

燃料电池金属双极板涂层综述

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摘要: 质子交换膜燃料电池 (PEMFC) 是一种新型的能源装置, 双极板是其主要的部件之一。金属双极板在成本和力学性能方面都具有优势, 因此逐渐占据市场主流, 但是其易腐蚀的特点也影响了燃料电池的性能。从后镀金属双极板、预镀金属双极板和免镀金属双极板 3 种不同的工艺路线出发, 系统总结了相关研究进展。对于不同工艺路线下的不同涂层, 通过接触电阻、腐蚀电流和表面形貌等指标进行了评价。发现后镀金属双极板的性能好于预镀金属双极板和免镀金属双极板, 但是其工艺路线最复杂, 成本最高, 而免镀金属双极板工艺最简单, 但是其防腐导电性能不能满足 DOE2025 标准, 预镀涂层介于两者之间, 是一种过渡的工艺路线。最后, 从涂层结构和元素掺杂角度对后镀涂层进行了展望, 从涂层晶体结构和涂层材料选择角度对预镀涂层进行了展望, 从箔材元素比例、预处理工艺角度对免镀金属双极板进行了展望。综述了燃料电池金属双极板防腐导电性的发展方向, 对金属双极板朝着更低的成本和更好的性能方向发展有着重要意义。

关键词: 腐蚀; 金属双极板; 预镀涂层; 后镀涂层; 免镀涂层

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A Review of Metal Bipolar Plate Coatings for Fuel Cells

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ABSTRACT: Proton exchange membrane fuel cell (PEMFC) is a new type of energy device, and bipolar plate is one of its main components. Metal bipolar plates have advantages in terms of cost and mechanical properties, and gradually occupy the mainstream of the market, but their easy corrosion characteristics also affect the performance of fuel cells. This paper systematically summarized the relevant research progress from three different process routes: post-coated metal bipolar plates, pre-coated metal bipolar plates and no-coated metal bipolar plates. Different coatings under different process routes were evaluated by contact resistance, corrosion current and surface morphology. It was found that the performance of post-coated metal bipolar plates was better than that of pre-coated metal bipolar plates and no-coated metal bipolar plates, but its process route was the most complicated and its cost was the most expensive; while the process of no-coated metal bipolar plates was the simplest, but its anticorrosive and conductive performance could not meet the DOE2025 standard; and the pre-coating was a transitional process route between the two. Finally, the outlook of post-coating from coating structure and element doping, the

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outlook of pre-coating from coating crystal structure and coating material selection, and the outlook of no-coated metal bipolar plate from foil element ratio and pretreatment process were presented.

This paper reviewed the development direction of the anti-corrosion conductivity of metal bipolar plates for fuel cells, which was of great significance for the development of metal bipolar plates toward lower cost and better performance. The process route for post-coated metal bipolar plates was to prepare a single plate by micro-stamping and forming in the first step, and in the second step to prepare a coating on the surface of the plate to improve its corrosion resistance and electrical conductivity under cathodic and anodic conditions. The advantage of this process was that it facilitated the fabrication of specimens and the high quality of the coating. There were many post-plating process routes and a wide range of coatings. Common coatings included precious metal coatings, carbon-based coatings, ceramic coatings, etc. The generation cost of the post-plating process route was high and could not adapt to the rapid development requirements of the new industry. In order to overcome the shortcomings of the post-plating process, some researchers envisaged the plating process in advance. Using the roll to roll method on the steel strip of the stainless steel substrate to first deposit corrosion-resistant conductive coating, and then micro-stamping forming flow channel study, eliminating the post-plating process while also simplifying the production process of bipolar plates was a cost-effective solution.

The coating deposited on the surface of metal bipolar plates is difficult to avoid defects in the deposition process, resulting in a reduced lifetime, and the coating itself increases the cost and production time of the bipolar plates. The no-coated metal bipolar plate solves the above problems perfectly. The advantages of post-coating are the wide variety of coating options and the sequence of processing and then coating ensures the integrity and quality of the coating, but the highest production cost and the slow and difficult deposition rate of the coating make it difficult to achieve large scale, batch and high standard production. Pre-coating has the advantage of producing coated strips on a large, fast, batch basis, greatly saving the cost and time of production, but the coated strips are prone to cracking and failure when processing the flow field. The advantage of no-coating is the elimination of the coating process, its cost is the lowest among the three routes, but the anticorrosive conductivity of no-coating is poor, its research data are few, and has not yet been widely used in a large area. The anticorrosive conductivity and mechanical properties of no-coated metal bipolar plates need to be further verified.

