

学校编码：10384

分类号\_\_\_\_\_密级\_\_\_\_\_

学号：B200025031

UDC \_\_\_\_\_

厦门大学  
博 士 学 位 论 文

原位快速时间分辨显微 FTIRS 的建立及其  
对 Pt 微电极表面动态过程的研究

Electrochemical in situ fast time-resolved microscope FTIR  
reflection spectroscopy and its applications in the studies of  
surface dynamic processes on nanostructured Pt electrodes

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论文提交日期：2004 年 6 月

论文答辩时间：2004 年 7 月

学位授予日期：2004 年 月

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2004 年 6 月

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厦门大学博硕士学位论文摘要

## 摘要

固液界面电化学原位红外反射光谱利用指纹特征和表面选律,检测电极表面吸附物种及其成键和取向,在分子水平上研究反应机理。时间分辨和空间分辨是原位红外光谱两个重要的发展方向。其中时间分辨光谱,在检测短寿命中间体,跟踪反应历程,获取分子水平层次的动力学规律等方面可提供独到的信息。

本论文自行设计并研制信号同步仪,采用微电极并与红外显微镜相结合,建立了外反射型电化学原位步进扫描时间分辨显微 FTIR 光谱 (*in situ* SSTR-MFTIRS),光谱的时间分辨率最快可达  $10\mu\text{s}$ 。利用纳米结构电极的异常红外效应,显著提高光谱检测灵敏度,克服了通常薄层电解池中电极对电位变化响应慢的不足,拓宽了快速时间分辨红外光谱的应用范围,为研究电化学快速反应动力学和表面动态过程奠定了基础,开展了以下研究:(1)运用 SSTR-MFTIRS 研究了纳米结构 Pt 微电极上桥式吸附态 CO 向线型吸附态 CO 转化的动态过程,观察到转化中间态 CO,初步提出转化过程的模型并获得定量的转化动力学数据。(2)设计并研制具有快速传质能力的流动电解池和微电极,实现了将 SSTR-MFTIRS 应用于不可逆电化学反应过程中的研究,发现纳米结构 Pt 微电极上吸附态 CO 的不可逆氧化经历“成核-成长”机理。(3)运用 SSTR-MFTIRS 研究了纳米结构 Pt 微电极上吸附态  $\text{SCN}^-$  的电位诱导取向转化动力学,发现  $\text{SCN}^-$  从 S 端吸附转为 N 端吸附的速度明显低于其逆过程。

此外还通过编制 EG&G263 型恒电位仪与红外光谱仪的同步控制软件,建立了电化学原位快速扫描时间分辨显微 FTIR 反射光谱(RSTR-FTIRS),实现循环伏安和红外光谱同时快速采集,在  $200\text{mVs}^{-1}$  电位扫描下,光谱的电位分辨率仍可达  $2.6\text{mV}$ ,获得碱性介质中甲醇电催化氧化动态过程的新信息。

本论文建立的两种原位快速时间分辨显微 FTIR 反射光谱,实质性地发展了外反射型电化学原位红外光谱技术,所获得的纳米结构微电极表面动态过程和反应动力学研究结果对于深入认识分子水平上的电极过程动力学规律、发展电催化及相关理论具有重要意义。

**关键词:** 原位 FTIRS; 时间分辨; 反应动力学

## Abstract

Electrochemical *in situ* infrared reflection spectroscopy, on the basis of its fingerprint and surface selection rules, can identify the nature of adsorbates and their surface bonding and orientation in electrode/electrolyte interfaces. The time-resolved and space-resolved spectroscopy have become currently two main directions of the development of electrochemical *in situ* IR spectroscopy. The former is unique in probing short lifetime intermediates, tracking reaction processes and providing dynamic information at molecule level in electrochemistry.

