

Modeling Mono- and Bi-functional Alkaline Electrocatalysts for Hydrogen Oxidation and Evolution Reactions on the Basis of First-Principles Calculations

ZhenHua Zeng, Jeff Greeley

School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

zheng@purdue.edu, jgreeley@purdue.edu

There has been increasing interest in the development of efficient electrocatalysts for alkaline environments. Among other advantages, non-precious metal catalysts have sufficient stability to be used in alkaline media, leading to lower system costs than acid devices. However, using Mono-functional catalysts, e.g. Pt, alkaline systems have often suffered from lower activity than corresponding acid-based systems. Recently, it has been shown that bi-functional Ni-(hydr)oxide/Pt(111) electrocatalysts manifest activities that approach those of acidic fuel cells. In spite of the promising properties of these and related systems, however, the atomic-scale details underlying their operation remain largely unknown, and the present study focuses on using atomistic computational techniques to elucidate these atomic-scale phenomena.

In this talk, we describe a combined thermodynamic and Density Functional Theory (DFT+U+vdW) analysis of oxidation/reduction of transition metal (hydr)oxides deposited on precious metal electrocatalyst surfaces. We show how this formalism can be used to develop Pourbaix diagrams and surface phase diagrams of thin (1-2 ML) Ni (hydr)oxide films/islands deposited on close-packed Pt substrates. We then extend these models to describe three-phase boundaries between the films, the Pt substrate, and the surrounding electrolyte, and we study the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) in alkaline media at these interfaces. We find that a few partially hydrated-Ni/Pt edges are the most likely candidates for the active phases. In the hydrogen oxidation region, there is a high coverage of OH adsorbed at the edges, while in the hydrogen evolution region there are enough vacancies to accommodate H₂O adsorption and dissociation. Kinetic analysis confirms that OH-H association and H₂O dissociation are promoted at these interfaces, in comparison to mono-functional Pt catalysts. We close with a discussion of the potential for further improvement of this and related bi-functional electrocatalysts in alkaline environments.

References

1. "Enhancing Hydrogen Evolution Activity in Water Splitting by Tailoring Li+-Ni(OH)₂-Pt Interfaces" R.Subbaraman, D.Tripkovic, D.Strmcnik, KC Chang, M.Uchimura, A. P. Paulikas, V.Stamenkovic, N, M. Markovic, *Science* 334 (2011) 1256
2. "Trends in activity for the water electrolyser reactions on 3d M(Ni,Co,Fe,Mn) hydr(oxy)oxide catalysts" R. Subbaraman, D. Tripkovic, K. Chang, D. Strmcnik, A.Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic, and N. Markovic. *Nature Materials* **11**(2012) 550.