KEY WORDS: corrosion; metal bipolar plate; pre-coated; post-coated; no-coated

质子交换膜燃料电池（PEMFC）相对于锂离子电池具有能量密度高、补能快、原材料丰富等优点，其作为汽车的动力电池具有非常广阔的发展前景^[1-3]。质子交换膜燃料电池是一种利用氢气和氧气反应产生电能的新型能源，双极板是其重要的组成部件之一，双极板占燃料电池总成本的 30%，占总质量的 60% 以上^[4-5]。双极板的主要作用是传输和均匀分配氢气、氧气，且兼具导电、水热管理等作用，在燃料电池酸性环境下，双极板必须兼具良好的耐腐蚀性和导电性^[6-10]。双极板目前的发展方向有石墨双极板、金属双极板、复合双极板。金属双极板具有良好的导电性、导热性、质量小、易加工成形等优点，可以大幅降低双极板的制造成本，因此成为研究的热点。但其易腐蚀会造成燃料电池内阻增大，降低电池的输出效率。金属双极板需在保证优异导电性的前提下具有良好的抗腐蚀性，因此对金属双极板进行涂层改性以达到要求。界面接触电阻（ICR）、腐蚀电流密度（ J_{corr} ）和涂层的力学强度等特性参数是金属双极板涂层的关键参数^[11-14]。本文将根据 3 种金属双极板涂层工艺路线（后镀金属双极板和预镀金属双极板和免镀金属双极板）来综述金属双极板涂层的研究进展。

1 后镀金属双极板

后镀金属双极板的工艺路线为：第一步微冲压成形制备单极板；第二步是在极板表面制备涂层，提高其在阴阳极环境下的耐腐蚀性和导电性。这种工艺的好处是有利于试样制造且涂层质量高。后镀工艺路线研究广泛，涂层种类多。常见的涂层有贵金属涂层、碳基涂层、陶瓷涂层等^[15-18]。

1.1 贵金属涂层

贵金属涂层有金、银、铂、铱等^[19-21]，它们具有优异的导电性和化学性质稳定性，能够抵抗燃料电池酸性电解液的腐蚀，但是昂贵的价格极大地增加了金属双极板的成本。

Wen 等^[22]通过电化学沉积方法在 316L 不锈钢上以 10 μm 厚 Cu 作为中间层，表层沉积 1 μm 厚 Au 涂层，在模拟燃料电池环境中（0.5 mol/L H_2SO_4 ，10 mg/L HF，80 $^\circ\text{C}$ ）分别浸泡处理 0、12、24、48 h 后，采用动电位极化试验，Au 涂层的腐蚀电流密度从 $1.716 \times 10^{-5} \text{ A/cm}^2$ 增加到 $2.243 \times 10^{-4} \text{ A/cm}^2$ 。在模

拟燃料电池环境中, 存在大量的 H^+ 、 SO_4^{2-} 和 F^- , 使得 Au 涂层表面发生电化学反应, 形成腐蚀坑, 随着 Au_2O_3 的形成, 腐蚀反应速率降低。Huang 等^[20]通过化学钝化制备了 316L 双极板表面的银涂层, 得到了表面缺陷和针孔更少的银涂层。测得该双极板在 0.8~1.2 MPa 的装堆压力下接触电阻值为 6.57~6.09 $\text{m}\Omega\cdot\text{cm}^2$, 满足 DOE2025 标准。新的涂层表面有更大的水接触角 (从 58° 增加到 104°), 表明其具有更好的疏水性。在极化电位为 0.4 V 时, 模拟燃料电池阴极环境中, 测得钝化前后的双极板腐蚀电流密度分别为 0.593、 4.44×10^{-2} $\mu\text{A}/\text{cm}^2$ 。Wang 等^[23]研究了氧化铱和铂对钛金属双极板的改性作用。通过对双极板的极化研究可知, 铂涂层钛双极板的性能优于氧化铱涂层。贵金属涂层高昂的价格很难达到 DOE2025 的标准如表 1 所示, 双极板的成本要降至 2 美元每千瓦以下。

表 1 2025 美国能源部门双极板标准^[24]
Tab.1 2025 Bipolar plates standard of America
DOE Department^[24]

Items	Unit	Target
Cost	Dollar/kW	<2
Anodic corrosion current density	$\mu\text{A}/\text{cm}^2$	<1
Cathodic corrosion current density	$\mu\text{A}/\text{cm}^2$	<1
ICR	$\text{m}\Omega/\text{cm}^2$	<10

1.2 碳基涂层

非晶碳 (Amorphous Carbon: a-C) 涂层价格低、性能优, 是双极板改性的理想材料之一, 得到了广泛的研究^[25-28]。按照碳杂化态 sp^3/sp^2 之比可分为类金刚石膜和类石墨膜。 sp^3 杂化居多的类金刚石膜具有优异的力学性能和良好的抗腐蚀性能。 sp^2 杂化居多的类石墨膜具有良好的导电性^[29-31]。因此调控涂层中的 sp^3/sp^2 杂化比例, 使其具有优异的导电性和良好的抗腐蚀性, 是金属双极板碳基涂层的重要研究方向。

