发现 N 掺杂梯度孔炭气凝胶有利于传质, 掺杂微量 Fe 元素后, 催化氧还原活性非常好, 起始电压和半波电压分别为 918 和 798 mV, 比相同条件下 Pt/C 催化剂分别高出 117 和 206 mV。

在 PEMFC 的使用过程中, 启动、急停都会加速碳载体的电化学腐蚀。Ouattara 等^[33]模拟 PEMFC 的启动和急停条件, 加速老化测试炭气凝胶抗电化学腐蚀性能, 相同条件老化 14 h 后, Pt/C 和 Pt/炭气凝胶活性比表面积分别减少了 17.57%、56.27%。炭气凝胶由于石墨化程度较低, 抗电化学腐蚀性比 Pt/C 催化剂要差。为了提高炭气凝胶石墨化程度, Singh 等^[34]通过高温高压凝胶、高温惰性气氛石墨化, 制备出中孔比表面积 $490\text{ m}^2\cdot\text{g}^{-1}$ 、平均孔径 4.9 nm 的炭气凝胶, PEMFC 的起始电位为 964 mV, 半波电位为 814 mV, 优于相同条件下 Pt/C 催化剂。

炭气凝胶上存在许多活泼碳悬空键, 比较容易发生电化学腐蚀反应。炭气凝胶表面改性可提高抗电化学腐蚀性和催化活性。Wang 等^[35]制备了 KOH 活化掺 N 炭气凝胶催化剂, 掺杂 N 引入了大量的缺陷结构, KOH 活化后进一步优化了炭气凝胶的孔结

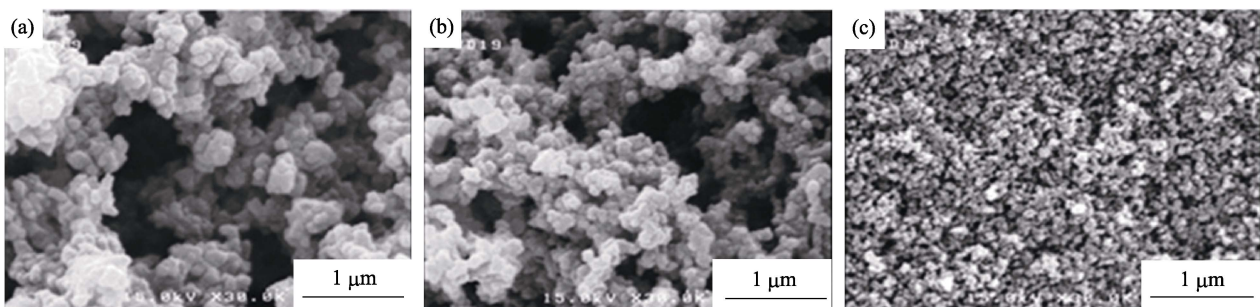
图4 炭气凝胶 CA20(a)、CA30(b)和 CA40(c)的 SEM 照片^[28]

Fig. 4 FESEM micrographs of carbon aerogel samples CA20(a), CA30(b) and CA40(c)^[28]

