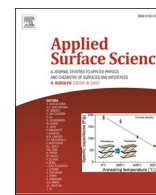




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Applied Surface Science

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## Full Length Article

First principles study of Ir<sub>3</sub>Ru, IrRu and IrRu<sub>3</sub> catalysts for hydrogen oxidation reaction: Effect of surface modification and ruthenium contentJeffrey Roshan De Lile<sup>a,1,\*</sup>, Ashkan Bahadoran<sup>b,1</sup>, Qinglei Liu<sup>b,\*</sup>, Seung Woo Lee<sup>c</sup>, Chanhoo Pak<sup>c</sup>, Jiujun Zhang<sup>d</sup>, Seung Geol Lee<sup>a,e,\*</sup><sup>a</sup> Department of Organic Material Science and Engineering, Pusan National University, 2, Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 26241, South Korea<sup>b</sup> State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China<sup>c</sup> Graduate Program of Energy Technology, School of Integrated Technology, Institute of Integrated Technology, Gwangju Institute of Science and Technology, Gwangju 61005, South Korea<sup>d</sup> Institute for Sustainable Energy/College of Sciences, Shanghai University, Shanghai 200444, China<sup>e</sup> School of Chemical Engineering, Pusan National University 2, Busandaehak-ro 63beon-gil, Geumjeong-gu, Busan 26241, South Korea

## ARTICLE INFO

## Keywords:

DFT calculation  
Ruthenium-Iridium  
Alloy catalyst  
Core-shell catalyst  
Segregation  
Hydrogen oxidation  
Fuel cell

## ABSTRACT

The catalysis of hydrogen oxidation reaction (HOR) at the anode is one of the most important topics in achieving high-performance proton exchange membrane fuel cells, especially in the presence of hydrogen fuel impurities and during the start-up/shutdown cycling and cell reversal. To improve catalytic HOR performance, Iridium-Ruthenium alloy (IrRu) catalysts have been explored to address the issues. For fundamental understanding of the catalytic HOR activities, this paper employs density functional theory (DFT) calculations to elucidate and interpret the surface modifications and Ru content effect on hydrogen adsorption energy of the IrRu alloys. The catalytic HOR activity trend of the alloyed IrRu catalysts is calculated to be Ir<sub>3</sub>Ru > IrRu > IrRu<sub>3</sub>, which is opposite to that experimentally observed. However, if the surface enrichment of Ir atoms on the IrRu surfaces to form core-shell type catalysts, the calculated trend becomes to IrRu<sub>3</sub> > IrRu > Ir<sub>3</sub>Ru, which is in agreement with the experiment result. In spite of higher surface energy on IrRu<sub>3</sub> core-shell surface, the compelling d-band downshift can attribute to the surface charge depletion, decreasing hydrogen adsorption energy, and resulting in the highest catalytic activity. For Ir<sub>3</sub>Ru core-shell catalyst, a relatively higher charge accumulation on the surface Ir is observed, which can up-shift the d-band and increase hydrogen adsorption, resulting the lowest catalytic activity. The IrRu catalyst has intermediate d-band downshift and hydrogen adsorption energy so that its catalytic activity remains between IrRu<sub>3</sub> and Ir<sub>3</sub>Ru for both alloyed and core-shell structures.

## 1. Introduction

Proton exchange membrane (PEM) fuel cells fed by hydrogen and air (oxygen) have been recognized as one of the most practical energy conversion devices particularly for electric vehicle applications due to their high energy/power densities, high energy conversion efficiency and zero emission [1,2]. In PEM fuel cells, two necessary electrocatalytic reactions are hydrogen oxidation reaction (HOR) at anode and oxygen reduction reaction (ORR) at cathode. The anode HOR can produce protons and electrons. The protons then migrate through PEM and the

electrons travel through an external circuit eventually combines with oxygen at the cathode to produce water (the whole reaction is: O<sub>2</sub> + 2H<sub>2</sub> → H<sub>2</sub>O). Due to the slow kinetics of both HOR and ORR, electrocatalysts are needed on the anode and cathode to catalyze the reactions to practical rates. Normally, the anode consists of carbon supported Platinum-Ruthenium alloy (PtRu) [3,4]. The main purpose of Pt alloying with Ru is to improve the anode tolerance to hydrogen fuel impurities such as carbon monoxide [3,5]. However, there are some drawbacks associate with PtRu catalysts, such as high-cost of Pt, less tolerance to start-up/shutdown cycles and cell reversal, specifically when PEM fuel cells are

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