Bi 等^[32]根据材料 E -pH 图, 通过封闭式非平衡磁控溅射沉积了以 Cr、Ti 和 Nb 3 种不同材料作为中间层的非晶碳膜, 相对于 Ti 和 Nb 元素, Cr 元素促进了 a-C 薄膜的石墨化, 得到了最高比例的 sp^2 杂化。因为 Cr 元素的溶解, Cr 种子层的非晶碳膜具有最高的腐蚀电流密度。而由于 Ti 和 Nb 层在电解液中的钝化作用, 带有 Ti 和 Nb 种子层的非晶碳涂层的腐蚀电流密度较低。Li 等^[33]通过直流平衡磁控溅射技术在 SS316L 基片上沉积了不同 Ti 掺杂量的非晶碳 (a-C) 薄膜, 探讨了 Ti 掺杂量对 a-C 薄膜导电性和抗腐蚀性的影响。Ti 掺杂量的增加可以促进 a-C 薄膜的 sp^2 杂化率, 掺杂的钛原子也可以与碳形成低电阻率的 TiC 相, 使薄膜的 ICR 从 5.64 $\text{m}\Omega\cdot\text{cm}^2$ 下降到 3.47 $\text{m}\Omega\cdot\text{cm}^2$ 。当钛靶材电流高于 1.2 A 时, 腐蚀电流

逐渐上升, 意味着达到一定掺 Ti 量时, 薄膜的耐腐蚀性开始下降。Li 等^[34]研究了不同频率的直流脉冲溅射电源对 PEMFC 中金属双极板上 a-C 薄膜结构和性能的影响。研究表明, 适度的频率有利于纳米石墨团块的形成, 进而提高薄膜的 sp^2 占比, 如图 1 所示。在 200 kHz 脉冲电流下制备的薄膜表现出最好的综合性能, ICR 分别为 1.35 $\text{m}\Omega\cdot\text{cm}^2$ (沉积时), 2.03 $\text{m}\Omega\cdot\text{cm}^2$ (0.84 V (vs. SHE) 极化 24 h 后) 和 2.39 $\text{m}\Omega\cdot\text{cm}^2$ (1.60 V (vs. SHE) 极化 1 h 后)。特别是在 0.84 V (vs. SHE) 极化 200 h 后, 在 200 kHz 下制备的薄膜的 ICR 为 2.44 $\text{m}\Omega\cdot\text{cm}^2$, 表明薄膜具有优良的耐久性。

Li 等^[35]利用直流磁控溅射 (DCMS) 技术在不同的溅射功率下在 SS316L 上沉积 a-C 薄膜, 研究显示在高溅射功率下, 沉积的 a-C 薄膜的 sp^2 含量明显下降, 导致 ICR 值显著增加。当溅射功率为 0.9 kW 时, 得到最佳的 a-C 薄膜, 腐蚀电流密度为 7.52×10^{-3} $\mu\text{A}/\text{cm}^2$, 接触电阻值为 2.91 $\text{m}\Omega\cdot\text{cm}^2$, 远低于 DOE2025 标准。Zhang 等^[36]利用直流磁控溅射技术通过基底偏置电压交替循环沉积 a-C 涂层, 在 a-C 涂层的表面有更多富含 sp^2 的团块, 增加了涂层的导电性。交变偏压周期的增加, 使 a-C 多层涂层中的界面更多, 夹层厚度更薄, 如图 2 所示。对于 15 个交替周期沉积的涂层, 在 0.6 V 恒电位极化下测得最低的腐蚀电流密度为 0.297 $\mu\text{A}/\text{cm}^2$ 、接触电阻值为 3.58 $\text{m}\Omega\cdot\text{cm}^2$ 。

Kumar 等^[37]利用沉积速率超过 100 nm/min 的电弧离子镀, 在钛箔表面快速沉积性能优异的 a-C 薄膜。实验结果表明, 在 1.4 MPa 的压力下, a-C 涂层的 ICR 下降到 1.125 $\text{m}\Omega\cdot\text{cm}^2$, 腐蚀电流密度约为 3.37×10^{-3} $\mu\text{A}/\text{cm}^2$ 。Umada 等^[29]通过脉冲等离子体化学气相沉积和不同的碳源 (C_2H_2 、 C_2H_4 、 CH_4) 制备了 3 种类型的氢化非晶碳薄膜, 研究了不同碳源对 sp^2 取向的影响, 通过 XES 和 XAS 光谱等检测, 表明由 C_2H_4 沉积的氢化无定形碳膜中的 sp^2 碳具有相对较高的取向, 作者猜测这种 sp^2 键的碳结构在薄膜中的取向也是一个重要的因素, 可能会影响一些薄膜的特性。Mi 等^[38]利用磁控溅射在 316L 上沉积的三层结构膜如图 3 所示, 通过调节 Ti 靶电流的大小得到 6 种不同的 Ti 掺杂含量, sp^2/sp^3 比率随着 Ti 电流的提高而增加。当 Ti 靶电流为 1 A 时, 测得 1.4 MPa 下最小接触电阻为 2.9 $\text{m}\Omega\cdot\text{cm}^2$ 。在恒电位 0.6 V (vs. SCE) 极化试验中测得最小腐蚀电流密度为 3.55×10^{-2} $\mu\text{A}/\text{cm}^2$, 表明涂层具有优秀的防腐导电性能。

