

Highly Stable Pt–Au@Ru/C Catalyst Nanoparticles for Methanol Electro-oxidation

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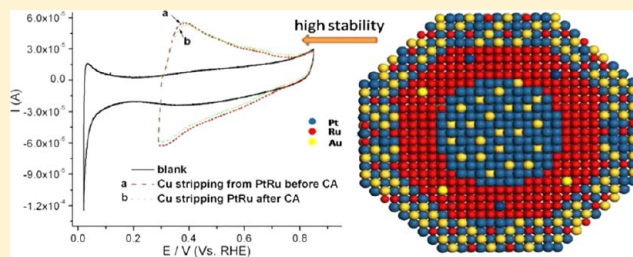
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Supporting Information

ABSTRACT: Among the major obstacles to the successful application of Pt–Ru alloys as anode electrocatalysts for direct methanol fuel cells are their low electrocatalytic activities and poor stability under demanding operating conditions. In particular, detrimental is the eventual dissolution of the more oxophilic Ru. In this work, a novel carbon-supported gold-stabilized Pt–Au@Ru catalyst was synthesized using the water-in-oil microemulsion method. The catalyst possesses an enhanced methanol oxidation activity in acid medium and significantly enhanced stability over a commercially available Pt–Ru/C catalyst (E-TEK, 60%). This work provides a representative example of stabilization of an oxophilic transition element, Ru, using a unique ternary structure with Au. The stabilized surface and bulk composition are determined through copper underpotential deposition, transmission electron microscopy, X-ray diffractometry, and X-ray photoelectron spectroscopy in conjunction with electrochemical measurements. In situ X-ray absorption spectroscopy analysis revealed that the addition of gold in the Pt–Au@Ru/C catalyst enhances the stability of the catalyst chiefly by interacting electronically with the Pt and Ru to raise their oxidation potentials.



1. INTRODUCTION

Despite the problems presently associated with their operation, direct-methanol fuel cells (DMFCs) continue as a high-potential energy source for portable devices and have been the subject of intense research over the last couple of decades.^{1–3} Whereas significant progress has been made on both the membrane and catalyst research fronts, the Pt catalyst efficiency is still largely limited by poisoning with CO, the principal intermediate carbonyl species during methanol oxidation.⁴ The state-of-the-art anode for electro-oxidation of methanol in DMFCs is a Pt–Ru bimetallic catalysts of spatially varying composition because it provides high tolerance to the products of direct methanol oxidation, such as adsorbed aldehydes and CO.⁵

Over the last three decades PtRu bimetallic catalysts have been synthesized in a wide variety of ways with varying initial activities and more importantly stabilities under both operating and startup/shutdown conditions. The latter conditions are perhaps most important due to the introduction of large and mixed potentials in the cell, which can cause the anode to intrude into unstable (for surface Ru) and dangerously high

overpotentials. In general, high initial activity leads to poor stability. Among the methods used to prepare PtRu (1:1 atomic ratio being preferred based on previous reports), the most widely used method is simultaneous deposition of Pt–Ru onto carbon supports (high loading in excess of 60% on C). Typically, a Pt salt (e.g., H₂PtCl₆) and a Ru salt (e.g., RuCl₃) are used to form PtRu clusters on carbon supports, followed by reduction with a variety of reducing agents.^{6,7} Over the years, modifications have been made with regard to precursors with less impurities,^{8,9} supports,^{10,11} solvents,^{12,13} reducing agents,^{14,15} and so on. Finally, a number of advanced synthesis procedures have evolved. Some of these methods, such as the thermal decomposition procedure,¹⁶ the colloid method,^{17–19} the ball-mill mechanochemical method,²⁰ and a few others^{21–23} have the possibility for large scale production.

The wealth of prior literature shows that the CO tolerance exhibited by PtRu catalyst is chiefly attained via a bifunctional

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