ENERGY STORAGE ON THE CHEAP: HOMOGENEOUS CATALYSTS FOR WATER OXIDATION

Reported by Seth Ensign October 28, 2013

INTRODUCTION

Although current fossil fuel reserves can meet global energy requirements for several centuries, the release of CO_2 from their consumption would have a *devastating* impact on the climate.[1,2] As such, renewable means of energy production are of great interest. Alternative energy sources often operate intermittently so efficient energy storage is essential to the expanded utilization of renewable energy sources. The catalytic oxidation and reduction of water, with earth-abundant metal-catalysts, would allow for climate stability in the coming centuries. This process is summarized in equations 1-3.

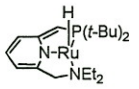
$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad E = -1.23\ V + 0.059\ (pH) \qquad (1)$$

$$4H^+ + 4e^- \leftrightarrow 2H_2 \qquad E = 0\ V - 0.059\ (pH) \qquad (2)$$

$$2H_2O \rightarrow 2H_2 + O_2 \qquad E = -1.23\ V \qquad (3)$$

WATER ELECTROLYSIS IN A TWO-PART SYSTEM

The first approach to water activation via hydrogen and oxygen evolution involves both an anode and cathode. Dividing water oxidation (Equation 1) and water reduction (Equation 2) into separate half-reactions allows for the design of different metal complexes that need to efficiently catalyze only one half-reaction. While metal complexes, such as **1**, have been shown capable of both oxygen and hydrogen evolution (Equation 3,) superstoichiometric amounts are required.[3]



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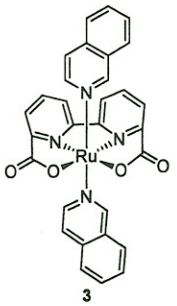
HOMOGENEOUS WATER OXIDATION

Water oxidation (Equation 2) is a challenging half reaction as it involves a four electron process and high energy intermediates. To avoid these intermediates, mechanistic steps for catalysts often involve proton coupled electron transfer to avoid charge buildup. Initial investigations in this field led to the "blue dimer," **2**, or $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{III}(H_2O(bpy)_2]^{4+}$.[4] While this complex was the only molecular catalyst capable of catalytic water oxidation for a great deal of time, it was limited by both low activity and rapid degredation.[5] Decades of improvement on this system has led to work by Sun *et al.*



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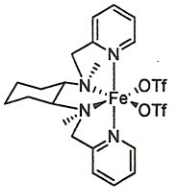

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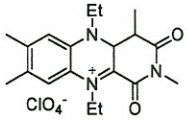

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which produced a water oxidation catalyst **3** that functions extremely quickly-at a rate comparable to Photosystem II.[6] However, ruthenium is a rare and costly metal. In contrast, water oxidation catalyst **4** published by Costas *et al.* has lower activity but utilizes iron as an abundant, low cost metal center.[7] Also of interest, the first report of organocatalytic water oxidation features flavin derivative **5.** While this complex is not efficient in is activity, it represents a novel alternative to metal complexes using earth-abundant carbon.[8] Despite the fact that there has been less research dedicated towards the optimization of both iron and simple organic molecules as for ruthenium, these fields remain promising areas of growth. Unfortunately, the limitations of traditional homogeneous catalysts is their ligands: catalytic activity is often rapidly lost under oxidizing conditions.

HETEROGENEOUS WATER OXIDATION AND POLYOXOMETALATES

Heterogeneous water oxidation catalysts, notably work that utilizes CoO_x thin films, represent a promising development.[9,10] While these complexes lack the activity of homogeneous catalysts and have proved demanding to study, these catalysts are noted for their durability, facile construction, and ease of use.[11,12] Similarly, polyoxometalate (POM) catalysts incorporate reactivity centers typically associated with heterogeneous catalysts and may serve as model systems for study. As stand-alone water oxidation catalysts, these complexes are self-assembled, carbon-free, durable, active, and are readily accessible from earth-abundant metals.[12–14]

SUMMARY

The electrocatalytic oxidation of water offers an efficient means of energy storage. Recent advances in this field have increased both the longevity of homogeneous catalysts and the reactivity of heterogeneous catalysts.

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