Pt Alloys as Electrocatalysts for Ammonia Oxidation Reaction

by

Chan Yat Tung

Date: 4 September 2019 (Wednesday)
Time: 14:00
Venue: Room 4472 (Lift 25-26)

Examination Committee:
Prof. Qing CHEN, Chairman
Prof. Minhua SHAO, Supervisor
Prof. Ping GAO

Abstract

Ammonia is a carbon free chemical energy source with hydrogen storage capacity of 17.7 wt% and energy density of 3000 W h/kg which is much higher than other small organic molecular fuels such as methanol. Meanwhile, its theoretical oxidation charge (4.75 Ah/g) is comparable with the electro-oxidation charge of methanol to CO₂ (5.01 Ah/g). Therefore, ammonia is a promising fuel candidate and has been successfully used in an alkaline fuel cell by directly feeding ammonia. However, the current technology of catalysts is inadequate to ensure large scale and commercial application of ammonia electro-oxidation reaction (AOR) from cost and performance points of view. Though Pt is expensive, it is the most active one for improving AOR kinetics. However, the high cost and scarcity of Pt hinder its wide application. Alloying Pt with other transition metals having comparable performance to Pt is promising to address the cost issue.

In this study, Pt-3d transition metal (Fe, Co, Ni, Zn) nanocubes were synthesized and the effects of addition of 3d transition metal to Pt were studied. It was found that the addition of Zn element can enhance the AOR activity on account of following reasons: (1) Eletrodissolution of Zn atoms. (2) Zn content could act as a promoting center for the generation of Zn-OH species thus resulting in more Pt sites being available for ammonia oxidation. (3) The negative shifted binding energy of Pt decreased the oxophilicity of Pt-Zn/C and strengthened the chemisorption of active intermediate NH₂. Furthermore, the addition of Fe, Co and Ni caused a decrease in AOR activity due to: (1) Increase of competitive adsorption of hydrogen against ammonia. (2) Increase of oxophilicity lead to more competitive adsorption of hydroxyl group against ammonia. (3) High activation energy barrier and binding strength of N for nickel and cobalt according to literature DFT calculations.