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High Performance Fuel Cell Catalyst and 5kW PEMFC Stack Without Humidification at Room Temperature and Atmosphere

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高性能燃料电池催化剂及其 5kW 常温常压免增湿电堆

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摘要: 应用高压有机溶胶法制得高性能的 Pt/C催化剂.该催化剂的活性颗粒度达 2.8 nm,活性比表面为 450 m^2/g,并进行了小批量试产(10 g).建立新型直接涂膜电极和免增湿技术,并制作了 275 cm^2 的膜电极,设计和组装 5 kW 质子交换膜燃料电池电堆,以氢气为燃料,空气为氧化剂在常温常压免增湿条件下试运行,电堆连续运行 10 h,输出功率基本稳定不变.

关键词: 有机溶胶法;直接涂膜;免增湿

中图分类号: TG174.418 **文献标识码:** A

常温常压免增湿质子交换膜燃料电池是现今国内外燃料电池研究的重要课题[1-5].常压运行可用低能耗的风机取代高能耗的空气压缩机;常温运行可使燃料电池在通常条件下迅速启动,无需预热,免去加热系统,从而使输出效率提高 8%~10%,成本节省 15%[6-9].

国内外在常温常压免增湿燃料电池以及常压燃料电池电堆方面已有大量的研究[10-13].

本文研制低温活性 Pt/C催化剂,建立直接涂膜技术和免增湿技术,设计并装配 5 kW 常温常压免增湿燃料电池电堆.

1 实 验

1.1 催化剂

采用有机溶胶法制备[14-18]. Pt/C催化剂,批量生产 10 g,含铂量 20%. XRD检测活性组分颗粒度;电化学方法测试活性比表面,甲醇氧化循环伏安法测催化剂电催化活性.

1.2 电 极

在红外灯光照射下,借助即涂即干直接涂膜,制备膜电极.这可有效防止膜的溶胀,使催化剂与膜结合紧密,并形成多孔的立体催化剂涂层[19-20].电极的性能由 ARBIN燃料电池测试系统检测.

1.3 免增湿技术与电堆设计

于催化层添加适量保湿剂,并设计合理的免增湿运行方式.

以国产石墨板作双极板,机械铣削流场,间隔块板设置采用冷却板模式;橡胶材料密封,用数字式压力机组装电堆.

1.4 电堆运行

使用 PALTONG 10kW 燃料电池测试系统观测电堆试运行.条件如下:空气及氢气均不加湿,不预热,满功率时空气流速为 350~400 L/min,空气从电堆流出后直接排空,氢气流速 60~70 L/min,间歇排放,每运行 10 s排放 1 s;空气和氢气输入压力分别为 10 kPa和 5 kPa;气体通入 3~5 s后,电堆即可满功率运行.

2 结果与讨论

2.1 Pt/C催化剂特性

上述 Pt/C催化剂经 XRD测试表明(图略),其主要衍射峰明显宽化,活性组分高度分散,按

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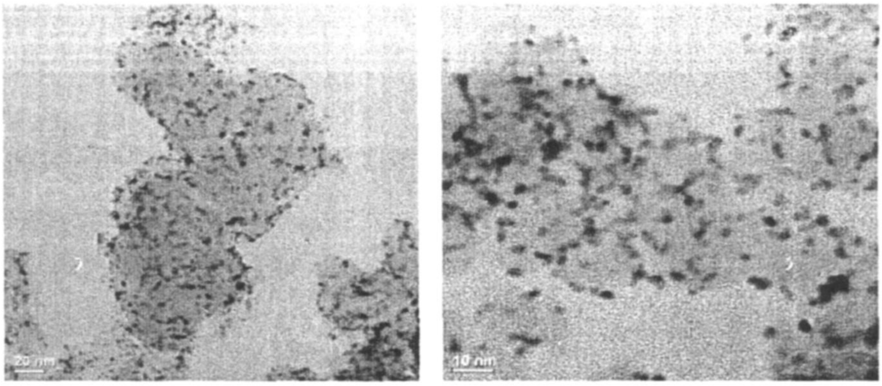

图 1　有机溶胶法制备的 20% (by mass) Pt/C催化剂的 TEM 照片

Fig 1　The TEM images of the 20% (by mass) Pt/C catalyst prepared by organic colloidal methed

SCHERRER公式估算的颗粒度约为 2.8 nm.