In this thesis, we have established an electrochemical *in situ* step-scan time-resolved microscope FTIR external reflection spectroscopy (*in situ* SSTR-MFTIRS). The setup consists of an infrared microscope working with microelectrodes, and a home-designed and fabricated signal synchronizer. The time resolution of *in situ* spectra can reach up to 10 $\mu$ s. Abnormal infrared effects (AIREs) of the nanostructured Pt microelectrode was used to improve significantly the IR determination sensitivity. The fast time-resolved FTIRS carried out in a thin-layer IR cell extended the possibility of using *in situ* SSTR-MFTIRS to study a wide variety of electrochemical reactions. It has been demonstrated that the SSTR-MFTIRS is a promising tool to be used in studies of kinetics and surface processes of fast reactions.

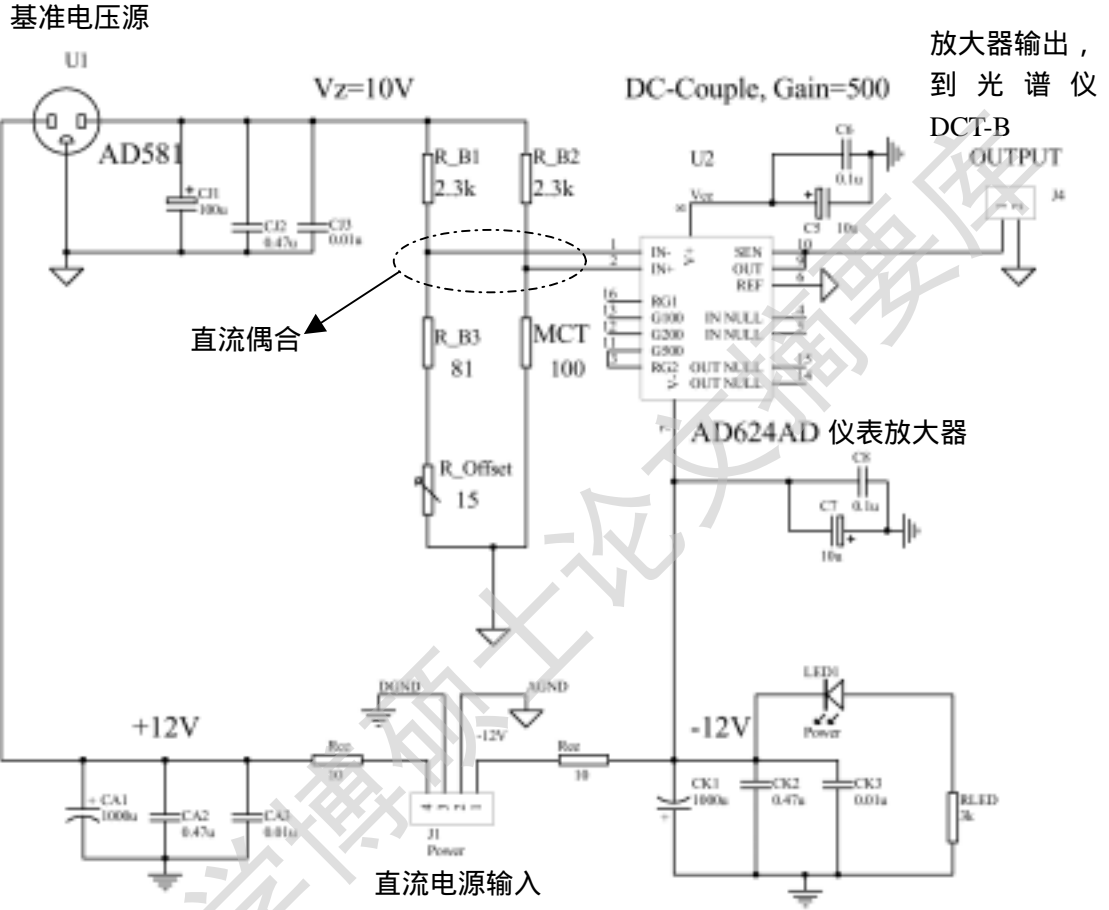
The studies include: (1) the dynamic processes of site conversion between bridge bonded CO (CO<sub>B</sub>) and linear bonded CO (CO<sub>L</sub>) on a nanostructured Pt microelectrode. Based on the determination of intermediate CO species in the site conversion processes and the acquisition of quantitative data of concerning the kinetics, a model of site conversion of adsorbed CO was suggested; (2) A novel spectroelectrochemical flow cell and a microelectrode possessing fast

