V.G.1 Structure and Function in Electrocatalysis of Reactions for Direct Energy Conversion

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Program Scope

We conduct studies of Pt monolayer electrocatalysts, and related core-shell catalysts for reactions of direct energy conversion including the O_2 reduction and O_2 evolution reactions, oxidation of ethanol and methanol, H_2 oxidation and evolution and CO_2 reduction. We aim at increasing our understanding of their kinetics and synthesizing ultimately low Pt content electrocatalysts with high activity and good stability. The results of some of our recent studies are highlighted below.

FY 2016 Highlights

Oxygen Evolution Reaction Mechanism and Enhanced Activity of the RuO_2@IrO_2 Core-Shell Nanocatalysts

Iridium dioxide is the gold standard for oxygen evolution reaction (OER) in proton exchange membrane water electrolyzers (PEMWE). However, iridium's low abundance restricts the application of PEMWE in carbon-free hydrogen production using solar- and wind-generated electricity. To maximize the performance of IrO_2-based catalysts we developed a facile synthesis method to prepare RuO_2@IrO_2 core-shell nanocatalysts, which has the specific activity RuO_2@IrO_2 for the OER is three-fold that of IrO_2. To further enhance activity, we studied the OER mechanism. There are controversial views on the reaction pathway and rate-determining-step, making rational design of advanced OER catalysts difficult. While it is generally agreed that the dominant pathway for hydrogen evolution involves the Tafel reaction that combines two adsorbed H in forming H_2, the OER pathways with the O-O bond formed from two adsorbed oxygen species are challenged by the density functional theory (DFT) studies suggesting that the activation barrier is lower with addition of a second O to an adsorbed one via sequential water dissociative adsorption on the O-adsorbed site. We resolved the controversy by fitting measured polarization curves for the RuO_2, RuO_2@IrO_2, and IrO_2 catalysts using a two-step kinetic equation for sequential water dissociation with adsorbed O as the major OER intermediate. Differing from the previous DFT predictions, we found the major role of free energy of O adsorption in determining the OER activity, and concluded that the rate-determining step on IrO_2 is the formation of O adsorbed phase, while the OOH formation limits the reaction rate on RuO_2. The new insight suggests that a more suitable oxide core should slightly strengthening the O-adsorption on the IrO_2 shell's for enhancing the OER activity, which will guide our future studies in developing highly active and low cost OER catalysts.

Elucidating Hydrogen Oxidation/Evolution Kinetics in Alkaline and Acid Solutions

Hydrogen oxidation and evolution reactions on Pt in acid are facile processes, while in alkaline electrolytes they are two orders of magnitude slower. This behavior is not understood. Thus, increasing the understanding of different kinetics and developing catalysts that are more active than Pt for these two reactions is important for advancing the performance of anion-exchange-membrane fuel cells and water electrolyzers. We found a four-fold enhancement in Pt mass activity for single crystalline Ru@Pt core-shell nanoparticles with two-monolayer-thick Pt shells, which doubles the activity on Pt-Ru alloy nanocatalysts. For Pt specific activity, the 2- and 1-monolayer-thick Pt shells, respectively, exhibited an enhancement factor of 3.1 and 2.3 compared to the Pt nanocatalysts in base, differing considerably from the values of 1 and 0.4 in acid. To explain such behavior and the orders-of-magnitude difference in activity in acid and base, we performed kinetic analyses of polarization curves over a wide range of potential, from -250 mV to 250 mV using the dual-pathway kinetic equation. From acid to base, the activation free energies increase the most for the Volmer reaction, resulting in a switch of the rate-determining step from the Tafel- to the Volmer-reaction, and a shift to a weaker optimal hydrogen-binding energy. The much higher activation barrier for the Volmer reaction in base than in acid is ascribed to one or both of the two catalyst-insensitive factors, slower transport of OH^- than H^+, and a stronger O-H bond in water molecules (HO-H) than in hydrated protons (H_2O-H^+).

Enhancing Oxidation Kinetics of Methanol and the C-C Bond Splitting in Ethanol on Pt Monolayer Under Tensile Strain

We demonstrated that the Pt monolayer under tensile strain on Au substrates has a highly enhanced activity for methanol and ethanol oxidation. In methanol oxidation formation of CO is precluded, while in oxidation of ethanol the C-C bond splitting facilitate enhanced activity [1]. The activity of Pt_{ML}/Au can be further improved by incorporating active co-catalysts, and the Ru/Pt_{ML}/Au/C and $RhSnO_2/Pt_{ML}$/Au/C electrocatalysts were designed and synthesized for practical application in a direct alcohol fuel cell. In situ infrared spectroscopy studies with single-crystal- and nanoparticle-based catalysts showed no adsorbed CO band (~2,090 cm^{-1}) in methanol oxidation, which proceeded to CO_2 This observation was in agreement with theoretical prediction by DFT calculation. Moreover, the addition of Ru co-catalyst in Ru/Pt_{ML}/Au/C successfully moved onset of CO_2 band (~2,343 cm^{-1}) to around 0.3 V vs. reference hydrogen electrode. During ethanol oxidation on Pt_{ML}/Au(111), the absence of both the CO_{ads} and CO_2 bands suggested that ethanol dissociative adsorption did not occur and that the reaction followed partial oxidation pathway without cleavage of the C−C bond. However, the splitting of C-C bond was observed on nanoparticles Pt_{ML}/Au/C and $RhSO_2/Pt_{ML}$/Au/C catalysts, as evidenced by the CO_2 band. Future work is needed to explain the difference and to further optimize these catalysts.

References

1. Li, M.; Liu, P.; Adzic, R.R., J. Phys. Chem. Lett. 3, 3480−3485. 2012.