

Photoelectrochemical Synthesis: Beyond Grätzel Cells

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Literature Seminar

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The exponential rise in energy demand and the environmental effects of using fossil fuels as civilization's primary energy source necessitate a shift towards more environmentally benign energy sources.^{1,2} All feasible energy options should be explored, but only solar energy promises both the near-term efficacy and long-term energy ceiling to presently slow the accumulation of atmospheric carbon dioxide and eventually bring anthropogenic carbon dioxide generation to a level which can be offset by natural processes.^{1,2}

The power of incident light at the Earth's surface is several thousand times greater than the rate of mankind's energy consumption.³ However, that energy must be converted to electricity or stored as a fuel before it can be used to satisfy societal needs. Solar energy can currently be converted to neither fuel nor electricity in a fashion which is competitive with fossil fuels. In order for either process to supplant hydrocarbons as the most economically practical energy source, a decrease in cost and/or increase in efficiency must be realized such that the final cost of solar-derived energy is decreased by an order of magnitude.¹ Grätzel cells, also referred to as dye-sensitized solar cells, have emerged as strong candidates to fulfill this goal due to their low cost and in spite of concerns regarding efficiency and stability.⁴⁻⁶

However, even if Grätzel cells become economically competitive with fossil fuels, they will still be incapable of providing energy with the consistency society demands due to both predictable and unpredictable localized shortages in solar flux. Thus, even in the most optimistic future, the Grätzel cell would need to be coupled to another device or replaced by a cell which utilizes light directly to create fuel. In order for solar energy to become society's primary energy source a means of storage must be devised which can be deployed on the scale of our energy economy while remaining cheap and efficient.⁷ Of the myriad of options for storing solar energy the two most promising are thermal and chemical storage.¹ While thermal storage appears feasible, this seminar will focus on the more chemically interesting possibility of using sunlight to create fuel.

Methods for storing solar-derived energy in chemical bonds can be divided into two classes: those which directly utilize light to drive uphill chemical reactions, and those which use electricity as an intermediate.⁸ Recently there have been numerous advances in both electrochemical^{9,11} and photoelectrochemical¹⁰⁻¹² syntheses of fuels primarily focused on conversion of water into hydrogen gas and oxygen gas, with the latter being the more challenging target. One of the most promising recent examples of water oxidation to

dioxygen is the report of a new class of water oxidation catalysts: cyclometalated iridium(III) aquo complexes as shown in Figure 1.

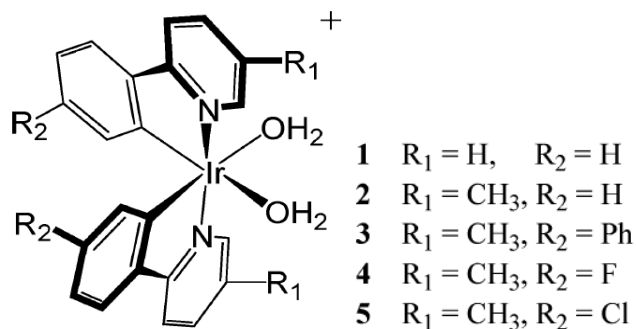


Figure 1: Cyclometalated iridium(III) aquo complexes have recently been found to catalyze water oxidation.¹²

These compounds have been shown to oxidize water to dioxygen in the presence of cerium(IV), which acts as a surrogate for a photosensitizer. This reaction utilizes the cerium(IV) at 66% efficiency and boasts turnover numbers from 2270 to 2760.¹² While iridium is prohibitively expensive, these compounds are still important catalysts primarily for two reasons. First, they are the first non-ruthenium catalysts for photochemical water oxidation to dioxygen which have a known structure. This suggests that other metals are most likely capable of performing this reaction given an appropriate selection of ligands. Second, their stability and ease of modification is amenable to kinetic and mechanistic studies which may provide insight regarding how catalyst and system design can be optimized for water oxidation.^{11,12}

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