碳基涂层通过调控碳的 sp^2 和 sp^3 杂化比例可以获得优秀的防腐导电性能, 并且碳资源丰富, 成本较低, 是非常具有发展前景的金属双极板涂层。然而, 纯碳基涂层与基底的结合力弱容易脱落, 且沉积速率慢, 容易出现针孔、大颗粒等缺陷, 因此提高沉积速率、加入元素掺杂和设计多层膜结构是主要的发展方向。

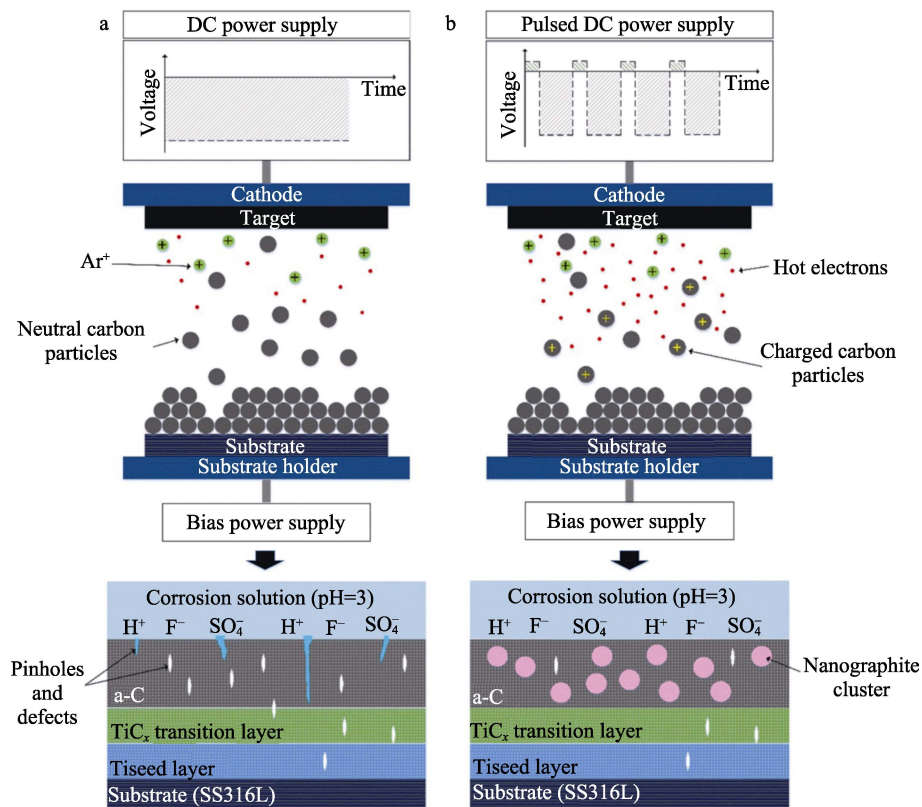


图 1 不同溅射电源在 a-C 膜中形成缺陷和纳米石墨团块的示意图: a) 直流电源; b) 脉冲直流电源^[34]
Fig.1 Schematic illustration for formation of defects and nanographite clusters in a-C with different sputtering power supply: a) DC power supply; b) pulsed DC power supply^[34]

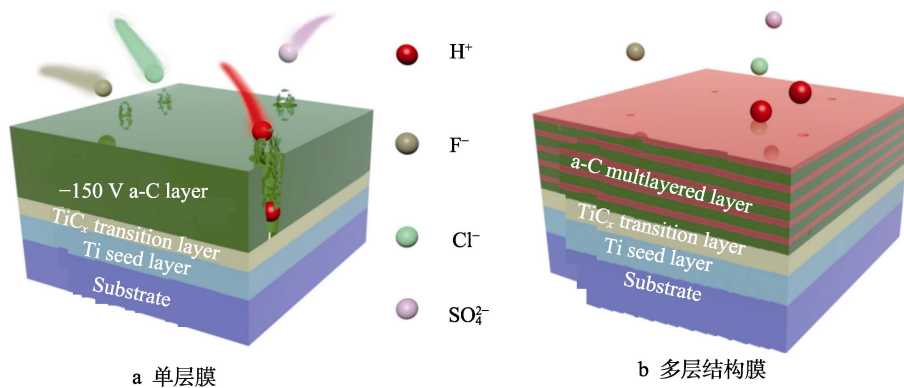


图 2 不同腐蚀状态的示意图^[36]

Fig.2 Schematic illustrations of different corrosion behaviors^[36]: a) single layer coating; b) multilayered coatings

