

# Electrocatalytic water oxidation to dioxygen in molecular Pd<sup>II/IV</sup> coordination environment.

## Investigators

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## Abstract

A new mechanistic approach to electrocatalytic water oxidation based on well-defined coordination complexes of Pd<sup>II-IV</sup> was designed. Its experimental studies to date included the development of a robust quantitative dioxygen assay suitable for screening target Pd complexes for catalytic activity in water oxidation.

## Introduction

Storage of photogenerated electricity in high energy-density renewable chemical fuels remains a critical stepping stone to large-scale transition to solar-based power in the low greenhouse gas future. Deployment of dihydrogen-based energy carriers, whose use is based on oxidation with atmospheric dioxygen, derives from the only renewable solar energy storage mechanism – natural photosynthesis – proven on the timescale and in volume relevant to those of the global energy needs. As in natural photosynthesis, *sustainable* production of anthropogenic dihydrogen-based solar fuels is only feasible from water, accompanied by formation of dioxygen. However, electrocatalytic oxidation of water to dioxygen is a long-standing catalysis problem that continues to undermine large-scale viability of photoelectrochemical storage of solar energy.

This research project aimed to explore a new mechanistic approach to electrocatalytic water oxidation based on well-defined coordination complexes of Pd<sup>II-IV</sup>. The proposed studies were designed to test the feasibility of key elementary steps of the proposed reaction mechanism and ultimately provide the foundation necessary for systematic improvement of water oxidation catalysis efficiency by design.

## Results

The work on the project was limited to the period from September through December 2008. During this time we developed a quantitative chemical assay for dioxygen suitable for screening candidate Pd complexes for catalytic activity in water oxidation. The assay is based on passive diffusion of dioxygen from the headspace of the reaction vessel to solid Mn<sup>II</sup>(OH)<sub>2</sub> kept under partial vacuum at 150°C for over 3 hrs. Quantity of dioxygen extracted from the reaction vessel (~0.1 mmol) is determined by iodometric titration of the oxidized Mn<sup>II</sup>(OH)<sub>2</sub>. Once fully validated, we expect this assay to amount to a robust, inexpensive and instrument-free method for dioxygen quantification applicable to various conditions of generation.

## Progress

The work completed during the active phase of the project produced auxiliary experimental knowledge that will facilitate future detailed reactivity studies of coordination complexes of Pd<sup>II-IV</sup> in the context of the original proposal goals. The main project hypotheses have yet to be tested and remain promising.

**Publications**

No publications resulted from this work as of yet.

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