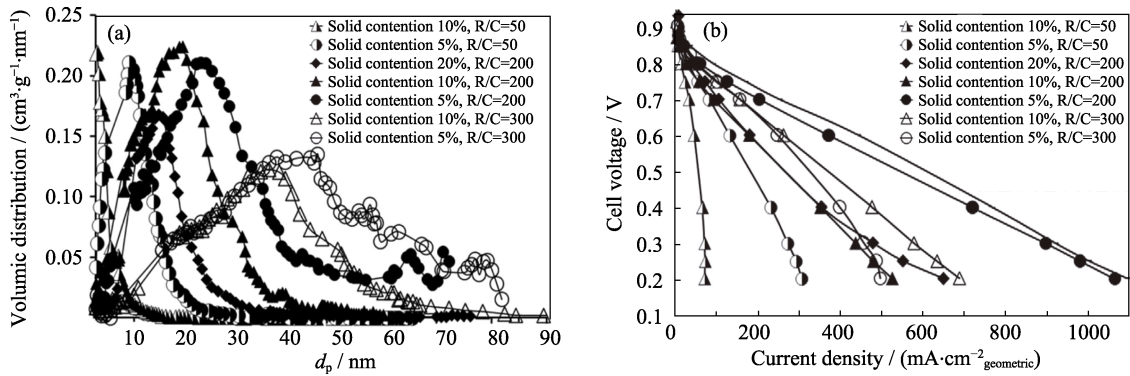


图 5 压汞法测定的不同固含量、不同间苯二酚(R)和碳酸钠(C)摩尔比的炭气凝胶孔径分布曲线(a), 及其对应的单电池极化曲线(b)^[29]

Fig. 5 Pore size distribution curves(a) of carbon aerogels determined by mercury porosimetry with different molar ratios of resorcinol (R) and sodium carbonate (C), and their corresponding single cell polarization curves(b)^[29]

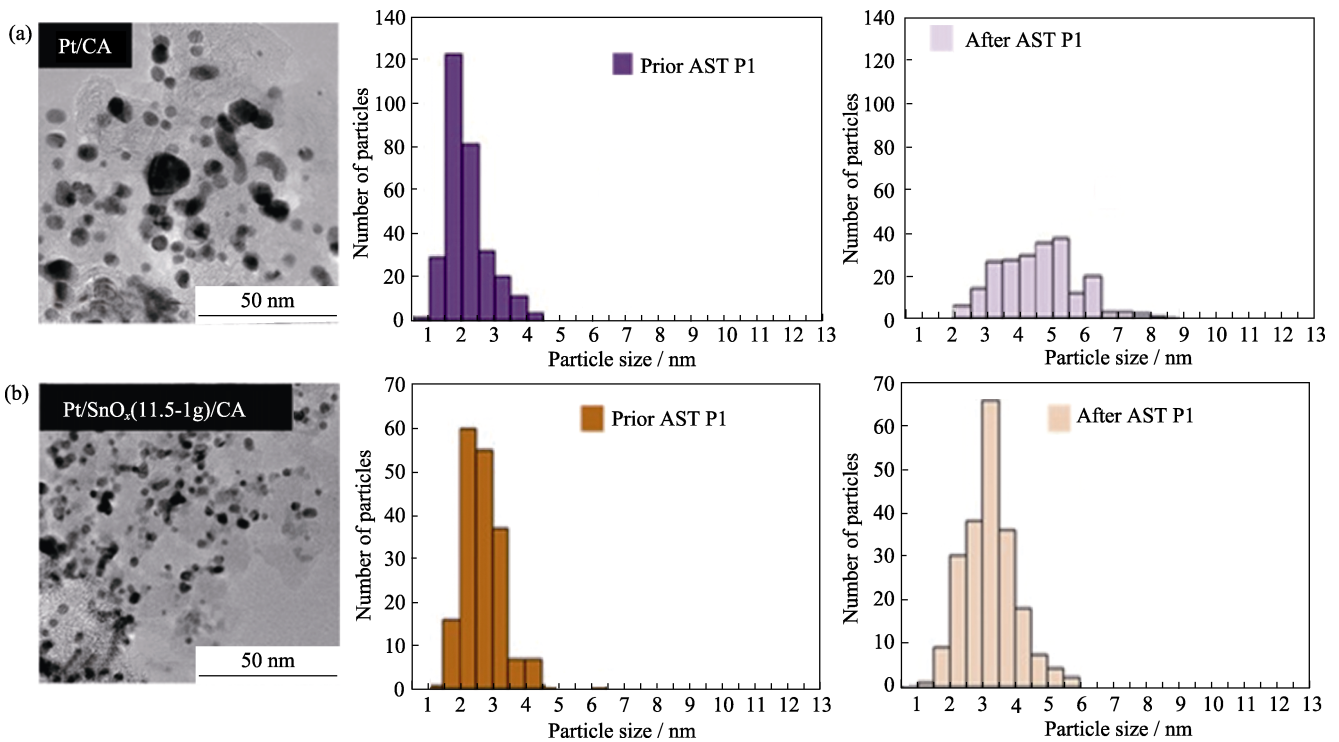


图 6 炭气凝胶(a)及 SnO₂ 涂覆炭气凝胶(b)负载 Pt 催化剂加速氧化测试(AST P1)后的 TEM 照片和加速氧化测试前后的 Pt 粒子统计分布图^[36]

