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硕 士 学 位 论 文

钉钴合金催化剂的制备与氧还原催化活性

Synthesis and Electrocatalytic Activity of Ruthenium Cobalt

Alloys toward Oxygen Reduction Reaction

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## 摘要

质子交换膜燃料电池具有工作温度低、启动快、比功率高等优点，被认为是电动汽车等的首选能源。现有的燃料电池技术需要使用价格昂贵的铂基催化剂，且阴极氧还原反应的过电位较大，严重阻碍了其商业化进程。因此，有必要研究同时具有高氧还原活性和良好稳定性的非铂阴极催化剂。钌基催化剂具有良好的氧还原活性，但钌硒化合物催化剂的稳定性较差，钌用量大，而钌基合金催化剂中钌的用量可调整，但存在氧还原活性较差，合成所用的金属先驱体较昂贵，甚至有毒，难于得到纯相等问题。本论文采用较廉价的金属氯化物为原料，探索浸渍还原法并结合热处理制备高氧还原活性和高稳定性的碳载钌钴（铁）合金催化剂的方法，系统研究了钌/钴比例、催化剂载体、热处理温度及时间对催化剂结构、组成及氧还原活性的影响，深入探讨了不同合成参数下合金化程度、活性位、载体石墨化程度与氧还原催化活性的关系。

结果表明，采用钌/钴摩尔比（Ru/Co）为 2.0，经 400℃ 热处理 2 小时制备得到了结晶良好、六方相的碳纳米管负载钌钴合金催化剂，在酸性介质中的氧还原峰电位（ $E_p$ ）为 0.631 V，氧还原反应电位（ $E_{ORR}$ ）为 0.708 V，转移电子数达到 3.7。经 500 圈循环测试后  $E_{ORR}$  值仅降低了 12 mV，活性和稳定性俱佳。而 Ru/Co=0.5 时得到的催化剂氧还原活性更好， $E_p=0.680$  V， $E_{ORR}=0.736$  V，转移电子数为 4.0，但经 500 圈循环测试后  $E_{ORR}$  值降低了 90 mV，稳定性较差。石墨烯负载的钌钴合金催化剂结晶性较差，同时存在钌单质及钌钴合金相，氧还原活性较差， $E_{ORR}=0.691$  V， $E_p=0.616$  V。

钌/钴比例显著影响钌与钴的合金化过程和载体石墨化程度，进而影响催化剂的活性位。钌钴合金的形成不但有利于减小催化剂的颗粒尺寸，而且可以改变与碳载体的相互作用。钌/钴摩尔比为 2.0 时合金化程度更完全，同时碳纳米管载体的石墨化程度较高，缺陷较少，因此氧还原活性和稳定性均较好；钌/钴摩尔比为 0.5 时催化剂的平均粒径最小，因此氧还原活性最好，但合金化程度不够完全，且碳纳米管载体的石墨化程度较低，缺陷较多，稳定性较差。

将铁取代钴得到碳纳米管负载钌铁纳米颗粒为核壳结构，内核为结晶性好的六方相钌铁合金，外壳为结晶性较差的铁和铁的氧化物，只有去除外壳的铁和铁的氧化物时，内核的钌铁合金催化活性与钌钴合金催化剂持平。

**关键词：**质子交换膜燃料电池；氧还原反应；钌基合金；稳定性

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## Abstract

Proton exchange membrane fuel cell (PEMFC) has been considered to be the preferred energy for electric vehicles due to its advantages of low working temperature, quick startup and high specific power density. Current technology in PEMFC usually requires the use of expensive platinum-based materials as catalysts. Furthermore, a large overpotential resulting from oxygen reduction reaction (ORR) at a cathode has significantly restricted the commercialization of PEMFC. It is, necessary, to investigate non-platinum cathode catalysts that exhibit both high activity and good stability. Ruthenium-based catalysts show good ORR activity, but poor stability was observed with ruthenium selenide compounds which also consume a great amount of ruthenium. Ruthenium-based alloyed catalysts could be prepared with the adjustable ruthenium contents. However, there existed several problems including low ORR activity, the use of expensive and toxic metal precursors, and difficulty to obtain single alloy phases.