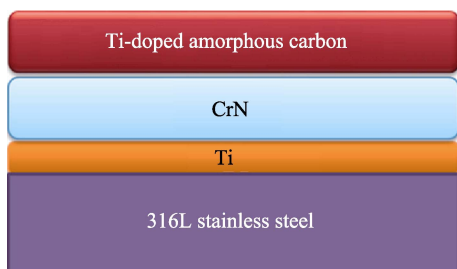


图 3 三层结构 (a-C/CrN/Ti) 涂层^[38]

Fig.3 Schematic diagram of three-layer coating structure (a-C/CrN/Ti)^[38]

1.3 陶瓷涂层

陶瓷涂层具有良好的导电性和防腐性,并且化学

性质稳定、硬度高、熔点高,适合用作金属双极板涂层。金属双极板陶瓷涂层主要分为氮化物陶瓷和碳化物陶瓷等。

1.3.1 氮化物陶瓷涂层

多种多样的氮化物陶瓷涂层^[39-42]被研究用来增加金属双极板的防腐导电性,如 CrN^[43-45]、ZrN^[44]、TiN^[43]等,其中 TiN 展示出更为优秀的防腐导电性,氮化物涂层在沉积过程中会出现如针孔、大颗粒等缺陷,设计多层涂层和加入元素掺杂可以阻止缺陷向柱状生长,并能获得更为致密的涂层结构。

Wang 等^[46]通过高功率脉冲磁控溅射在不同的 N₂ 流速下沉积 TiN 涂层,在 N₂ 流速为 8 mL/min 时, TiN 涂层表现出高紧实度和最佳的表面微观结构,具

有优异的耐腐蚀性, 腐蚀电流密度为 $0.278 \mu\text{A}/\text{cm}^2$, 界面接触电阻值低至 $3.51 \text{ m}\Omega\cdot\text{cm}^2$, 满足 DOE2025 目标。Jannat 等^[41]通过物理气相沉积 (PVD) 技术在 316L 不锈钢上沉积致密的纳米钛/氮化钛 (Ti/TiN) 多层涂层。在 1.4 MPa 下, 测得接触电阻为 $11 \text{ m}\Omega\cdot\text{cm}^2$, 明显优于未镀涂层的金属板。在模拟燃料电池阴极环境下, 在 0.6 V 恒电位极化下测得最低的腐蚀电流密度为 $0.93 \mu\text{A}/\text{cm}^2$ 。Fan 等^[47]将金掺杂到 TiN 涂层上形成新型复合涂层 (Au/TiN/SS), 得到的 TiN 涂层界面接触电阻从 $5.48 \text{ m}\Omega\cdot\text{cm}^2$ 降低到 $1.72 \text{ m}\Omega\cdot\text{cm}^2$, 符合 DOE2025 标准。Yan 等^[48]通过磁控溅射在 SS 基材上沉积 TiN-Ag 纳米复合涂层, 研究了沉积温度为 $200\sim 350^\circ\text{C}$ 时涂层的性能。在 350°C 下, 涂层显示出了最小的接触电阻 $4.18 \text{ m}\Omega\cdot\text{cm}^2$ 和最小的腐蚀电流 $0.596 \mu\text{A}/\text{cm}^2$ 。

1.3.2 碳化物陶瓷涂层

碳化物陶瓷涂层^[13,25-26,39,49-51]包括 CrC、TiC、NbC、TaC 等, 相比较于氮化物陶瓷涂层, 碳化物陶瓷涂层拥有更好的导电性, 但是防腐性较低。单一的碳化物涂层的防腐导电性能并不能满足 DOE2025 的要求, 因此越来越多的研究集中在纳米涂层、复合涂层和多层膜结构等。

Pan 等^[52]利用反应式射频磁控溅射技术 (RF-MS) 在 304 不锈钢 (304SS) 上制备双层 CrC/CrN 涂层。双层结构的协同作用有效地阻止了腐蚀性物质通过缺陷的渗透, 大大增加了基材的抗腐蚀能力。双层 CrC/CrN 涂层的接触电阻约为 $7 \text{ m}\Omega\cdot\text{cm}^2$, 腐蚀电流为 $0.538 \mu\text{A}/\text{cm}^2$, 满足 DOE2025 目标。Li 等^[53]利用磁控溅射制备了 TaC/TiC/TaC/C 多层涂层, 与纯 TiC 和 TiC/C 涂层相比, TaC/TiC/TaC 结构表现出最低的腐蚀电流密度, 为 $0.28 \mu\text{A}/\text{cm}^2$, 抗腐蚀性能最优。Zhang 等^[54]研究了 NbC 改性的 Ti 板, 在 1.4 MPa 下, NbC-Ti 双极板腐蚀电流密度为 $0.32 \mu\text{A}/\text{cm}^2$, 接触电阻值为 $16.6 \text{ m}\Omega\cdot\text{cm}^2$, 低于裸 Ti 板的 $91.9 \text{ m}\Omega\cdot\text{cm}^2$, 然而其接触电阻大于 DOE2025 目标值。

