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基于微电极芯片局域增强电势研究及 AuPd 合金纳米催化剂制备和性质

Study of Locally-Enhanced Interfacial Potential Based on Microelectrode Chips and Preparation of AuPd Alloy Nanocatalystfor Ethanol Electrooxidation

刘涛

指导教师姓名：孙 世 刚　教授
专　业 名 称：物理化学
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By

Tao Liu

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Prof. Shi-Gang Sun

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摘要

铂基金属纳米催化剂广泛应用于燃料电池、汽车尾气处理、石油化工、化学工业等其他领域。由于铂资源匮乏，价格昂贵，因此提高铂金属的利用率和寻找其替代金属，以减少铂金属的使用是现阶段研究的重大问题。

研究表明，高指数铂纳米催化剂由于其表面原子配位数少，具有较高的催化活性。本课题组在长期研究过程中发展了电化学流动反应体系（EFRS：Electrochemical Flow Reaction System），实现了在液相中连续可控合成高指数纳米 Pt/C、Pd/C 以及 PtPd/C 等负载型金属纳米催化剂，不仅提高了铂的催化活性和利用率，而且使电化学制备铂族金属纳米催化剂规模化生产迈进了一大步。对于体系中的所涉及的电化学机理，进行了深入的研究和探索。

近几年，Pd 作为一种 Pt 的代替材料已被广泛研究。Pd 纳米催化剂的成本相对较低，在碱性电解质溶液中对醇类电氧化的催化活性较高，尤其对乙醇电氧化的催化性能具有独特的优势。

本工作采用微机电系统（MEMS）加工制作了一系列微电极芯片，探究了电化学连续合成的新机理，研究了局域增强电势（LEIP：Locally-Enhanced Interfacial Potential）的性质。此外，为了减少 Pt 的使用，对 Pt 的替代金属 Pd 进行研究，探究 Pd 以及 AuPd 合金纳米催化剂对乙醇的催化性能。主要研究结果如下：

1、根据电化学流动反应体系中炭黑粒子周围所处的环境以及结构特点，设计微电极芯片，利用 MEMS 平台制作加工所需芯片，用于研究电化学流动反应体系中炭黑粒子的行为。改变微电极芯片的参数以及微电极芯片的结构，记录导电粒子周围电势变化情况，探究导电粒子周围电势分布规律。

2、改变电化学测试条件，对三电极芯片 MEC-2 进行不同方波电位，不同频率，不同电解质溶液浓度测试。局域增强电势随着测试条件不同，展现出不同的特征。局域增强电势随着外加方波电位的增加而增加，与方波电位变化频率完全保持一致，以上两个变化都呈现线性相关性。随着电解质溶液浓度增加，局域增强电势表现出先增加后减小的趋势，在 $NaClO_4$ 溶液浓度为 30 mmol/L 时，局域增强电势最大。外加方波电势是诱导局域增强电势的产生原因，说明局域增强电势可以用外加方波电位调制，同时优化电解液的浓度可以得到合适的局域增强电

势。

3、运用电化学恒电位法在 ITO 基底上沉积制备出不同组成的 AuPd 合金纳米粒子，通过改变电解液中前驱体的比例组成控制合金纳米粒子的组成，进而调变其对乙醇的电氧化的催化活性。研究显示，沉积电位影响纳米粒子的粒径和分布密度，通过优化制备条件，控制沉积电位-0.3 V 制备的 Au_1Pd_3 合金纳米粒子对乙醇电氧化表现出最高的催化活性和稳定性: Au_1Pd_3 合金纳米粒子上测得的乙醇氧化峰电流密度为 34.36 mA cm^{-2}，是相同条件制备的 Pd 纳米粒子上的峰电流密度（4.46 mA cm^{-2}）的 7.7 倍。在固定氧化电位-0.3 V，稳定测试 1800 s，Au_1Pd_3 合金纳米粒子给出的乙醇氧化稳态电流密度为 1.05 mA cm^{-2}，是相同条件下制备的 Pd 纳米粒子的（0.02 mA cm^{-2}）52.5 倍。

本文所探究的 EFR 中炭黑粒子的电化学行为以及所涉及的反应机理，对认识电化学液相反应过程具有指导性意义。本文所研究 AuPd 合金纳米催化剂的结果对设计制备高性能直接乙醇燃料电池合金催化剂具有重要意义，并在光电化学和醇类分子传感检测等方面具有应用价值。

关键词：电催化；微电极芯片；局域增强电势；AuPd 合金；氧化铟锡（ITO）；乙醇氧化

Abstract

Pt-based metal nanocatalysts are widely applied as catalysts in a variety of fields such as fuel cell, automobile exhaust purification, petrochemical industry and chemical industry. Due to the rare reserves and the high price of platinum group metal, therefore,how to improve their utilization efficiency and find an alternative to Pt-based catalysts has been an important scientific and engineering issue.