This work explored the preparations of high ORR activity and high stability RuCo(Fe) alloyed catalysts using less expensive metal chlorides as precursors by an impregnation reduction method followed by heat treatment. The influences of Ru/Co ratio, supporting material, heat treatment temperature and time on structures, compositions and ORR activities of catalysts were systematically investigated. The relations between alloying degree, ORR active site, degree of graphitization and catalytic activity were studied.

The results demonstrated that the carbon nanotubes (CNTs) supported RuCo catalysts with good crystallinity and pure hexagonal RuCo alloy phase were obtained using the Ru/Co ratio of 2.0, the heat treatment temperature of 400°C and the heat treatment time of 2 h. In an acidic medium, the peak potential ( $E_p$ ) was 0.631 V, the potential corresponded to ORR ( $E_{\text{ORR}}$ ) reached 0.708 V, and the transfer electron number ( $n$ ) was 3.7. After 500 potential cycles, the catalyst degraded only 12 mV in  $E_{\text{ORR}}$ , indicating both good ORR activity and good stability. The CNTs supported RuCo catalysts prepared with Ru/Co=0.5 showed the  $E_p$  of 0.680 V,  $E_{\text{ORR}}$  of 0.736 V and  $n$  of 4.0, suggesting the better ORR activity than that prepared with Ru/Co=2.0. However, the stability was poorer with the degradation of 90 mV in  $E_{\text{ORR}}$  after 500 potential cycles. On the other hand, the graphene supported RuCo catalyst prepared with Ru/Co=2.0 revealed poor crystallinity

and a mixed phase structures consisting of metallic Ru and alloyed RuCo, resulting poorer ORR activity with the  $E_p$  and  $E_{ORR}$  values of 0.616 V and 0.691 V, respectively.

The Ru/Co ratio showed significant impacts on the formation of alloys and the degree of graphitization in support, which ultimately affected the catalytic ORR active site of RuCo catalysts. The formation of RuCo alloy was not only beneficial to reduce the particle size, but also changed the interaction between metals and support. More complete degree of RuCo alloying, higher degree of graphitization and less defect presented in CNTs support were achieved for the RuCo catalyst prepared with Ru/Co=2.0, resulting in both high activity and good stability. The smallest mean particle size was observed for the RuCo catalyst prepared with Ru/Co=0.5, which contributed to the best ORR activity. However, less complete degree in RuCo alloying, lower graphitization and more defect in CNTs led to poorer stability as compared to that prepared with Ru/Co=2.0.

The CNTs-support RuFe catalyst, prepared using the same method as RuCo by substitution of Co with Fe, demonstrated a core-shell structure. The inner core composed of well crystallized and hexagonal RuFe alloy, while the outer shell poorly crystallized iron and iron oxide. When the iron and iron oxide in the shell was removed, the ORR activity associated with the inner RuFe alloy was almost identical to that of RuCo alloyed catalyst.

**Key words:** Proton exchange membrane fuel cell; Oxygen reduction reaction; Ruthenium-based alloy; Stability

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## 第一章 引言

目前对燃料电池研究的关注，主要在于其能量转换效率以及环境友好的特点。燃料电池（Fuel cell）是指将燃料储存的化学能直接转变为电能的原电池装置。质子交换膜燃料电池是燃料电池中的一种，属于低温燃料电池，有望应用于交通运输领域<sup>[1]</sup>。本文研究对象为应用于质子交换膜燃料电池的阴极催化剂。

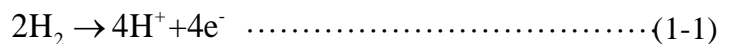
### 1.1 质子交换膜燃料电池概述

#### 1.1.1 组成及原理

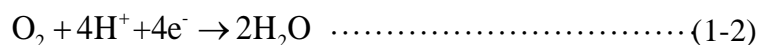
图 1.1-a 为单电池结构示意图，主要由膜电极组（membrane electrode assembly, MEA），表面刻蚀的双极板（流道板）（1 和 9），防漏垫片（2 和 8），集流板和端板组成。作为核心部分的膜电极组为三明治式多层结构，由多个薄层组成，包括最中间的质子交换膜（Teflon membrane）（5），两边的催化剂电极层（catalyst electrodes layer）（4 和 6），以及外侧的气体扩散层（gas diffusion layer）（3 和 7），其结构示意图如图 1.1-b 所示。电化学反应就发生在高聚物电解质膜电极区域内<sup>[2]</sup>。