Fig. 6 TEM images after accelerated stress tests (AST P1) and Pt nanoparticles statistical distributions before and after accelerated stress tests (AST P1) of carbon aerogels (a), SnO₂ coated carbon aerogels (b) supported Pt catalysts^[36]

构, 无需负载 Pt, 催化氧还原反应半波电压为 790 mV. Fabien 等^[36]在炭气凝胶表面涂覆 SnO₂ 载体的抗电化学腐蚀性较好, 加速氧化测试后负载催化剂的活性比表面积和质量比活性不降反增; 由图 6 可知, 相比于炭气凝胶而言, SnO₂ 涂覆炭气凝胶负载 Pt 催化剂加速氧化测试后, Pt 粒子团聚现象减少。强氧化剂与炭气凝胶悬空键结合, 有利于在动力学上减缓电化学腐蚀。Berthon 等^[37]制备了氟化炭气凝胶, 5×10³ 次循环测试后氟化载体催化剂活

性比表面积仅减小 10%, 远低于相同条件下 Pt/炭气凝胶(25%)和 Pt/C(15%)。

炭气凝胶具有中孔比表面积高、活性位点多、传质阻力小等特点, 非常适合作为 PEMFC 载体。可控的纳米多孔三维网络结构是炭气凝胶作为载体最具有吸引力的特点。然而, 炭气凝胶目前存在抗电化学腐蚀性较差等缺点。表面改性、提高石墨化程度是增强炭气凝胶抗电化学腐蚀性的主要方法。目前, 以炭气凝胶为载体的 PEMFC 正处于应用前期。

2 碳纳米管

碳纳米管是呈六边形排列的碳原子层构成的无缝管, 是一种特殊的一维纳米结构, 具有阻抗低、导电性高、稳定性好的特点。根据管壁中碳原子层数目, 碳纳米管可分为单壁碳纳米管和多壁碳纳米管^[38], 结构如图 7 所示。很多研究^[39-42]表明, Pt/碳纳米管电催化活性、抗电化学腐蚀性和抗 CO 毒性均优于同条件下的 Pt/C, 是很有潜力的载体材料。近年来, 研究者在增强碳纳米管负载催化剂的稳定性、增大碳纳米管比表面积等方面开展了深入的研究。

Pt 与碳纳米管掺杂的杂原子之间的电子转移可增强催化活性。Zhao 等^[43]制备了含 Fe 的 N 掺杂碳纳米管, 催化氧还原反应半波电压为 850 mV, 密度泛函理论模型研究表明结构中大量的吡啶 N 加快了电子传递速度。二氧化钛稳定性较好、具有一定催化活性, Mohammad 等^[44]合成了一种 TiSi_2O_x 涂覆碳纳米管, 负载 Pt 后催化氧还原反应, 半波电压比 Pt/碳纳米管高出 30 mV。Gao 等^[45]研究表明, 利用高度分散晶体 Ta_2O_5 修饰的碳纳米管作为载体, 稳定性非常好、催化活性也较好, 10^4 次循环伏安测试之后, 半波电压和活性比表面积基本不发生变化, Pt- Ta_2O_5 /碳纳米管电催化活性比表面积为 $78.4 \text{ m}^2 \cdot \text{g}^{-1}$, 0.9 V 时的质量比活性为 $0.23 \text{ A} \cdot \text{mg}^{-1}_{\text{Pt}}$, 是相同条件下 Pt/C 和 Pt/碳纳米管的 2.2 和 3.4 倍。 Ta_2O_5 和碳纳米管协同作用, 改变了 Pt 电子结构, 形成了 Pt-O-Ta 化学键, 使得 Pt 变得更加稳定。

