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博 士 学 位 论 文

**Pt 单晶及 Sb 修饰晶面上 CO<sub>2</sub> 还原  
电催化的表面结构效应**

**Surface Structure Effects in Electrocatalysis of CO<sub>2</sub> Reduction  
on Pt Single Crystal and Sb Modified Planes**

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## 摘要

CO<sub>2</sub>的电催化还原是环境科学，能源科学，电化学等研究领域的前沿课题。金属单晶电极具有明确的表面原子排列结构，为认识界面微观结构，电催化反应的表面过程提供了一个理想模型。两者结合不仅把 CO<sub>2</sub> 还原反应的研究从宏观唯象推进到表面微观过程，而且为在微观层次设计、筛选和研制高性能电催化剂提供指导。

本论文研制了 Pt(100)、Pt(110)、Pt(111)、Pt(510)、Pt(310)、Pt(210)、Pt(320) 和 Pt(991)等八个 Pt 单晶电极，并通过表面处理获得同一电极的不同表面结构，运用电化学循环伏安方法 (CV)，程序电位阶跃暂态技术和原位 FTIR 光谱，研究了在上述不同表面结构的 Pt 单晶电极及 Sb 修饰的 Pt 基础单晶面上 CO<sub>2</sub> 电催化还原的表面过程和反应动力学，以甲酸为探针分子进一步研究了电催化的表面结构效应。取得如下重要结果：

1. CO<sub>2</sub> 电催化还原的表面结构效应。Pt 单晶电极上 CO<sub>2</sub> 的电催化还原是表面结构敏感的反应。当电位扫描上限  $E_u = 0.75 \text{ V}$  (vs SCE) 时，即电极表面保持确定结构的条件下，三个基础晶面中，Pt(110)给出最高的反应活性，Pt(100)的反应活性略低，而 Pt(111)则相对“惰性”。阶梯晶面的电催化特性表现为该晶面所含各种结构表面位的电催化特性的组合。不同冷却气氛得到的 Pt(hkl)- I (Ar + H<sub>2</sub>) 与 Pt(hkl)- II (空气)上 CO<sub>2</sub> 还原吸附态产物的氧化电量 ( $Q_{OX}^{r-CO_2}$ ) 和覆盖度 ( $\theta_{r-CO_2}$ ) 呈现相同的变化趋势，但具有较为开放结构的 Pt(hkl)- II 对 CO<sub>2</sub> 的还原活性要高于表面结构更为有序的 Pt(hkl)- I。当  $E_u = 1.25 \text{ V}$  时，由于氧的吸脱附导致电极表面重构，各单晶电极的电催化性能发生了不同的变化。定义

$$\frac{\Delta Q}{Q} = \frac{Q_{r-CO_2(1.25V)}^{OX} - Q_{r-CO_2(0.75V)}^{OX}}{Q_{r-CO_2(0.75V)}^{OX}}$$

能：Pt(111)上得到最大的  $\frac{\Delta Q}{Q}$ ，即其对 CO<sub>2</sub> 还原的电催化活性得到最大程度的提

高；电极上 (110) 表面位密度小于 (等于) 50% 的四个单晶电极的  $\frac{\Delta Q}{Q}$  值为正，

即催化活性提高，而电极上 (110) 表面位密度大于 50% 的三个单晶电极的  $\frac{\Delta Q}{Q}$  值

为负，指示电催化活性降低。这一结果说明对于  $\text{CO}_2$  还原反应，具有开放结构的 (110) 表面位具有较高的电催化活性，而相对有序的 (100) 表面位则具有较高的稳定性。

2. 电极电位和表面结构对  $\text{CO}_2$  还原的影响规律。 $\text{CO}_2$  在 Pt 单晶电极上还原平均速率的最大值 ( $\bar{v}^{\text{max}}$ ) 均位于 -0.20 V 附近，即对  $\text{CO}_2$  电催化还原，电极电位对同一材料基底的电极所产生的影响是相同的，但不同的表面结构对反应动力学的影响具有显著的差异。

