

# **Developing solid-state electrocatalysts based on design principles from nature: The oxidation of water and the reduction of CO<sub>2</sub> to fuels**

## **Investigators**

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## **Abstract**

This project involves the exploration of promising catalyst materials for two energy conversion reactions of interest, the electrochemical reduction of CO<sub>2</sub> and the electro-oxidation of water. If effective catalyst materials can be developed for both reactions, an efficient energy storage device based on liquid fuels could potentially be coupled to intermittent renewable energy sources such as wind or solar. This project recently commenced in January 2010 and Jaramillo and Nørskov have been coupling experimental and theoretical methods in order to tackle challenges involving catalyst development for these reactions.

## **Future Plans**

Experimental work has recently begun. Here, we outline our plans for the initial stages of the project:

- Study small-cluster Fe-Ni-S mimics of the active center of carbon monoxide dehydrogenase (CODH) for the CO<sub>2</sub>-reduction reaction.
  - We have already obtained Fe-Ni-S cubane clusters from Prof. Ed Solomon (Chemistry) who generously shared some of his chemical inventory with us.
  - We will deposit these small-molecule mimics of the CODH active center onto HOPG supports, aiming for sub-monolayer coverage.
  - We will image the supported clusters by scanning tunneling microscopy (STM) in order to quantify their coverage and to ensure that the cubanes remain apart (i.e. no sintering)
  - We will establish their stability in different solvents, aqueous and non-aqueous.
  - We will measure catalytic properties in optimal electrolytes.
  
- Study thin films of Fe-Ni-S for the CO<sub>2</sub>-reduction reaction.
  - We have begun to synthesize thin films of Fe-Ni-S onto inert, electrically conductive supports.
  - We will gain control of film stoichiometry and morphology by controlling electro-deposition parameters.
  - We will prepare different crystal structures through selective heat treatments
  - We will examine crystal structure and stoichiometry by X-Ray Diffraction and X-Ray Photoelectron Spectroscopy
  - We will measure catalytic properties of these targeted surfaces and structures and correlate activity and selectivity to structure and composition.

- Study metal oxide surfaces for water electro-oxidation (oxygen evolution).
  - We will focus first on RuO<sub>2</sub> as this material is known to be the best catalyst for this reaction.
  - We will prepare nanostructured thin films of RuO<sub>2</sub> by surfactant templating.
  - We will measure surface and catalytic properties and aim to understand how the geometric and electronic effects of the nanostructure impact catalyst activity.

The theoretical work on the project will start this summer when Jens Nørskov joins Stanford. An experienced and very talented postdoc, Lars Grabow, will start September 1st and we expect that progress will be fast. This is particularly so because we have already started exploring both the oxygen reduction reaction and the CO<sub>2</sub> reduction reaction theoretically based on funding from the Danish Ministry of Research through the "Catalysis for Sustainable Energy" initiative at the Technical University of Denmark. Two projects will be initiated this summer:

- Studies of water splitting on oxides.
  - We will choose rutile oxides, eg. RuO<sub>2</sub>, TiO<sub>2</sub>, IrO<sub>2</sub>, as the starting point and study the structure-dependence of the free energy of the intermediates.
  - We wish in this way to establish the optimum structure for this process as a complement to the experimental studies in the Jaramillo group on similar systems.
- Studies of CO<sub>2</sub> reduction over metals and metal sulfides.
  - Cu is the only known catalyst for the electrochemical reduction of CO<sub>2</sub> to form hydrocarbons. By studying the reaction over a stepped Cu(211) surface we have established the reaction mechanism and an understanding of the origin of the large overpotential observed experimentally. We will study how these parameters depend on the structure of the Cu surface. We wish in this way to contribute to establishing the parameters determining the catalytic activity for this process.
  - We will continue this work by looking at transition metal sulfides as CO<sub>2</sub> reduction catalysts. We will start by establishing the reaction mechanism for the reaction at the reactive edges of finite size MoS<sub>2</sub> and depending on the results will move to other sulfide surfaces.

We are excited to have commenced this GCEP project and we look forward to obtaining results which will be communicated in the form of scientific articles, future GCEP reports, and presented at technical meetings including GCEP conferences.

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