为增大碳纳米管比表面积, Sahoo 等^[46]将多层碳纳米管上层沿轴向打开, 制备出了具有石墨烯“翅膀”的石墨烯-碳纳米管杂化材料。研究表明, 相比于 Pt/C 催化剂, Pt/石墨烯-碳纳米管杂化材料具有高催化活性, 阴极 Pt 负载量为 $0.3 \text{ mg} \cdot \text{cm}^{-2}$ 时, 最大功率密度高达 $1000 \text{ mW} \cdot \text{cm}^{-2}$ 。石墨烯-碳

纳米管杂化材料兼具石墨烯片层和碳纳米管一维结构, 电导率高、反应活性位点多, 碳纳米管和石墨烯片层协同作用有利于 Pt 分散, 是一种新型载体材料。Priji 等^[47]研究了 Pt-Sn/石墨烯-碳纳米管载体催化剂, 当 Pt、Sn 原子比为 3:1 时, $60 \text{ }^\circ\text{C}$ 功率密度为 $568 \text{ mW} \cdot \text{cm}^{-2}$, 比同等条件下 Pt/碳纳米管高出 23% 且阴极催化剂负载量远低于性能相当的 Pt/C。Meenakshi 等^[48]报道了具有高活性和稳定性的 Pt_3Sc /石墨烯-碳纳米管催化剂, $60 \text{ }^\circ\text{C}$ 时的功率密度为 $760 \text{ mW} \cdot \text{cm}^{-2}$, 加速氧化测试前后的质量比活性均高于 Pt/C。

碳纳米管的导电性和稳定性优异, 抗电化学腐蚀性较好。然而, 碳纳米管的活性比表面积较小, 表面惰性导致负载 Pt 催化剂能力较弱。近年来, 研究者们通过制备碳纳米管杂化材料、碳纳米管-过渡金属复合材料等方法, 极大地增强了碳纳米管负载 Pt 催化剂的催化活性和稳定性, 增大了碳纳米管载体的活性比表面积, 增强了 Pt 负载能力。但是对于工业化生产, 碳纳米管作为 PEMFC 催化剂载体还面临着合成方法和价格的问题。

3 石墨烯

石墨烯具有二维平面结构, 其理论比表面积大 ($2630 \text{ m}^2 \cdot \text{g}^{-1}$)、电导率高 ($106 \text{ S} \cdot \text{cm}^{-1}$)、抗电化学腐蚀性好^[49], 是很有应用前景的 PEMFC 载体材料。大量研究表明, 以石墨烯作为 Pt、Pt 合金和非贵金属催化剂载体的催化剂, 性能均优于商业 Pt/C。

石墨烯具有诸多优异性能, 但其本征二维结构的片层间范德华力较强, 容易发生重组、团聚, 导致负载的 Pt 随之团聚、脱落和失活。通过二维片层石墨烯架构而得到的具有三维结构的石墨烯材料, 能避免片层间团聚。Liu 等^[50]制备了具有三维结构和缺陷的石墨烯泡沫, 比表面积高达 $1500 \text{ m}^2 \cdot \text{g}^{-1}$, 载体催化剂的电化学活性比表面积为 $101 \text{ m}^2 \cdot \text{g}^{-1}$ (比 Pt/C 高 50%), 质量比活性为 $176 \text{ A} \cdot \text{g}^{-1}_{\text{Pt}}$ (比 Pt/C 高 30%)。石墨烯气凝胶具有本征纳米多孔三维网络结构。Eylul 等^[51]使用超临界 CO_2 溶剂将 Pt 负载在石墨烯气凝胶上, 载体催化剂电化学活性比表面积为 $102 \text{ m}^2 \cdot \text{g}^{-1}$, 质量比活性为 $30.6 \text{ A} \cdot \text{g}^{-1}_{\text{Pt}}$ 。