陶瓷涂层的沉积方式主要为各式各样的物理沉积, 可以得到可控的涂层厚度。但是陶瓷涂层的防腐导电性较差, 需要设计多层膜结构或复合材料膜以提高其性能, 从而满足 DOE2025 标准。

上海治臻新能源有限公司的 S05C 型后镀金属双极板采用 SS316L 不锈钢基材, 产品性能优异, 流场区接触电阻为 0.6 MPa 小于 $10 \text{ m}\Omega\cdot\text{cm}^2$, 满足 DOE2025 标准。

后镀金属双极板的金属基材种类选择广, 如不锈钢、钛合金等, 涂层种类多, 但是由于双极板流道的存在, 后镀金属板在沉积涂层过程容易出现涂层均匀性和致密性不一的问题, 并且涂层表面容易出现点蚀缺陷。

2 预镀涂层金属双极板

后镀层工艺路线的生成成本高, 无法适应新产业的快速发展要求, 为了弥补后镀层工艺的缺点, 有研究者设想将镀层工艺提前, 在不锈钢基材钢带上采用 roll to roll 的方法先沉积耐腐蚀导电涂层, 然后进行微冲压成形流道研究, 省去了后续的涂层制备同时也将双极板的生产工艺流程简化, 是一种经济有效的解决方案。在不锈钢基材钢带上容易沉积致密的涂层, 但在后续的成形过程中涂层会出现条状的裂纹和少量的涂层分层和剥落, 导致涂层失效。

Peker 等^[55]研究了 1 000 块无涂层和 1 000 块有预镀 $1 \mu\text{m}$ 厚 ZrN 涂层的 316L 钢带冲压成双极板, 无涂层的预镀涂层的双极板平均腐蚀电流密度为 $2.05 \mu\text{A}/\text{cm}^2$, 远低于无涂层的 $7.04 \mu\text{A}/\text{cm}^2$ 。无涂层和预镀涂层的双极板平均接触电阻值分别为 293 、 $132 \text{ m}\Omega\cdot\text{cm}^2$, 都不满足 DOE2025 标准的要求。试验结果表明, 预镀 ZrN 涂层的钢带在冲压成形后在耐腐蚀和接触电阻方面要优于未涂层, 而两者成形后的表面形貌没有显著不同。Turan 等^[56]采用 PVD 镀膜技术、3 种金属氮化物涂层材料 (CrN、TiN、ZrN) 和 3 种厚度 (0.1 、 0.5 、 $1 \mu\text{m}$) 对 316L 钢带进行预镀涂层后成形和先成形后镀涂层实验, 研究不同工艺顺序对接触电阻的影响, 其中 TiN 涂层表面形貌如图 4 所示。对于 CrN 涂层, 预镀相对于后镀有更小的接触电阻, 但都高于 DOE2025 标准。对于 TiN 涂层, 后镀相较于预镀有更小的接触电阻, 而且都满足 DOE2025 标准。在腐蚀实验后, TiN 涂层的接触电阻显著上升。预镀和后镀对于 ZrN 涂层的接触电阻, 没有显著差异。对于 2 种工艺成形的双极板在 SEM 下进行观测, 发现先成形后镀的涂层有更清晰的点蚀缺陷, 预镀后成形的涂层有更清晰的条状裂纹 (流道的顶端和壁上的裂纹要多于底部) 和少量的涂层分层和剥落, 不同厚度的涂层显示了不同形状的裂纹。

Dur 等^[57]在 316L 钢带上用 3 种涂层材料 (CrN、TiN、ZrN) 进行预镀涂层后成形和先成形后镀涂层, 研究不同工艺顺序对双极板耐腐蚀的影响。腐蚀实验测试结果显示, 对于 ZrN 涂层, 先预镀涂层后冲压的双极板比先冲压成形后镀的双极板耐腐蚀性低; 无论工艺顺序如何, $1 \mu\text{m}$ 厚的 CrN 和 ZrN 涂层的双极板都达到了 DOE 的要求, TiN 涂层的耐腐蚀性最差。Müller 等^[58]利用阴极电弧脉冲在 316 不锈钢板上沉积 Cr/a-C 涂层, 研究预镀涂层和后镀涂层的金属双极板对燃料电池在启停工况下的影响。在 2 000 次启停工况后: 1) 预镀和后镀的 Cr/a-C 涂层都只有轻微的破损; 2) 预镀和后镀的 Cr/a-C 涂层的粗糙度在阴极侧增加且形貌都有所改变; 3) 相对于后镀, 预镀的涂层在后成形过程中有所损坏, 导致中间层 Cr 被暴露, 但是暴露的 Cr 并没有产生腐蚀产物或引起双

