学校编码：10384

学　　号：20520061151975　　密级_____

厦门大学

硕 士 学 位 论 文

直接甲醇燃料电池膜电极电化学表征装置及其应用

Electrochemical Devices Applied for Analysis of Membrane Electrode Assembly in Direct Methanol Fuel Cells

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论文提交日期：2010 年 6 月

论文答辩时间：2010 年 6 月

2010 年 6 月

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A Thesis Submitted for the Degree of Master of Science

at Xiamen University

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May 2010

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摘 要

对膜电极进行寿命表征通常采用传统三电极体系或单电池。为结合两种体系的优点，弥补其不足，本论文设计并加工了适用于实验室条件下使用，能在与实际运行环境接近的条件下评价燃料电池膜电极材料电化学性能和稳定性的表征装置。通过不断改进和优化，保证了该装置在寿命表征过程中的稳定性。利用该装置进行了模拟直接甲醇燃料电池(DMFC)全电池寿命实验、E-TEK阳极气体扩散电极(GDE)半电池加速老化实验和Pd掺杂Nafion膜作为支持电解质膜的阳极半电池加速老化实验。将电化学分析手段和ICP-MS相结合，获得了相互印证的电化学和元素分析数据，从而验证了膜电极电化学表征装置的稳定性和实用性。

结果表明，商用 E-TEK 阳极 GDE 中 Ru 的溶出发生在模拟 DMFC 正常寿命运行过程中，尤其是电池运行的初始阶段；循化伏安加速老化和高电位活化处理会加剧 Ru 的溶出，改变催化剂表面元素分布及氧化态，从而影响甲醇氧化活性。在阳极半电池加速老化实验中，用 Pd 掺杂 Nafion 膜作为质子交换膜，会出现 Pd 流失的现象，表明 Pd 在燃料电池运行环境中不稳定。

阳极GDE中原有的钌氧化物种是导致电池运行初始阶段钌溶出的主要原因，高电位活化处理可以通过：(1) 改变催化剂表面 Pt:Ru 值；(2) 减少不利于甲醇氧化活性的钌氧化物种含量，提高催化剂抗甲醇氧化中间物种毒化的能力，从而大幅度提高甲醇电氧化活性，但同时也加速了钌元素的溶解流失。本工作中设计并加工的电化学表征装置适用于对膜电极在接近燃料电池实际运行过程中的寿命及电化学性能研究，并可用于阻醇膜的性能研究。

关键词：直接甲醇燃料电池；膜电极；电化学装置；钌溶出；活化处理

Abstract

Degradation of membrane electrolyte assemblies (MEAs) is commonly analyzed either in traditional three-electrode systems or in single cells. In order to combine the advantages of both three-electrode systems and single cells, as well as to overcome their limitations, the improved electrochemical devices applied for MEAs' analysis were designed and implemented in this work. This type of electrochemical devices, which satisfies the testing conditions in laboratories, establishes an environment as close as possible to that of actual fuel cells and meets the requirements for degradation analysis. Mutual verification results were acquired by combinations of electrochemical and ICP-MS analyses in durability tests of simulated direct methanol fuel cell (DMFC), accelerated degradation tests of E-TEK anode gas diffusion electrode (GDE), accelerated degradation tests in anode half-cells with Pd-modified Nafion membranes as proton exchange membranes (PEM), thus confirmed the stability and applicability of the electrochemical devices.

Ruthenium dissolution from anode GDE was found during the normal operation of DMFC, especially during the initial period. The accelerated degradation tests and high potential activation treatments enhanced Ru dissolution and changed the distribution and oxidation states of surface elements of catalyst, which affect methanol oxidation activity. The instability of Pd in DMFC operating conditions was evidenced by Pd dissolution from Pd-modified Nafion membranes which served as PEM during the accelerated degradation tests in anode half-cells.

Ruthenium oxides originally existed in the E-TEK anode GDE were the main causes of Ru dissolution during the initial DMFC operation period. High potential activation treatments dramatically improved methanol oxidation activity by promoting the ability of anode catalysts to tolerant poisonous intermediates of methanol oxidation through (1) changing surface Pt:Ru ratios, and (2) reducing the amount of Ru oxides detrimental to methanol oxidation. However, high potential treatments also

simultaneously worsen Ru dissolution. The electrochemical devices are either suitable for electrochemical performance and degradation analyses of MEAs in conditions as close as possible to those of actual fuel cells or suitable for the performance evaluation of methanol inhibiting membranes.

Key words: Direct methanol fuel cell; Membrane electrode assemblies; Electrochemical devices; Ru dissolution; Activation treatments