

学校编码: 10384

分类号 _____ 密级 _____

学号: 200325107

UDC _____

廈門大學

碩 士 学 位 论 文

直接甲醇燃料电池中
甲醇渗透的电化学研究

An Electrochemical Investigation of Methanol Crossover
in Direct Methanol Fuel Cells

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论文提交日期: 2006年5月

论文答辩时间: 2006年5月

学位授予日期: 2006年 月

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2006年5月

An Electrochemical Investigation of Methanol Crossover in Direct Methanol Fuel Cells



A Thesis Presented for the Degree of
Master of Science at Xiamen University

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May 2006

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摘要

直接甲醇燃料电池 (DMFC) 具有能量密度高、安全、无污染等优点, 是近年来新开发的一类燃料电池。甲醇来源丰富, 价格便宜, 易于存储, 是便携式电子设备和电动汽车的理想动力源。然而, 甲醇渗透造成电池性能衰退, 是阻碍 DMFC 商业化的主要问题之一。因此, 开展甲醇渗透的研究工作, 建立适宜的表征方法, 对阐明甲醇渗透和阻醇机理, 推进 DMFC 的商业化进程有着重大的理论指导意义和实际应用价值。

本论文工作的主要思路是通过考察不同条件下甲醇的电氧化行为, 获得甲醇电氧化的动力学参数及影响因素, 并利用甲醇电氧化来研究甲醇渗透行为和操作条件对甲醇渗透的影响。因此, 采用循环伏安和计时电流测试技术考察了甲醇浓度、扫描速度、温度等对甲醇电氧化的影响及甲醇电氧化反应的动力学行为, 然后通过建立 H-Cell 来模拟燃料电池, 获得不同时间后阴极侧的甲醇电氧化行为, 考察了静态和搅拌情况下甲醇从阳极通过质子交换膜渗透到阴极的过程及不同温度时模拟 DMFC 运行的开路电位变化情况, 并在测试结束后对相应的 Nafion[®] 膜进行了 XRD 和 FTIR 表征。

实验结果表明, 室温条件下测得 Nafion[®]117 膜中甲醇的渗透速率约为 $4.4 \times 10^{-6} \text{cm}^2/\text{s}$, 甲醇浓度和温度等对甲醇电氧化峰电流及峰电位的影响较为明显。甲醇电氧化峰电流随浓度或温度的增加而增加, 峰电位随浓度或温度的增加而发生正移。室温下, 当甲醇浓度从 0.1mol/L 增加到 1.0mol/L 时, 甲醇在 Pt/C/GC 电极上的氧化峰电流密度从 $22.0 \text{mA}/\text{cm}^2$ 增加到 $54.5 \text{mA}/\text{cm}^2$, 同时峰电位从 0.61V 正移至 0.77V (vs. SCE)。80°C、甲醇起始浓度为 1.0mol/L 时, 峰电位进一步正移, 且只在扫描第一圈时得到完整的氧化峰, 扫描至第四圈时, 氧化峰消失并出现电流振荡现象。甲醇在 PtRu/C/GC 电极上的电氧化速率相对于甲醇浓度约为 0.4 级, 传递系数为 0.36~0.39; 甲醇起始浓度为 1.0mol/L 时模拟 DMFC 开路运行 10h 后在阴极侧检测出甲醇, 其氧化峰电流密度约为运行前的 14%, 小于相同渗透时间时静态条件下测得的甲醇渗透量。甲醇渗透量随着时间的延长而增加, 但是 Nafion[®] 膜的主链和支链结构相对比较稳定。

关键词: 直接甲醇燃料电池; 甲醇渗透; 甲醇电氧化

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ABSTRACT

Direct methanol fuel cell (DMFC) has advantages of high power density, safety, low or zero emission and has been developed in recent years. Using methanol as a fuel, it is inexpensive, obtainable, convenient to carry and store. DMFC has become one of the most promising candidates as power sources in portable electronic products and electric vehicles. However, the degradation of cell performance due to methanol crossover from anode side to cathode side is one of the major problems that impedes the commercial development of DMFC. It is, therefore, both theoretically and practically important to elucidate mechanism of methanol crossover and inhibition of fuel crossover through proton exchange membrane by investigating methanol crossover and developing appropriate characterization methods.

The main approaches in this work were to investigate methanol electrooxidation under different conditions and to obtain kinetic parameters of the reaction, as well as to examine its influencing factors. The behavior of methanol crossover and the effects of operating conditions on methanol crossover were studied through methanol electrooxidation. The effects of methanol concentration, scan rate and temperature on methanol electrooxidation and the kinetic process of the reaction were investigated using cyclic voltammetry and chronoamperometry. Through the H-shape cell tests, the methanol electrooxidation curves were obtained after different periods of time under a stationary or a stirring condition and simulative DMFC tests were also carried out to study the effect of methanol crossover on OCV at different temperatures. The corresponding Nafion[®] membranes were studied by FTIR and XRD after each H-Cell test.