It has reported that high-index Pt nanocatalysts perform better electrocatalytic properties for the low accordance number of surface atoms. Through long-term research, our group has developed an electrochemical flow reaction system (EFRS), which realized the electrochemical synthesis of Pt/C, Pd/C, PtPd/C and other supported metal nanocatalysts with high-index facets in solution. The EFRS not only improve the performance of catalysts but also achieve mass production of catalysts. However, the electrochemical behavior and the involved reaction mechanism of the system remains to be explored further.

In recent years, Pd-based catalysts emerging as an alternative to Pt-based catalysts have been widely investigated. The price of Pd is cheaper and it possesses superior catalytic activity toward the anodic alcohols electrooxidation in alkaline electrolyte especially for ethanol.

In this thesis, we use the microelectrode chips prepared by micro-electro-mechanical system (MEMS) to explore a new principle of electrochemical continuous synthesis in solution, and study the properties of LEIP (Locally-Enhanced Interfacial Potential). Besides, to reduce the use of Pt, we explore Pd-based nanocatalysts and their catalytic activity toward ethanol electro-oxidation. The main results are listed as below:

1. Based on the requires of the experiments and the structural characteristics of electrochemical flow reactor (EFR), we designed and fabricated two kinds of microelectrode chips by MEMS technology for researching the electrochemical behavior in EFR. By changing the parameter and structure of microelectrode chips,

we observe the variation of potential near the conductive particles to explore the regularity of potential distribution near the conductive particles.

2. By changing the test condition, such as potential of SWP, frequency of SWP and concentration of electrolyte solution to study the properties of LEIP. LEIP is increased with the increase of potential of SWP and the variation of frequency of LEIP is completely agreement with varying of frequency of SWP. LEIP increase first then decrease with the increase of concentration of electrolyte solution, and when concentration of $NaClO_4$ is 30 mmol/L, LEIP presents the maximum. We discover that external SWP is the direct factor which inducing the LEIP of conductive particles, and the intensity of LEIP can be modulated by external SWP. Also, we can get the required LEIP by optimizing the concentration of the electrolyte solution.

3.Using electrochemical potentiostatic deposition to deposit AuPd alloy nanoparticles on indium tin oxide (ITO) substrates. Emphasis was put upon systematic studies of effects of the composition and preparation conditions of the AuPd alloy nanoparticles to electrocatalytic properties. The results demonstrated that the deposition potential affects the size and dispersion of AuPd alloy nanoparticles. It has found that the AuPd alloy nanoparticles exhibited higher electrocatalytic activity and stability than Pd nanoparticles towards ethanol electrooxidation, ranking in the order of $Au_1Pd_3 > Au_1Pd_1 > Au_1Pd_9 > Pd$. The Au_1Pd_3 nanoparticles produced at -0.3 V yielded the highest catalytic activity and the most stability towards ethanol electrooxidation. The anodic peak current density of ethanol oxidation on Au_1Pd_3 nanoparticles was measured at 34.36 mA cm^{-2} that is 7.7 times of that measured on the Pd nanoparticles (4.46 mA cm^{-2}). Moreover, after a run of 1800 s for ethanol oxidation at -0.3 V, the steady-state oxidation current on the Au_1Pd_3 nanoparticles was determined to be 1.05 mA cm^{-2}, which is 52.5 times of that on the Pd nanoparticles (0.02 mA cm^{-2}).

Herein, the exploration of the reaction mechanism involved in EFR is of great importance in the study of the electrochemical reaction in solution.The study about

AuPd alloy nanocatalysts has thrown new insight into the design and preparation of high performance electrocatalysts for direct ethanol fuel cells, and presents potential applications in relevant fields such as photoelectrochemistry and alcohol sensors.

Keywords: electrocatalyst; microelectrode chips; local-enhanced interfacial potential; AuPd alloy; ITO; ethanol oxidation

目录

Table of Contents