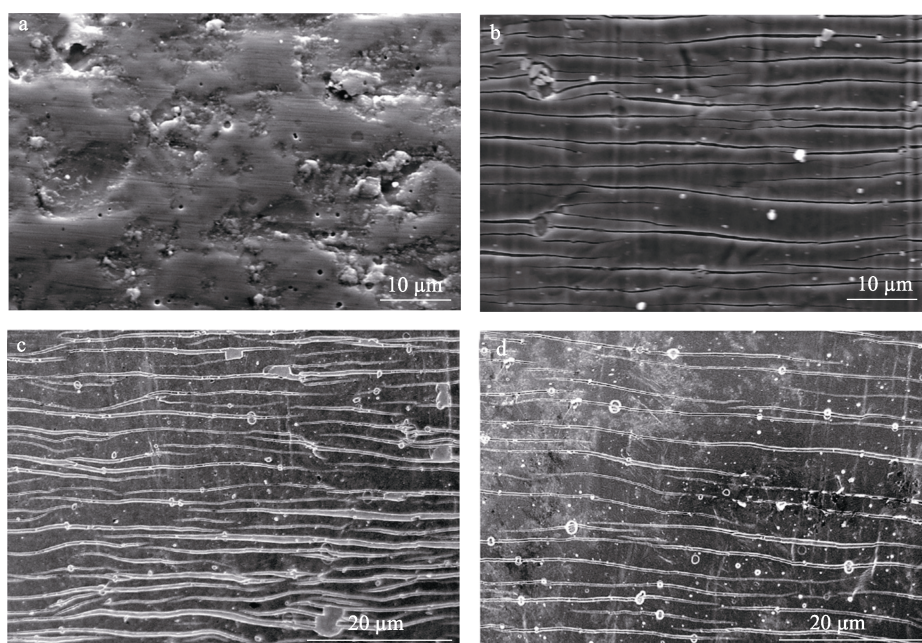


图4 SEM图像和涂层表面形貌: a) 后镀1 μm 厚度的TiN涂层; b~d) 预镀1、0.5、0.1 μm 厚度的TiN涂层^[56]
Fig.4 SEM images and coating surface morphology: post-coated 1 μm thick TiN coating;
b-d) pre-coated 1, 0.5, 0.1 μm thick TiN coating^[56]

极板金属离子的逸出。研究表明,预镀和后镀的Cr/a-C涂层双极板可以用于燃料电池的启停工况。Novalin等^[59]将TiN涂层预镀在不锈钢带上,对钢带进行拉伸试验来观察涂层的表面形貌,并测试其抗腐蚀能力。试验结果表明,涂层上的裂纹数量随着涂层厚度的增加而减少。在应变达到一定值之后,涂层横向裂纹变成了斜向裂纹。预镀TiN涂层钢带的抗腐蚀能力因后续成形而下降,但仍好于未镀涂层的钢带。

山特维克公司研发了另一种适用于质子交换膜燃料电池的预镀涂层金属双极板Sanergy™ LT,该预镀双极板涂层以类石墨碳基涂层为顶层,具有较低的接触电阻(1.4 MPa的压力为3~6 $\text{m}\Omega\cdot\text{cm}^2$)和表面电阻,以及良好的耐腐蚀性和涂层附着力。该预镀涂层在成形双极板后会有12%的双向应变。

相对于后镀工艺,预镀工艺可以极大地降低金属双极板的开发成本,但是双极板的制备需要在带材上压制出不同的流场形式,这些流场的成形需要经过模具冲压或拉伸成形,材料在伸长的过程中涂层的延展性不足会导致涂层开裂失效,在燃料电池环境下易发生腐蚀,导电性降低。如何避免涂层带材在冲压成形过程中的开裂问题是制备预镀金属双极板的关键,开发一种适合冲压成形的不锈钢预测涂层带材是燃料电池产业化过程中急需解决的问题。

3 免镀金属双极板

金属双极板表面沉积的涂层难以避免沉积过程中出现的缺陷,导致寿命降低,并且镀膜本身就增加

了双极板的成本和生产时间。免镀涂层的金属双极板完美解决了以上问题。免镀涂层金属双极板的金属基材主要是不锈钢,其防腐导电原理是不锈钢金属双极板表面形成的钝化膜具有防腐导电性,铁的钝化膜防腐导电性较差而Cr的复合钝化膜防腐导电性较好,通过提高钝化膜中Cr的复合钝化膜比例,从而达到免镀金属板防腐导电的目的。

Brady等^[60]研究了Fe-20Cr-4V合金和2205型不锈钢箔材通过预氧化和氮化处理后的防腐导电性。在模拟燃料电池阴极环境下极化7.5 h后,预氧化/氮化处理后的Fe-20Cr-4V和2205箔材都表现出比未处理的材料更低的腐蚀电流密度(6、1 $\mu\text{A}/\text{cm}^2$)。2种箔材极化之前的接触电阻都满足DOE2025标准,但是在极化后,测得接触电阻分别在20~25 $\text{m}\Omega\cdot\text{cm}^2$ 范围内和25~62.5 $\text{m}\Omega\cdot\text{cm}^2$ 范围内,远超DOE2025标准的10 $\text{m}\Omega\cdot\text{cm}^2$ 。