The experimental results showed that methanol permeability of Nafion[®]117 membrane was evaluated to be approximately about $4.4 \times 10^{-6} \text{ cm}^2/\text{s}$ at room temperature. Concentrations and temperatures had evident influence in the peak current density and peak potential for methanol electrooxidation. The peak current densities or peak potentials rose or shifted more positively with an increase in

methanol concentration or temperature. At room temperature, when the methanol concentration increased from 0.1mol/L to 1.0mol/L, the peak current density of methanol oxidation on Pt/C/GC electrode rose from 22.0mA/cm² to 54.5mA/cm². At the same time, the peak potential shifted positively from 0.61V to 0.77V(vs.SCE). Under the conditions of 80°C and 1.0mol/L starting concentration for methanol, the peak potential further shifted positively so that the whole oxidation peak was only observed during the first scan. The oxidation peak disappeared and current oscillations occurred during the fourth scan. The kinetic parameters for methanol electrooxidation on PtRu/C/GC electrode were also calculated. The reaction order with respect to methanol was 0.4, the transfer coefficient was 0.36~0.39. The peak of methanol electrooxidation was detected in the CV curve obtained from the cathode side of H-cell operated at OCV for 10h. Its peak current density was about 14% of that observed from the 1.0mol/L standard methanol solution, and the amount of methanol crossed through Nafion[®] 117 from anode to cathode was smaller than that under stationary condition for the same permeation time. The amount of methanol in the cathode side increased with the extension of permeation time. However, the backbones and side chains of Nafion[®] membrane were relatively stable.

Key Words: DMFC; Methanol Crossover; Methanol electrooxidation

第一章 引言

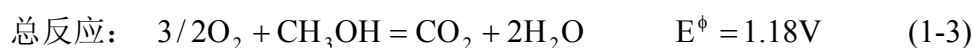
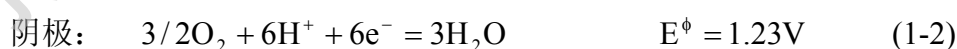
燃料电池(fuel cell)是一种将持续供给的燃料和氧化剂中的化学能连续不断地转化为电能的电化学装置。以电解质来区分,可以分为五类:碱性燃料电池、磷酸型燃料电池(PAFC)、固体氧化物燃料电池(SOFC)、熔融碳酸盐燃料电池(MCFC)和质子交换膜燃料电池(PEMFC)。

以甲醇作为燃料的燃料电池称为直接甲醇燃料电池(DMFC)。DMFC是一种清洁能源,具有高效、安全、无污染等优点^[1]。使用廉价易得的液体甲醇作燃料,系统简单,运行方便,在当今能源危机和环境污染日趋严重的情况下,直接甲醇燃料电池的深入研究尤为重要,具有很广阔的商业化前景。燃料便于存储和运输,可以作为便携电源广泛应用于移动通讯如手机、笔记本电脑、摄像机等;由于其能量密度大、无噪音,还可以广泛应用于军事领域,如单兵作战系统、潜艇等;DMFC还可以作为动力电源和辅助动力电源用于交通工具,如汽车、火车的空调电源等^[2]。本章主要介绍四个部分:(1) DMFC简介;(2) 甲醇渗透研究进展;(3) 甲醇渗透研究方法;(4) 表面与结构表征方法。

1.1 DMFC简介

1.1.1 工作原理

DMFC的工作原理如下:



由以上数据可以看出DMFC标准状态下的理论电压较高,但由于在实际使用时电极极化和电池内阻引起欧姆极化,DMFC输出电压远小于标准状态下的理论电压。

1.1.2 基本结构

DMFC的基本结构主要由阳极、质子交换膜、阴极等组成(如图1.1^[3]所示)。其中,催化层促进燃料的电氧化反应;质子交换膜传输质子,隔离燃料;气体扩

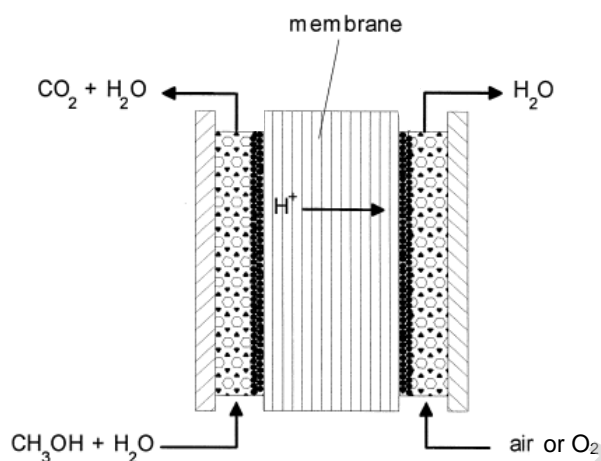


图 1.1 直接甲醇燃料电池基本结构示意图

散层为电极反应提供气体通道、电子通道和排水通道，同时还起到支撑催化剂层稳定电极结构的作用。

DMFC 工作时燃料甲醇通过燃料入口进入燃料电池的阳极催化层后，在阳极催化剂的作用下发生电化学氧化反应，反应产物水和二氧化碳从阳极出口排出，同时，反应产生的质子穿过电解质（质子交换膜）迁移至阴极并与达到阴极催化层的氧化剂（氧气或空气）反应生成水，水从阴极出口端排出，电子从阳极经外电路转移至阴极形成直流电。

1. 1. 3 存在问题

尽管 DMFC 具有很多优点，应用前景广阔，并已经有单位推出用于笔记本电脑、电动自行车、汽车的 DMFC 样机。然而，长期以来 DMFC 的商业化却受到两个关键问题的困扰^[4]：一是阳极对甲醇电化学氧化催化活性低；二是由于质子交换膜的选择透过性较差，存在甲醇渗透现象。甲醇渗透带来一系列的危害，其中表现在：（1）影响阴极性能。渗透到阴极的甲醇在阴极催化剂作用下与 O_2 发生非均相反应，形成混合电位，同时，甲醇还会使阴极催化剂中毒，造成阴极性能下降。（2）造成燃料的浪费。透到阴极的甲醇在阴极催化剂作用下与 O_2 直接发生反应，造成化学短路，这部分燃料不能提供电流而被白白浪费。（3）影响膜的导电性能。由于膜内甲醇分子的存在和迁移使膜的质子传导能力下降^[5]。以下主要对近年来甲醇电氧化及其渗透方面的研究进展作详细的综述。

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