3.  $\text{CO}_2$  电催化还原的表面机制。Pt 单晶电极上直接吸附 CO 的氧化电量 ( $Q_{\text{sat}}^{\text{CO}}$ ) 和饱和覆盖度 ( $\theta_{\text{sat}}^{\text{CO}}$ ) 均明显大于  $\text{CO}_2$  还原吸附态产物的氧化电量 ( $Q_{\text{sat}}^{r-\text{CO}_2}$ ) 和饱和覆盖度 ( $\theta_{\text{sat}}^{r-\text{CO}_2}$ )，证明  $\text{CO}_2$  还原需要邻近 Pt 表面位的参与，并且其还原产物在电极表面呈均匀分布。Sb 吸附在电极表面改变了 Pt 单晶电极对  $\text{CO}_2$  还原的电催化活性，并且随 Sb 覆盖度 ( $\theta_{\text{Sb}}$ ) 改变，其相应的反应活性也随之变化。Sb<sub>ad</sub> 对 Pt(100)和 Pt(110)电极表面的修饰均在不同程度上抑制了  $\text{CO}_2$  在电极表面还原反应，但其抑制程度随  $\theta_{\text{Sb}}$  的变化规律不同。Sb/Pt(100)电极上， $\text{CO}_2$  还原吸附态产物 (r- $\text{CO}_2$ ) 的氧化峰电流 ( $j_p$ ) 和氧化电量 ( $Q_{\text{OX}}^{r-\text{CO}_2}$ ) 随  $\theta_{\text{Sb}}$  的增大呈峰形变化，并在  $\theta_{\text{Sb}} = 0.19$  处取得最大值，即  $\theta_{\text{Sb}} = 0.19$  的 Sb/Pt(100)电极对  $\text{CO}_2$  还原具有最高的催化活性；Sb/Pt(110)电极上，r- $\text{CO}_2$  的  $j_p$  和  $Q_{\text{OX}}^{r-\text{CO}_2}$  随  $\theta_{\text{Sb}}$  增加单调递减。与此相反，Sb 在 Pt(111)电极表面吸附显著提高了对  $\text{CO}_2$  还原的催化活性，且 r- $\text{CO}_2$  的  $j_p$  和  $Q_{\text{OX}}^{r-\text{CO}_2}$  均随  $\theta_{\text{Sb}}$  增大线性增加。

4.  $\text{CO}_2$  电催化还原反应机理和活性中心结构。运用原位 FTIR 光谱检测到在 Pt 单晶及 Sb 修饰的 Pt 基础单晶面上  $\text{CO}_2$  的还原吸附态产物均是 CO 物种，主要以线式和桥式两种方式吸附在电极表面。综合 CV 研究结果，提出了 Pt 单晶电极上  $\text{CO}_2$  电催化还原的反应机理，并探讨了  $\text{CO}_2$  与电极表面的相互作用机制，进一步提出阶梯晶面上形成的特殊“椅式”和“船式”立体表面位体现了电催化活性中心的结构特征。

5. 甲酸电氧化对催化活性中心结构的验证。甲酸氧化同样为表面结构敏感的电催化反应。甲酸氧化对 (110) 表面结构的变化更为敏感。同一电极的不同

表面结构对甲酸氧化的性能指出,相对开放的表面结构构成高催化活性的基本要素,但相对有序的表面结构则提供较好的稳定性。与  $\text{CO}_2$  还原研究中获得的规律一致,即阶梯晶面对甲酸氧化的电催化活性并非随其相应的(100)和(110)表面位的密度线性变化,而与表面上“椅式”立体位的密度密切相关,进一步证实阶梯晶面上形成的这种特殊的表面位构成了催化活性中心。

本论文的研究工作在表面原子排列结构层次揭示了催化剂的表面结构与反应性能之间的内在联系规律,提出了电催化活性中心的结构模型,对于发展电催化的基础理论,指导设计和研制高催化活性和高稳定性的电催化剂具有重要意义。

**关键词:** Pt 单晶电极; 电催化;  $\text{CO}_2$ ;  $\text{HCOOH}$ ; 表面结构效应

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## Abstract

Electrochemical reduction of CO<sub>2</sub> is closely related to environment, energy and electrocatalysis. Single crystal electrodes can provide well-defined surface structure of atomic arrangement, which have been used as model electrocatalysts to study the intrinsic structure function relationship of electrocatalysis. The study of electrocatalytic reduction of CO<sub>2</sub> on Pt single crystal electrodes can reveal, on the one hand, the surface processes at a microscopic level, and direct the designing and screening electrocatalysts of high performance, on the other hand.

Three basal planes, Pt(100), Pt(110) and Pt(111), five stepped surfaces, Pt(510), Pt(310), Pt(210), Pt(320) and Pt(991) were prepared in this work. Different treatments were applied to these Pt single crystal electrodes, which lead to produce different surface structure of the same electrode. The surface processes and kinetics of CO<sub>2</sub> reduction on above surfaces, as well as on basal planes modified with irreversibly adsorbed (IRA) Sb adatoms, were investigated. Besides HCOOH oxidation was used as a probe reaction to confirm further the structure effects in electrocatalysis. Cyclic voltammetry, programmed potential step technique and *in situ* FTIR spectroscopy were employed in the study. The main results are summarized below.

1. Surface structure effects in electrocatalytic reduction of CO<sub>2</sub>. It has found that the electrocatalytic reduction of CO<sub>2</sub> depends strongly on Pt surface structure. When the upper limit potential ( $E_u$ ) was 0.75 V (vs SCE), the activity order is ranked Pt(110) > Pt(100) » Pt(111) for the three basal planes; the electrocatalytic property of a stepped surface may be considered as a certain combination of the properties of different surface sites presented on the surface. The oxidation charge of the reduced CO<sub>2</sub> species (r-CO<sub>2</sub>) ( $Q_{OX}^{r-CO_2}$ ) and the coverage of r-CO<sub>2</sub> ( $\theta_{r-CO_2}$ ) on both Pt(hkl)- I , cooled in Ar + H<sub>2</sub>, and Pt(hkl)- II , cooled in air after flame annealing, show the same trend of variation, while the Pt(hkl)- II with a structure that is more open than Pt(hkl)- I is more active than Pt(hkl)- I . When  $E_u$  was raised to 1.25 V, the surface of electrodes has been reconstructed because of oxygen adsorption at high potentials. Such surface reconstruction resulted in the change of electrocatalytic activity of Pt

