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**C1 分子电催化中纳米材料和 Pt 单晶电极的  
表面结构和组成效应研究**

**Effects of Surface Structure and Composition of  
Nanomaterials and Pt Single Crystal Planes in  
Electrocatalysis of C1 Molecules**

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厦门大学博硕士学位论文摘要库

# **Effects of Surface Structure and Composition of Nanomaterials and Pt Single Crystal Planes in Electrocatalysis of C1 Molecules**

A Dissertation Submitted for the Degree of Doctor of Philosophy

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## 摘要

近年来, 纳米材料由于其特殊的光、电、热、催化、磁和力等性能引起了广泛关注。纳米材料在腐蚀、电子、燃料电池、光电等多个领域得到了广泛研究。在能源安全和环境问题的驱动下, 对直接有机小分子燃料电池的研究成为其中最重要的课题之一。由于催化剂价格昂贵、以及易中毒而引起的低效率使得燃料电池在实际应用极其有限。同时催化剂材料的很多性质很大程度上取决于其表面结构和组成。因此, 本论文工作主要目的在于研究 CoNi 薄膜的异常红外性能, 合成对 C1 分子氧化的高活性铂基纳米催化剂并进一步提高它们的性能, 揭示 CO 在纳米材料和模型催化剂(铂单晶体电极)上的吸附行为及氧化反应动力学。本论文的主要结果如下:

1. 测定了不同材料电极的零全电荷电位(pztc)和CO覆盖度。采用微乳液法(w/o)合成四种具有不同择优取向的纳米粒子: 球形 ((Poly)Pt, ~4.5 nm), 立方体 ((100)Pt, ~8.2 nm), 六边形((100-110)Pt, ~11.5 nm)和四面体或八面体((111)Pt, ~8.6 nm)。使用Clavilier设计的单晶制备仪, 分别制备了半球形Pt多晶、具有(111)平台和不同(110)或(100)台阶密度的单晶电极。采用CO电荷置换法测定了所制得的不同电极在不同表面处理及修饰条件下的pztc。

(Poly)Pt、(100)Pt、(100-110)Pt和(111)Pt四种纳米粒子在0.5 M H<sub>2</sub>SO<sub>4</sub>中的pztc分别0.261、0.279、0.269和0.255 V, 而在0.1 M HClO<sub>4</sub>分别为0.292、0.336、0.305和0.276 V。结果表明pztc是个表面结构敏感的参数, 随着(100)位的减少(110)位的增加逐渐减小, 同时阴离子的吸附也会使pztc发生负移。半球形Pt多晶电极上pztc也有类似的变化规律。CO在不同电极上氧化的循环伏安特征随表面活性位的差别发生明显变化, 表明CO氧化是个对表面结构极其敏感的反应。利用pztc校正了双电层及CO氧化过程中阴离子重新吸附的电量, 获得CO的实际氧化电量。以0.06 V全电荷的绝对值即纯H的近饱和吸脱附电量为参比, 测得不同电极在0.5 M H<sub>2</sub>SO<sub>4</sub>和0.1 M HClO<sub>4</sub>中CO的覆盖度非常一致、与电解质无关。而传统双电层校正法由于无法区别阴离子吸附, 测得H的吸脱附电量在不同电解质中差别较大, 因此获得的CO在不同电解质中的覆盖度差别也比较大、不够准确。

由(111)平台和不同密度的(110)台阶组成的Pt(554)和Pt(221)电极以及由(111)平台和不同密度的(100)台阶组成的Pt(544)和Pt(533)电极, 它们的pztc随着台阶密度的增加而减小。这是由于Smoluchowski效应在台阶处形成一个底部带负电而顶部带正电的偶极子, 随台阶密度增加、负电荷密度增加, 因此pztc相应减小。当吸附原子Bi或Te选择性地吸附在(110)或(100)台阶位时, 由于吸附原子中和了台阶位的负电荷, 而对平台位(111)几乎没有影响, 因此pztc发生正移。缺陷位修饰Bi的(111)Pt纳米粒子也有相似的变化。借助于pztc和Bi的选择性修饰, 通过修饰前后CO和H的吸脱附电量的变化, 测定了类Pt(111)单晶电极及(111)Pt纳米粒子上CO在台阶/缺陷、平台和整个平面上的覆盖度。CO在(110)和(100)台阶位上的覆盖度相差很大, 分别为0.70和0.40。原位红外反射吸收光谱研究表明CO在(110)位上以 $\text{CO}_L$ 吸附为主而在(100)位上主要为 $\text{CO}_B$ , 进一步证明了CO在不同台阶位上吸附行为的显著差异。CO在(111)Pt纳米粒子的缺陷位(主要为(110)位)上的覆盖度为0.66, 与Pt(554)的(110)台阶位上的一致。

2. CO在不同电极上的氧化机理研究。当单晶电极的台阶位及纳米粒子的缺陷位修饰吸附原子后, CO的CV氧化峰发生正移, 同时从CA测得的表观氧化速率常数减小, 表明台阶/缺陷位是CO氧化的活性位。Pt(554)电极的台阶位修饰Bi或Te后, CO氧化的速率常数降低的幅度比具有相似台阶密度的Pt(544)电极大, 说明(110)台阶位对CO氧化的催化活性大于(100)台阶位。CO在各种类Pt(111)单晶电极上氧化的时间电流曲线, 无论是否修饰其他原子都可以用均场近似进行模拟, 而在(111)Pt纳米粒子及Bi修饰的电极上可以用改进的均场近似模型进行模拟。测得的Tafel斜率在 $60\sim 90 \text{ mV dec}^{-1}$ 表明CO氧化机理相同, 即都通过含有一个较慢的化学反应步骤的Langmuir-Hinshelwood模型进行。

3. 测定了多晶Pt的表面活化面积。对四个用火焰烧制的Pt多晶球分别进行火焰处理、不同扫速循环伏安氧化还原等处理, 采用传统的双电层校正法测定其在 $0.5 \text{ M H}_2\text{SO}_4$ 和 $0.1 \text{ M HClO}_4$ 中H区的吸脱附电量密度, 在硫酸溶液中其实还包含有阴离子的吸脱附。从四个不同多晶球上测得的结果重现性很好, 随着CV对表面扰乱程度的增加, H吸脱附电量密度逐渐增大。经过系统的研究, 我们建议以经火焰处理、表面光滑的Pt多晶球为参考, 在不同电解质溶液中采用不同的单位面积H吸脱附电量来计算Pt电极表面活化面积, 即硫酸溶液中的氢区电量为230



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