

The departments of Chemical Engineering, Chemistry & Biochemistry, and the Partnership for International Research in Electron Chemistry and Catalysis at Interfaces are pleased to announce a

SPECIAL SEMINAR

Fe-promoted NiO based oxygen evolution electrocatalysts

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Oxygen evolution is an enabling technology in the fields of catalysis, separations and energy conversion. In many (photo)electrochemical reactions, e.g. photosynthesis, hydrogen production by water splitting or CO₂ reduction to fuels, oxygen evolution from the oxidation of water occurs at the anode, and it limits the efficiency of the process. The challenges in efficiently converting water to oxygen lie in the multistep mechanism requiring four electron transfer steps, and in the highly oxidizing electrochemical potentials required to drive the reaction; many materials are simply not stable under the reaction conditions. Transition metal oxides are commonly used as oxygen evolution electrocatalysts. Decades of research have developed concepts of oxide reactivity in the form of volcano plots using bulk reactivity principles. However, due to limitations of available data, and the limited relevance of bulk data to the electrochemical reaction conditions occurring at surfaces these approaches are not easily extended to multicomponent or mixed metal oxide materials. Furthermore, it remains unclear whether better materials can still be found or how to find them.

We will show how that mixed metal oxides can have superior activity compared to the parent metals. We illustrate the principle through mixed iron/nickel oxides. We observed a significant increase in the electrocatalytic oxygen evolution activity for the mixed metal oxide at approximately 10% iron compared to either of the parent oxide materials. We found clear evidence that spinel phases form that likely are responsible for the enhanced oxygen evolution rates. X-ray diffraction and Raman spectroscopy clearly showed the existence of spinel phases, and in situ electrochemical EXAFS suggests that Fe atoms are directly involved in the oxygen evolution reaction. Temperature programmed reaction spectroscopy indicate that the Fe-promoted NiO catalysts are superior oxidation catalysts for methanol, and that addition of Fe increases the number of basic sites on the oxide surface.

Finally, we will present a generalized mechanism of the oxygen evolution reaction. We have used density functional theory to compute the reaction energies for each step in the mechanism on a class of metal oxides. In conjunction with complementary data from collaborators, we showed there are systematic correlations between the reaction energies of each step in the mechanism on all of the oxide materials examined. These correlations suggest an upper bound on the activity of oxide-based electrocatalysts that is far from the ideal electrocatalyst. Furthermore, we showed that the rate determining step in the oxygen evolution mechanism is determined by the difference in two reaction energies, leading to the volcano in activity observed experimentally.