以炭黑为阻隔和连接石墨烯片层的“空间桥梁”, 形成具有三维结构的石墨烯-炭黑杂化材料, 能够阻止石墨烯片层团聚^[52-54]。Li 等^[55]使用聚苯并咪唑将炭黑和石墨烯片层结合, 制备炭黑-石墨烯杂化材料, 研究表明以这种材料为载体的催化剂, 质量比活性为 $183 \text{ A} \cdot \text{g}^{-1}_{\text{Pt}}$ (Pt/C 为 $149 \text{ A} \cdot \text{g}^{-1}_{\text{Pt}}$), 膜电极开

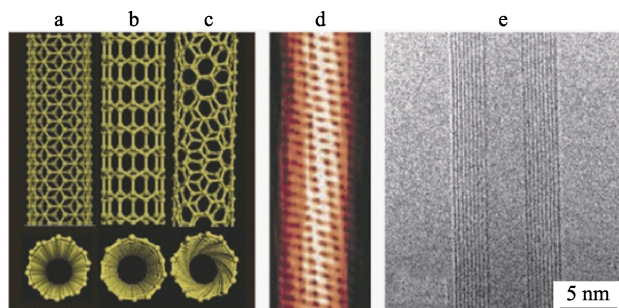


图 7 碳纳米管原子结构示意图(a~c), 隧道电子显微镜照片(d), TEM 微观形貌照片(e)^[38]

Fig. 7 Schematic illustrations of the structures(a-c), tunneling electron microscope image(d), transmission electron microscope image (e) of carbon nanotubes^[38]

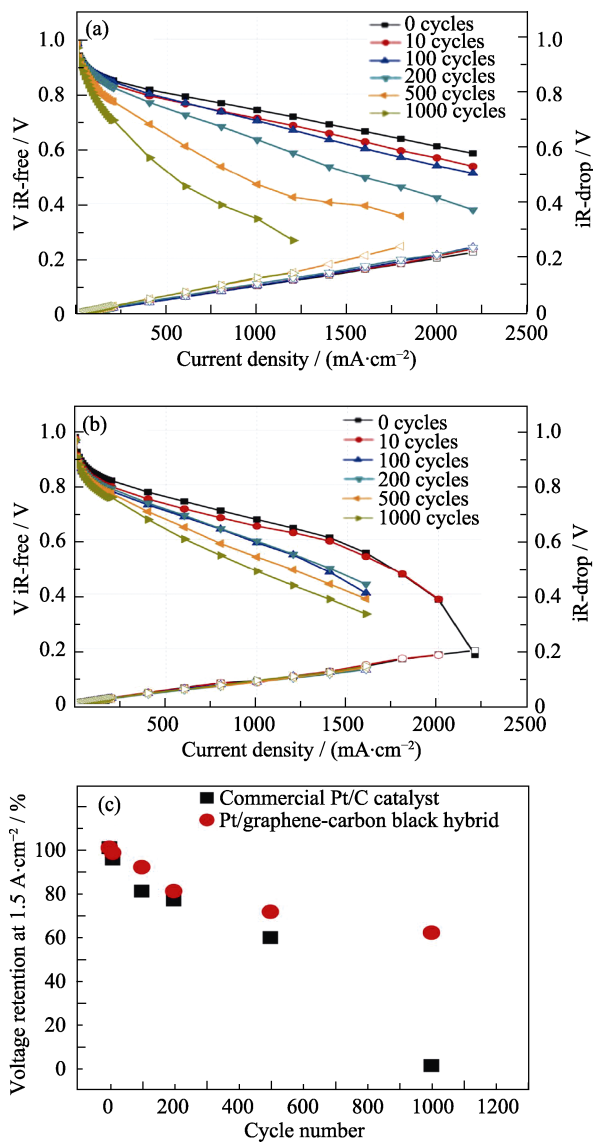


图 8 商业 Pt/C(a), Pt/炭黑-石墨烯杂化材料(b)为阴极催化剂的 PEMFC 经加速氧化测试后的极化曲线; 不同循环次数后的电压保留值(c)^[55]

Fig. 8 PEMFC polarization curves recorded after accelerated stress tests with cathode catalysts of commercial Pt/carbon black (a) and Pt/carbon black-graphene hybrid material (b); Voltage retention normalized with respect to initial performance after 10, 20, 100, 200, 500, and 1000 cycles(c)^[55]

