First principles studies of stability and reactivity of bifunctional electrocatalysts

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It has long been known that degradation of electrocatalysts presents a significant impediment to the widespread deployment of these materials in fuel cells and electrolyzers. While such phenomena have been extensively analyzed using a variety of experimental techniques, an atomistic understanding of many physical and chemical aspects of degradation is lacking. First principles electronic structure calculations, in turn, are well positioned to provide such atomic-scale insights into these technologically critical processes.

In this talk, we describe a combined thermodynamic and Density Functional Theory (DFT) analysis of oxidation and dissolution of metal and alloy electrocatalyst surfaces. We describe how this formalism may be used to describe the effects of local structure and composition on surface oxidation and dissolution, and we develop Pourbaix diagrams of the surface structure of Pt-based binary alloys, which we in turn use to describe the formation process of the well-known Pt-skin and Pt-skeleton alloys for Oxygen Reduction Reaction catalysis. We subsequently show how the method may be extended to generate surface phase diagrams of bifunctional catalysts with thin (1-2 ML) oxy/hydroxide islands deposited on close-packed Pt and Au substrates. We close with a mechanistic analysis of the fascinating bifunctional electrocatalytic processes that occur, in alkaline solutions, at the three-phase interfaces of these oxy/hydroxide islands, the metal substrates, and the surrounding electrolytes.

1. Reference: “Designing 3d-M(Ni,Co,Fe,Mn)-hydr(oxy)oxide catalysts for the water electrolyzer reactions by tuning OH---Mn+ energetics.” 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.