实验发现该催化剂经活化处理,除去催化剂表面吸附杂质后,其结晶形态无明显变化,但颗粒度增大至 3.0 nm.图 1为 10 g批量制备的 Pt/C催化剂的 TEM照片.

2.2　Pt/C催化剂电催化活性

图 2示出 10 g批量制备的 Pt/C催化剂电极在甲醇溶液中的循环伏安曲线.如图可见:该催化剂 (曲线 b)对甲醇的电氧化具有良好的催化活性,其催化性能远远高于商品 Pt催化剂 (曲线 a、c).

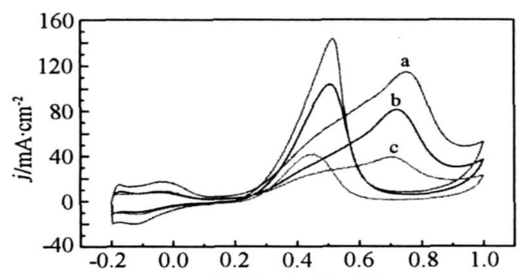

图 2　不同 Pt催化剂在甲醇溶液中循环伏安曲线

Fig 2　Cyclic voltammograms of the different Pt catalysts in methanol solution

a) Pt/CNTs　b) Pt/C;　c) John matthey Pt/C

2.3　免增湿膜电极的结构及性能评价

图 3a给出由 CCM技术制备的膜电极的极化曲线.与传统涂碳纸法膜电极 (图 3b)相比,显示出更好的性能.

在电池温度 75℃和加湿温度 70℃条件下,本文自制的膜电极已达到几乎与国内外膜电极相同水平 (见图 4).

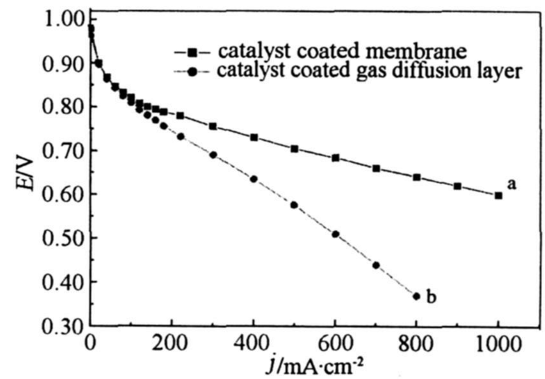

图 3　直接涂膜法制备的膜电极性极化曲线

Fig. 3　Polarilation curves of the MEA prepared by CCM methods with Lab-prepared catalyst

the operation condition: cell temperature 70℃, humidification temperature 80℃, back pressure 4.35 kPa

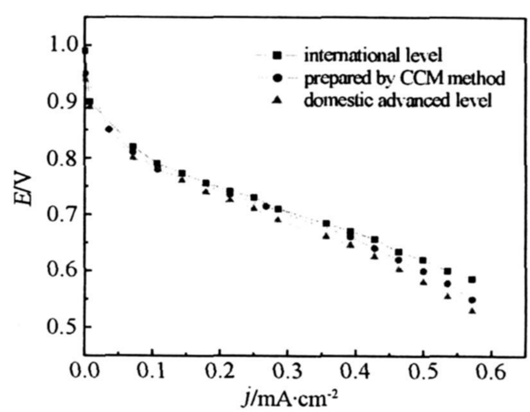

图 4　直接涂膜法制备的膜电极极化曲线

Fig. 4　polarilation curves of the MEA prepared by CCM cell temperature 75℃, humidification temperature 70℃, no back pressure