始工作后, 最大电流密度由 $500 \text{ mA}\cdot\text{cm}^{-2}$ 增大到 $2250 \text{ mA}\cdot\text{cm}^{-2}$; 由图 8 可知, 1000 次循环伏安测试之后, 电流密度保持在 $1500 \text{ mA}\cdot\text{cm}^{-2}$, 峰电压为 $1.0\sim 1.5 \text{ V}$, 而 Pt/C 峰电压值降低为 0 V 。聚苯并咪唑可锚定 Pt, 且石墨烯抗电化学腐蚀性较好, 故而炭黑-石墨烯载体性能优异。除炭黑之外, 碳纳米管、碳纤维等也可以作为阻隔并连接石墨烯片层的“空间桥梁”^[56-61]。

石墨烯表面呈化学惰性, 活性位点少, 负载催化剂能力较弱, 在石墨烯表面加入杂原子、官能团

或大分子, 能够在平面引入具有电化学活性的缺陷结构, 增大活性比表面积, 增强催化活性^[62-64]。Sergey 等^[65]制备了掺氟、掺氧的氧化石墨烯, 掺氧氧化石墨烯负载的 Pt 颗粒粒径较小, 掺氟、掺氧石墨烯载体催化剂性能均高于 Pt/C。

近年来, 研究者在杂原子掺杂石墨烯作为非贵金属催化剂载体, 用于催化氧还原做了大量工作^[66]。氮掺杂石墨烯增加了每摩尔氧气的电子转移数, 使氧气能在低电压下形成 OH^- 。Xu 等^[67]研究了 Co-B-N 掺杂多孔石墨烯催化剂的电化学活性, 起始电位和半波电位分别为 904 和 792 mV , 仅比商业 Pt/C 催化剂低 0.06 和 0.04 V , 而 Tafel 斜率为 $58 \text{ mV}\cdot\text{dec}^{-1}$, 低于 Pt/C ($71 \text{ mV}\cdot\text{dec}^{-1}$)。Lei 等^[68]报道了 N 掺杂石墨烯气凝胶用于氧还原反应, 起始电压仅比相同条件下 Pt/C 低 0.1 V , 稳定性和对甲醇的耐受性好于 Pt/C。同时, Wang 等^[69]还通过研究表明, 石墨烯上吡啶 N 掺杂缺陷处催化氧还原活性较高, 产生的超电势最低为 0.28 V , 大量吡啶 N 缺陷掺杂石墨烯在碱性环境中半波电位为 850 mV , 催化活性较好。Yang 等^[70]设计掺 Fe、掺 N 单层石墨烯为氧还原催化剂, 揭示了催化反应活性位点为 Fe 与吡啶 N 结合的缺陷位置。

石墨烯电导率高、抗电化学腐蚀性好且比表面积大。然而, 其在使用过程中易团聚、表面呈化学惰性。制备具有三维结构的石墨烯可以阻止片层团聚; 杂原子掺杂石墨烯, 可在表面引入具有催化活性的缺陷结构, 调节缺陷数目、尺寸和形状等, 改善石墨烯表面活性, 增强其负载能力和催化活性。单独的石墨烯片层较难在 PEMFC 中应用, 而三维结构的石墨烯材料和原子杂化石墨烯具有非常优异的性能, 有望成为 PEMFC 载体。

4 其他新型碳材料

碳纤维具有优异的导电性和独特的物理化学性质, 是一种很有潜力的电催化剂载体。Wang 等^[71-73]研究了氮掺杂多孔碳纤维、中空多孔碳纤维等不同形态的碳纤维, 多孔碳纤维负载 Pt 的抗电化学腐蚀性和催化活性均优于 Pt/C, 电化学活性比表面积为 $52 \text{ m}^2\cdot\text{g}^{-1}$ (Pt/C 为 $41 \text{ m}^2\cdot\text{g}^{-1}$), 起始电压和半波电压分别为 891 和 739 mV , 比 Pt/C 分别高出 44 和 25 mV ; 其最大功率密度为 $130 \text{ mW}\cdot\text{cm}^{-2}$, 是同等条件下 Pt/C 的二倍。Song 等^[74]制备了一种直径 100 nm 、孔径 $5\sim 30 \text{ nm}$ 的超细多孔碳纳米纤维负载的 Pt 催化剂, 电化学活性比表面积为 $71.9 \text{ m}^2\cdot\text{g}^{-1}$ (Pt/C 为