mass transfer were specially designed and fabricated, which allow irreversible electrochemical reactions to be studied by SSTR-MFTIRS. It has illustrated that the irreversible oxidation of CO adsorbed on nanostructured Pt microelectrode occurred according a nucleation and growth mechanism; (3) The potential induced orientation conversion of  $\text{SCN}^-$  adsorbed on nanostructured Pt microelectrode was also investigated by using the SSTR-MFTIRS. It was found that the conversion rate from S-bonded  $\text{SCN}^-$  to N-bonded  $\text{SCN}^-$  is considerably slower than that of the reverse reaction.

Through a home-developed software to realize the synchronization between 263A potentiostat (EG&G) and FTIR spectrometer, we have developed an electrochemical *in situ* rapid-scan time-resolved microscope FTIR reflection spectroscopy (RSTR-FTIRS), by which the collection of infrared spectra with an interval 2.6mV and the acquisition of cyclic voltammograms at a scan rate as large as  $200\text{mVs}^{-1}$  can be done simultaneously. By using the RSTR-FTIRS, new information on the kinetics of methanol electrocatalytic oxidation in alkaline media was obtained.

The establishment of the two types of electrochemical *in situ* fast time-resolved microscope FTIR reflection spectroscopy have progressed substantially the technique of electrochemical *in situ* external reflection infrared spectroscopy. The results concerning surface dynamic processes and kinetics obtaining in the present study have thrown a light in understanding at the molecular level the principle of electrode kinetics, and to develop the theory of electrocatalysis and relevant disciplines.

**Key Words:** *in situ* FTIRS; time-resolved; reaction kinetics



Appendix 2. Circuit of DC-coupled MCT amplifier

## 第一章 绪论

### § 1-1 概述

电化学作为物理化学的一个分支,主要研究两相之间的界面结构和电荷传递过程<sup>[1]</sup>,广泛应用于化工(如氯碱工业,电有机合成<sup>[2]</sup>)、电化学能源,材料,环境等领域。电化学动力学研究主要是从20世纪四十年代开始,A. N. Frumkin 学派抓住电极和溶液净化对电极反应动力学数据重现性有重大影响这一关键性问题,从实验技术上开辟了新局面,提出迟缓放电理论,使得电极过程动力学逐渐成为电化学科学的主要发展方向。研究电极过程动力学的主要目的在于探索影响电极反应速度的基本因素,从而可能有效地按照我们的主观愿望去影响电极反应进行的方向与程度。传统电化学研究方法主要通过电信号作为激励和检测手段,通过电流、电压和电荷的测量获得电极|电解质溶液界面结构、电化学反应机理和动力学性质等信息。虽然这些方法具有高灵敏度的优点,如可以检测千分之一的单层吸附,但都存在着一个明显局限性:不具有分子表征能力,对于复杂反应,仅能提供各种微观信息的平均总和,难以准确鉴别电化学反应过程中的各种反应物,中间物和产物,并提出可靠的反应机理。20世纪60年初开始发展的原位光谱电化学技术,将光谱技术与电化学方法相结合,能在电化学反应进行的同时对电极|电解质溶液界面过程进行原位光谱检测,从而提供分子水平上的信息,使得电化学研究从宏观深入到微观,从唯象,统计平均提升到分子水平<sup>[3-8]</sup>。随着仪器性能的提高,原位光谱测量也逐渐地从稳态测量向暂态(时间分辨)测量发展。快速时间分辨光谱能够检测双电层动态过程,短寿命中间体,直接测量复杂电极反应的基元反应动力学,揭示电化学反应机理,从而实现在分子水平上研究电极反应动力学<sup>[4, 6, 9]</sup>。

### § 1-2 传统电化学的动力学研究方法

电化学反应一般由反应物液相传质、前置表面转化、电荷转移、后置表



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