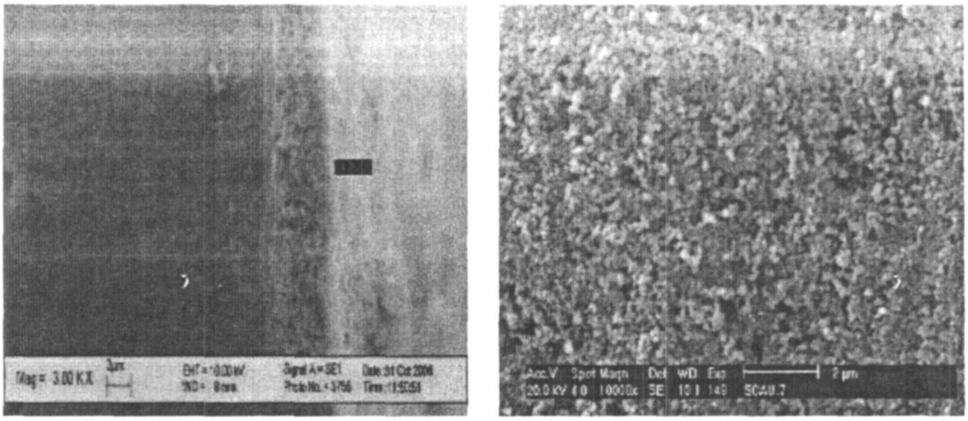

图 5 直接涂膜技术制备的膜电极的 SEM 照片

Fig. 5 SEM images of the MEAs prepared by CCM method

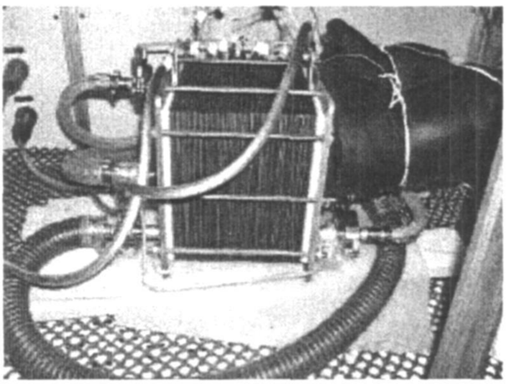

图 6 免增湿 5 kW 电堆照片

Fig 6 The image of 5 kW stack without humidification

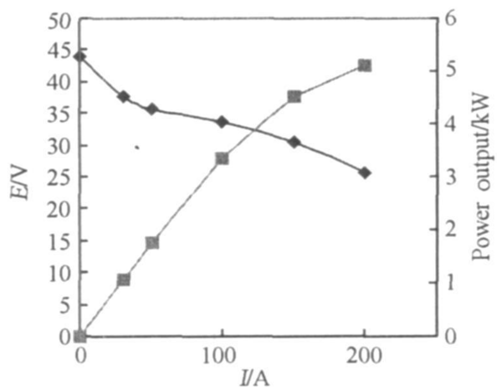

图 7 常温常压免增湿 5 kW 电堆运行特性

Fig. 7 A 5 kW stack run at room temperature, atmosphere and without humidification

还需指出，本文自制膜电极具有良好的低温活性，如在室温下运行其输出功率密度几乎可以达到与 75℃下运行的水平.

图 5示出直接涂膜电极的 SEM 照片. 从图可以看出，催化剂层呈多孔蓬松，厚度为 4.6 μm，质子交换膜结合十分紧密.

2.4 5 kW 燃料电池电堆

图 6示出免增湿 5 kW 燃料电池电堆的照片. 图 7给出常温常压免增湿 5 kW 电堆的运行特性.

电极先进行过预活化处理，而后组装成电堆. 电堆运行条件：电堆节数 50片；空气流量 400 L/min，氢气流量 75 L/min，空气直接排放，氢气间歇排放. 电堆无需预热，空气、氢气也无需加湿. 电堆连续运行 10 h，输出功率基本稳定不变 (见图 7).

参考文献 (References):

[1] Uchida H, Ueno Y, Hagihara H, et al. Self-humidifying electrolyte membranes for fuel cells: Preparation of highly dispersed TiO_2 particles in Nafion 112 [J]. J Electrochem Soc, 2003, 150(1): 57-62.

[2] Singaram Vengatesan, Hyoung-Juhn Kim, Sang-Yeop Lee, et al. Operation of a proton exchange membrane fuel cell under non-humidified conditions using a membrane-electrode assemblies with composite membrane and electrode[J]. Journal of Power Sources, 2007, 167(2): 325-329.

[3] Han M, Chan S H, Jiang S P. Investigation of self-humidifying anode in polymer electrolyte fuel cells[J]. International Journal of Hydrogen Energy, 2007, 32: 385-391.

[4] Zhu Xiao-bing, Zhang Hua-min, Zhang Yu, et al. A multilayer PTFE-reinforced self-humidifying membrane for fuel cell with dry H_2/air under ambient pressure [J]. Chinese Journal of Power Sources, 2007, 31(4): 291-295.

[5] Liu Fuqiang, Yi Baolian, Xing Danmin, et al. Development of novel self-humidifying composite membranes for fuel cells[J]. Journal of Power Sources, 2004, 124: 81-89.