图 1.2 给出了质子交换膜燃料电池的工作原理，包含多个物理过程，相互关联的非线性传输过程以及电化学反应过程<sup>[3]</sup>：

- （1）氢气和空气分别从阳极和阴极管道加压传送；
- （2）氢气和氧气分别通过多孔的气体扩散层和扩散进彼此的催化层
- （3）氢气在阳极催化层被氧化，生成质子和电子，反应式（1-1）；



- （4）质子在电解质溶液中移动通过质子交换膜；
- （5）电子通过双极板引导流向阳极集流板，随后通过外部循环到达阴极集流板；
- （6）氧气在阴极催化层被还原与质子和电子生成水，反应式（1-2）



- （7）产物水运输从阴极催化脱离，然后通过扩散层，离开膜电池组

(8) 产生的热量通过双极板被带离电池组。热量的产生主要是由于在阴极催化层上发生缓慢的氧还原反应，不必要的热量生成会造成能源效率的降低。

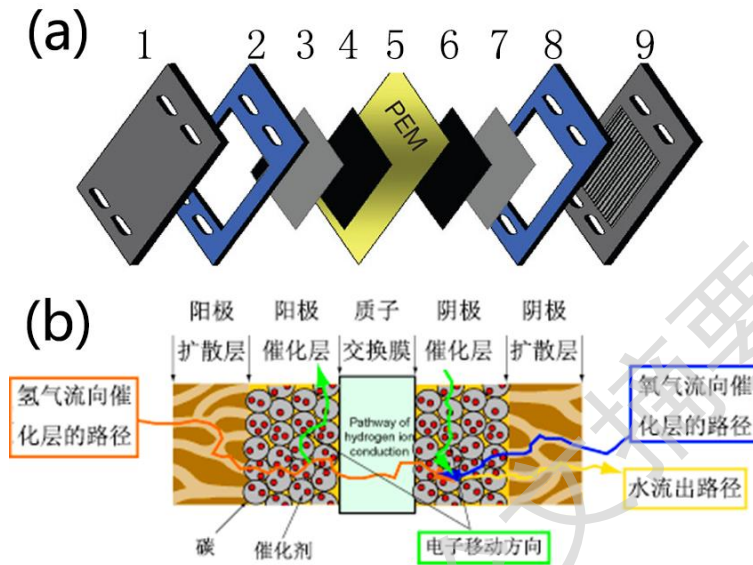


图 1.1 (a) 质子交换膜单电池和 (b) 膜电池组结构示意图  
 Figure 1.1 Schematic diagram of PEMFC (a) and MEA (b)

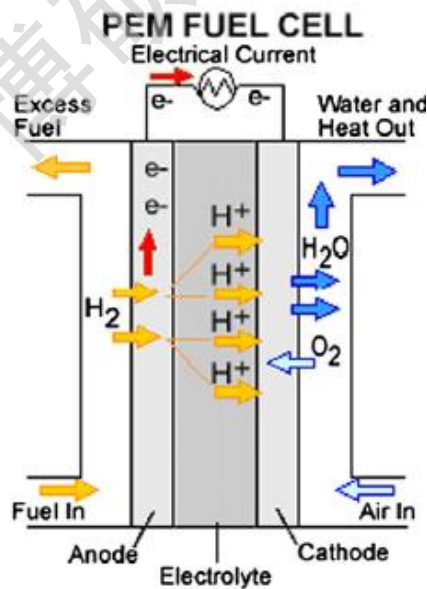


图 1.2 质子交换膜单电池工作原理图  
 Figure 1.2 Operation principle of MEA<sup>[4]</sup>

以上为质子交换膜燃料电池工作原理。另外，因为氢和氧的流道通常垂直于质子通过膜迁移的方向，也垂直于气体在扩散层扩散的方向，所以整个迁移过程是三维方



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