54.6 m²·g⁻¹), 起始电位和半波电位分别为 969 和 763 mV 均高于 Pt/C, 功率密度为 165 mW·cm⁻², 是 Pt/C 的 1.25 倍。

空心碳表面具有有序的介孔结构、内部中空, 电导率在 0.003~1.4 S·cm⁻¹ 之间。Ying 等^[75]合成了 Co-Pt 二元合金催化剂, 并将其植入氮掺杂的空心碳中, 相同条件下质量比活性是 Pt/C 的 13.5 倍, 电化学活性比表面积为 64.6 m²·g⁻¹(Pt/C 为 57.6 m²·g⁻¹), 半波电位为 883 mV(Pt/C 为 864 mV), 加速氧化测试之后半波电位仅降低 19 mV(Pt/C 降低 67 mV), 催化活性和耐久性都较好。Chen 等^[76]制备了氮掺杂石墨碳负载微量 Co 催化剂, 微孔、介孔结构和掺杂石墨 N、吡啶 N 使得材料具有催化氧还原活性。

近年来研究表明, 碳纤维、空心碳等新型碳材料作为电催化剂载体性能优异, 但由于制备方法复杂, 难以工业化生产和大规模应用, 成本较高, 故而研究较少。

5 结语

炭黑是商业 PEMFC 中被广泛使用的 Pt 载体, 性能基本满足要求, 但微孔含量高、导电性较差、比表面积较小, 易发生电化学腐蚀、催化剂利用率低, 导致 PEMFC 性能持续性较差。通过研发具有特殊结构和优异性能的新型碳载体, 有望克服炭黑载体的缺点。

炭气凝胶具有可控的纳米多孔网络结构, 活性比表面积大, 能够均匀有效地负载 Pt、缓解 Pt 失活、降低传质阻力, 然而抗电化学腐蚀性较差。表面改性和增强结构中石墨化程度, 是提高炭气凝胶抗电化学腐蚀性的有效措施。碳纳米管导电性和稳定性好, 抗电化学腐蚀性较好, 然而比表面积较低, 负载 Pt 能力较弱。碳纳米管杂化材料、碳纳米管-过渡金属复合材料极大地增大了碳纳米管载体的活性比表面积和负载 Pt 的能力。石墨烯电导率高、抗电化学腐蚀性好且比表面积大。然而, 其在使用过程中易团聚、表面呈化学惰性。制备三维结构石墨烯可以阻止片层团聚; 杂原子掺杂石墨烯, 可在表面引入具有催化活性的缺陷结构, 增强其负载能力和催化活性。本文综述的各类碳载体优缺点, 总结如表 1 所示。

PEMFC 要求载体有大量的三维互通中孔结构、丰富的表面活性位点、具有高导电性和稳定性的特点, 同时能够大规模工业化生产。具有丰富中孔结构的高度石墨化炭气凝胶、改性炭气凝胶、三维结构石墨烯材料、高比表面积碳纳米管杂化材料等,

表 1 不同碳载体的性能比较

Table 1 Comparison of some properties for four carbon supports

Property	Carbon black	Carbon aerogel	Carbon nanotubes	Graphene
Oxygen reduction reaction activity		✓ ✓	✓ ✓	✓ ✓
Proton transport	✓	✓	✓ ✓	✓ ✓
O ₂ transport	✓	✓	✓ ✓	✓ ✓
Water transport	✓	✓	✓ ✓	✓ ✓
Pt dispersion		✓ ✓		
Carbon corrosion	✓		✓	✓ ✓
Particle coalescence		✓ ✓		

理论上满足大多数理想电催化剂载体的条件, 性能较好, 有望成为新一代 PEMFC 电催化剂载体。

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