[6] Minkmas V Williams, Russell Kunz H, et al. Operation of Nafion®-based PEM fuel cells with no external humidification: influence of operating conditions and gas diffusion layer[J]. Journal of Power Sources, 2004, 135: 122-134.

[7] Viral Mehta, Joyee Smith Cooper. Review and analysis of PEM fuel cell design and manufacturing[J]. Journal of Power Sources, 2003, 114: 32-53.

[8] Wang C, Liu Z X, Maoa Z Q, et al. Preparation and evaluation of a novel self-humidifying Pt/PFSA composite membrane for PEM fuel cell[J]. Chemical Engineering Journal, 2005, 112: 87-91.

[9] Vengatesan S, Kima H J, Choa E A, et al. Operation of a proton-exchange membrane fuel cell under non-humidified conditions using thin cast Nafion membranes with different gas-diffusion media [J]. Journal of Power Sources, 2006, 156: 294-299.

[10] Jüurgen Stumper, Charles Stone. Recent advances in fuel cell technology at Ballard[J]. Journal of Power Sources, 2008, 176: 468-476.

[11] Yang Tao, Shi Pengfei, Du Chunyu. Study on self-humidified PEMFC with reactant circulation[J]. Electrochimica Acta, 2006, 51: 5618-5625.

[12] Zhang Yu, Zhang Huamin, Zhu Xiaobing, et al. Fabrication and characterization of a PTFE-reinforced integral composite membrane for self-humidifying PEMFC [J]. Journal of Power Sources, 2007, 165: 786-792.

[13] Zhang Liyan, Pan Mu, Quan Shuhai. Model predictive control of water management in PEMFC[J]. Journal of Power Sources, 2008, 180: 322-329.

[14] Yi Baolian(衣宝廉), Yu Hongmei(俞红梅), Hou Zhongjun(侯中军), et al. Electrocatalysts for proton exchange membrane fuel cells in Dalian Institute of Chemical Physics, Chinese Academy of Sciences-Study on the Pt/C Electrocatalyst[J]. Precious Metals, 2002, 23(3): 1-7.

[15] Zhu Hong(朱红), Ge Feng-juan(葛奉娟), Kang Xiao-hong(康晓红), et al. The study on carbon nanotube-loaded Pt catalysts for proton exchange membrane fuel cells [J]. Electrochemistry, 2003, 9(4): 445-450.

[16] Liao S, Holmes K A, Tsaprailis H, et al. High performance PtRuIr catalysts supported on carbon nanotubes for the anodic oxidation of methanol[J]. J Am Chem Soc, 2006, 128(11): 3504-3505.

[17] WANG Ning-kate(王宁卡特), LIU Jun-min(刘军民), LIAO Shi-jun(廖世军), et al. Preparation of high dispersion and high performance PtRu/CNTs catalyst by an organic colloid method[J]. Battery, 2006, 36(5): 371-374.

[18] YIN Shi-bin(尹诗斌), MU Shi-chun(木士春), PAN Mu(潘牧), et al. Research on catalyst supports for low-temperature fuel cell[J]. Chinese Battery Industry, 2007, 12(4): 281-284.

[19] Zhou Chen(周琛), Liu Jun-min(刘军民), Liao Shi-jun(廖世军). A CCM type of membrane electrode assembly prepared by direct spraying method[J]. Journal of Wuhan University of Technology, 2006, 28(Ⅱ): 462-466.

[20] Zhou Chen(周琛), Liu Jun-min(刘军民), Liao Shi-jun(廖世军). A CCM type of membrane electrode assembly prepared by direct spraying method: CN: 200610035275.4 [P]. 2006.

High Performance Fuel Cell Catalyst and 5kW PEMFC Stack Without Humidification at Room Temperature and Atmosphere

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Abstract: The Pt/C catalyst with high dispersion and high performance was prepared successfully by an organic colloidal method and small batch production (10g) of Pt/C catalyst has been realized. The particle sizes of the active components in the catalyst could be as small as 2.8 nm and the active surface area was up to 450 m^2/g. A high performance membrane-electrode assembly (MEA) with surface area of 275 cm^2 has been prepared by using the home-made catalyst with a catalyst coated membrane method invented in the lab, and a 5 kW stack has been assembled. The stack showed working 10 h at room temperature, atmosphere and without humidification.

Key words: organic colloidal method; catalyst coated membrane; without humidification