single crystal electrodes. The difference in electrocatalytic activity towards CO<sub>2</sub> reduction for a given Pt single crystal electrode with different surface structures has been depicted by the quantity  $\frac{\Delta Q}{Q} = \frac{Q_{r-CO_2(1.25V)}^{OX} - Q_{r-CO_2(0.75V)}^{OX}}{Q_{r-CO_2(0.75V)}^{OX}}$ . The largest  $\frac{\Delta Q}{Q}$  was obtained on Pt(111), i.e., the activity of Pt(111) has been augmented the most significant after its reconstruction.  $\frac{\Delta Q}{Q}$  on those Pt single crystal electrodes with a (110)-site density below 50% is positive, illustrating that the activity of corresponding electrodes increased; while  $\frac{\Delta Q}{Q}$  on those electrodes with a (110)-site density over 50% is negative, indicating a loss of activity. The results revealed that the (110) sites with relatively more open structure exhibit a high activity, and the (100) sites with relatively more order structure provide a better stability.

2. The effects of electrode potential and surface structure in CO<sub>2</sub> reduction. it has measured that the maximum average rate ( $\bar{v}^{\max}$ ) of CO<sub>2</sub> reduction on all Pt single crystal electrodes regardless of the surface structure is at around -0.20 V, which implies that the electrode potential has the same effect for CO<sub>2</sub> reduction on the Pt electrode, however, different surface structure can affect significantly the kinetics of this reaction.

3. Surface mechanism of CO<sub>2</sub> reduction. Both the charge of oxidation of directly adsorbed CO in saturation ( $Q_{sat}^{CO}$ ) and the corresponding coverage ( $\theta_{sat}^{CO}$ ) are larger than the oxidation charge of adsorbed product in saturation from CO<sub>2</sub> reduction ( $Q_{sat}^{r-CO_2}$ ) and the corresponding coverage ( $\theta_{sat}^{r-CO_2}$ ), which illustrated that adjacent sites are necessary for assisting the reaction. The electrocatalytic properties of Pt single crystal electrodes were altered by the presence of IRA Sb<sub>ad</sub> on electrodes surface. The activity of Sb/Pt(hkl) is the function of coverage of Sb<sub>ad</sub> ( $\theta_{Sb}$ ). IRA Sb<sub>ad</sub> on Pt(100) and Pt(110) electrodes has decreased the activity of these surfaces. The peak current ( $j_p$ ) and  $Q_{OX}^{r-CO_2}$  of r-CO<sub>2</sub> on Sb/Pt(100) electrode are varied with  $\theta_{Sb}$ , yielding a

volcano-type distribution. The maximum  $j_p$  and  $Q_{OX}^{r-CO_2}$  were measured at  $\theta_{sb} = 0.19$ , indicating that such surface displays the highest activity for this reaction. With the decrease of  $\theta_{sb}$ , the  $j_p$  and the  $Q_{OX}^{r-CO_2}$  of r-CO<sub>2</sub> on Sb/Pt(110) electrode decreased monotonically. However, Sb<sub>ad</sub> on Pt(111) has increased the activity. With the increase of  $\theta_{sb}$ , the  $j_p$  and the  $Q_{OX}^{r-CO_2}$  of r-CO<sub>2</sub> on Sb/Pt(111) electrode increased linearly.

4. Reaction mechanism and active center of CO<sub>2</sub> reduction. The adsorbed products of CO<sub>2</sub> reduction on Pt single crystal electrodes and IRA Sb modified basal planes were determined by *in situ* FTIR spectroscopy as linear- and bridge-bonded CO species. Based on these results, a reaction mechanism of CO<sub>2</sub> reduction on Pt single crystal electrodes was proposed. It has revealed that the active sites on Pt single crystal electrodes for CO<sub>2</sub> reduction consist of “Chair” and “Boat” sites on stepped surface. Such steric sites represent the characters of active centers for this electrocatalytic reaction.

5. Structure of active centers was confirmed by HCOOH oxidation. HCOOH oxidation depends also strongly on Pt surface structure. This reaction was more sensitive to the change of (110) structure and employed to confirm further the active centers. The different surface structure of the same Pt single crystal electrode displayed different reactivity, which showed that relatively open surface structure exhibits a higher performance, but at the same time relatively ordered surface structure provides a better stability. The results are in accordance with those obtained in studies of CO<sub>2</sub> reduction. It has found that the electrocatalytic property of (100) and (110) sites on stepped surfaces do not present a linear relation with the surface density of these sites, but are related to surface density of active sites, i.e., the “Chair” sites. This result further confirmed that the active centers in electrocatalysis are those sites of steric structure as formed on stepped surfaces.

Key words: Pt single crystal electrode; Electrocatalysis; CO<sub>2</sub>; HCOOH; Surface structure effect

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