Pugal等^[61]通过电化学氮化处理316L不锈钢双极板,发现当氮化电压为0.5 V时样品的防腐导电性能最好,并且均好于未氮化处理的样品。在1.5 MPa的压强下测得氮化处理的样品接触电阻值为7 $\text{m}\Omega\cdot\text{cm}^2$,在模拟燃料电池阴极环境下,测得氮化处理的样品腐蚀电流密度为0.158 $\mu\text{A}/\text{cm}^2$ 。电化学氮化处理使得不锈钢双极板表面形成的复合膜(CrN,Cr₂N,Cr-O-N)厚度为5.8 nm,提升了316L不锈钢双极板的防腐导电性。

Zhang等^[62]研究了Fe-Ni-Cr合金(Fe、Ni、Cr的原子数分数分别为35.84%、32.34%、29.17%)双极板在三步表面预处理(酸化、热处理、电化学处理)

之后的防腐导电性, 表面形貌如图 5 所示。酸化处理是指在室温下将合金浸没在 HF 溶液中, 这一步处理增加了 C 原子在合金表面的积聚; 热处理是在 250 °C 氧气环境中进行的, 这一步使得合金表面形成了 FeO/Cr₇C₃ 复合膜; 电化学处理使得合金表面形成了 Cr₂O₃/Cr₇C₃/C 复合膜。实验测得该合金双极板的接触电阻在 240 N/cm² 为 9.4 mΩ·cm², 腐蚀电流密度为 4.62×10⁻² μA/cm²。DOE2025 标准为 1.4 MPa 下接触电阻小于 10 mΩ·cm², 而作者在测试中的压强为 2.4 MPa, 由于越高的测试压强会得到更低的接触电阻, 所以推测该合金的接触电阻值不满足 DOE2025 标准。

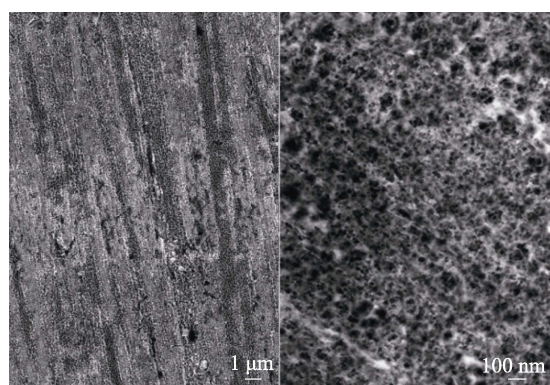


图 5 FESEM 图: 样品在三步表面预处理后的表面形貌^[62]

Fig.5 FESEM image: surface morphology of sample after three steps of surface pretreatments^[62]

韩国浦项大为现代汽车 NEXO 提供的免镀金属双极板, 其金属基材为 Poss470FC 钢, 厚度为 0.08~0.1 mm, 防腐导电性能优异。

免镀金属双极板的关键在于调控箔材中各元素的成分比例, 并通过酸浸处理、热处理、电化学处理等方式, 调整不锈钢表面钝化膜的成分、厚度和表面粗糙度等, 从而提高表面钝化膜的导电性和耐腐蚀性能, 达到免涂层的目的。从现有的研究中发现, 免镀金属双极板防腐导电性离满足 DOE2025 标准还有一定的距离, 技术研究尚未成熟。

4 展望

本文回顾了后镀涂层、预镀涂层和免镀涂层 3 种金属双极板涂层的加工工艺路线。后镀涂层的优势在于涂层可选种类广泛, 先加工后镀涂层的顺序保证了涂层的完整和质量, 但生产成本最高, 且涂层的沉积速率慢, 难度大, 难以实现大规模、批量化、高标准的生产。预镀涂层的优势在于可大面积、快速、批量化地生产涂层带材, 大大节约了生产的成本和时间, 但是涂层带材在加工流场时容易出现开裂失效。免镀涂层的优势在于省去了镀膜工序, 成本是 3 种路线中

最低的, 但是免镀涂层的防腐导电性能较差, 研究数据少, 且尚未得到大面积的推广应用。免镀金属双极板的防腐导电性、力学性能等有待进一步验证。未来双极板涂层的发展可以考虑以下几个方面:

1) 后镀涂层: 1) 设计多层膜结构和元素掺杂的涂层; 2) 研发沉积速率快、防腐导电性能优的涂层。预镀涂层: 1) 设计利于滑移晶体体系的晶相结构; 2) 开发适合冲压成型的不锈钢预镀涂层带材。

2) 免镀涂层: 1) 通过调控箔材中元素的比例和加入不同预处理工艺, 研制防腐导电性能能够满足 DOE2025 标准的箔材种类; 2) 可以考虑加入涂层工艺, 进一步改善金属双极板的防腐导电性。

然而, 在燃料电池的高比功率要求背景下, 双极板的设计不仅在防腐导电性方面, 而且对传质、水管理和成本等方面提出了更高的要求。

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