



In situ X-ray absorption spectroscopy on probing the enhanced electrochemical activity of ternary PtRu@Pb catalysts



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ABSTRACT

The cumulative synergistic effect generated by the combination of the components is a promising route for developing active ternary catalysts with reduced Pt content. In this article, synthesis, electrochemical property and in situ X-ray absorption spectroscopy (XAS) of a novel ternary catalyst PtRu@Pb/C have been reported. This ternary PtRu@Pb/C catalyst shows tenfold increase in the peak current density for methanol oxidation reaction (MOR) in comparison to the commercial state-of-the-art PtRu catalyst. To understand the mechanistic pathways and plausible reasons behind higher current density of PtRu@Pb, XAS and $\Delta\mu$ analysis in combination with ab initio FEFF8 calculations have been performed. The results reveal the direct evidence of strong charge transfer from lead to platinum shedding the light on this enhanced activity. The electrochemical study in conjunction with the in situ spectroscopy affirms the different role played by Pb and Ru, where ligand mechanism is induced by Pb and the bi-functional mechanism is mostly operated by ruthenium both being responsible in the enhancement of high current density for MOR.

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1. Introduction

Direct oxidation of alcohols remains the Holy Grail for electrochemists for more than four decades of research on this subject. In all these years, PtRu in various forms have remained the electrocatalyst of choice especially for systems in acidic pH scale, particularly those using proton exchange membranes with potential application in fuel cells and direct electrolysis of alcohols. Use of Ru to promote the oxidation of C₁ moieties has been explained by well-accepted mechanism such as bi-functional [1–3] and direct oxidation [4,5]. It has been affirmed that alloying enables modification of electronic and structural property of platinum with direct effects on CO-tolerance [6–8]. The bi-functional mechanism ascribes the oxides and oxy hydroxides formation on the more oxidative metal such as Ru, assisting the oxidative removal of CO bound on the platinum surfaces [3,9,10]. On the other hand, direct mechanism (enabled by the ligand effect), emphasizes that alloying metal modifies the electronic structure of the Pt, thus weakens Pt–CO bond and enhances the easy removal of CO [11,12,13]. In particular, Hammer et al. establishes a strong correlation between the CO chemisorption energy and the d-band nature of the surface by

developing a two-level model describing the coupling of the CO 5 σ and 2 π^* states to the metal d valence states [11,14]. Thus the representative d-band properties such as d-band center, d-band width, or d-band filling can be used to evaluate the metal–CO bond strength. Hence, while designing a platinum-based catalyst, ability to modify the d-band properties of platinum becomes an important consideration.

Here we report a novel ternary PtRu@Pb catalyst which combines the strong bi-functional property of PtRu with the ligand effect induced by a third metal Pb. Addition of Pb to Pt have been studied in the context of oxidation of small organic molecules, most of which have focused on formic acid [7,15] with relatively few regarding alcohols [15–17]. The large difference of work function between Pb and Pt promotes charge transfer from former to later [18] resulting in the enhancement of catalytic activity (e.g. dramatic increment of formic acid oxidation in under potentially deposited (UPD) Pb adatoms on Pt surface [19,20]). The density functional theory studies on intermetallic PtPb alloys suggests that shift in d-band center of Pt to lower energy due to the upward shift of Fermi level because of the presence of *sp* electrons from Pb [21]. Thus, both experimental and theoretical calculation indicates Pb as a suitable alloying component for Pt-based electrocatalysts. However, the instability of Pb at higher cycling potential and subsequent dissolution of Pb from intermetallic alloys is highly detrimental for overall fuel cell performance [22,23].

For the optimization and stability of the catalysts, the controlled composition and effective alloying of Pb-based catalysts should be

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