2018

Water Oxidation: Replicating the Power of Photosynthesis

Flora Denton
Parkland College

Recommended Citation

Denton, Flora, "Water Oxidation: Replicating the Power of Photosynthesis" (2018). *Natural Sciences Poster Sessions*. 139.
https://spark.parkland.edu/nsps/139

WATER OXIDATION

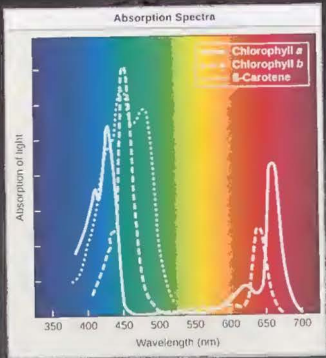
Replicating the Power of Photosynthesis

Photosynthesis: the Basics

Oxygenic photosynthesis (often referenced as simply 'photosynthesis', although there is an anoxygenic process in certain organisms) is well known as the method by which plants, green algae, and certain bacteria create their own food from water, carbon dioxide, and energy absorbed from the sun's rays. The net equation can be summarized as:

$$6CO_2 + 12H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O.$$

The products of the reaction are glucose ($C_6H_{12}O_6$), which is the energy source for the plant, water (which is re-formed at the end of the process), and oxygen—hence the name 'oxygenic'. The complete and intricate process of photosynthesis is not this simple, however. There are multiple chemical reactions that occur within the organism, which may be divided into light-dependent (or simply "light") reactions, and light-independent ("dark") reactions. The light reactions of the organism serve to synthesize oxygen gas, adenosine triphosphate (known as ATP), and NADPH. Both ATP and NADPH are energy-rich and used by the plant in dark reactions, in which glucose is formed by the plant for long-term energy storage (Vidyasagar).

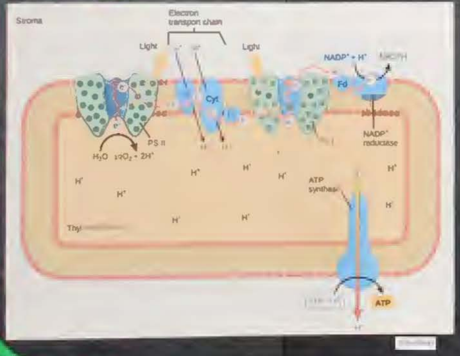


This is the absorption spectra of three pigment molecules found within the thylakoid membrane. Notice the lack of absorption of light by both chlorophylls in the green spectrum: this reflection of light is responsible for the green appearance of many chlorophyll-containing organisms. A combination of these pigment molecules in each reaction center creates the optimal absorbance for wavelengths of 680nm in PSII and 700nm in PSI (OpenStax).

Light Reactions: Creating Oxygen

Light reactions require sunlight to facilitate a reaction. There are two systems involved in the conversion of sunlight into energy, known as photosystem I and photosystem II (or PSI and PSII, respectively). The active centers within these systems are composed of an outer membrane of antenna proteins (known as the thylakoid membrane), separating the outer stroma from the inner lumen (OpenStax).

This barrier contains several membrane-bound substances, including the special photoreactive chlorophyll pairs—P_{680} in PSII and P_{700} in PSI—named for the wavelength of light associated with the highest rate of absorbance in each reaction center. These pigment molecules are responsible for the light reactions of the organism (Cuffari).



Each system acquires electrons from a different source and deliver their electrons to a different place. The process begins with PSII, when light enters the plant's reaction center and stimulates the release of an electron from a pigment molecule, creating an electron acceptor and an electron donor (in the form of a free electron). This electron is then sent through an electron transport system to PSI. Meanwhile, the pigment molecule in PSII is still lacking an electron. This vacancy is known as an "electron hole", which attracts nearby electrons. PSII fills this vacancy by stealing an electron from a water molecule. For every one water molecule, two electron holes are filled and half of a diatomic oxygen molecule are formed:

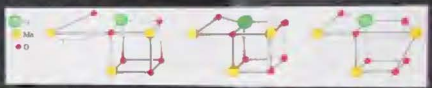
$H_2O \rightarrow 2e^- + \frac{1}{2}O_2 + 2H^+$ (Vidyasagar)

Only about 10 percent of the oxygen gas produced is used by the organism producing it, and the rest is released into the atmosphere and used by other oxygen-dependent organisms. The two hydrogen ions formed are kept within the lumen of the reaction center, lowering the pH of the lumen and creating a pH gradient between the lumen and the stroma. The energy created by the gradient of electrically repelled H^+ is harnessed by the ATP synthase channel (fused to the membrane) as the protons rush through the passageway to diffuse the gradient. ATP synthase then uses that energy to bond a third phosphate group to ADP, creating the high-energy compound ATP, which is stored in the glucose formed in later reactions and used for energy by the organism's cells (OpenStax).

Uncovering the Composition and Processes of PSII

Photosynthesis has been extensively studied, however the oxygen-evolving PSII is still relatively unclear in terms of chemical structure—and arguably the most fascinating and beneficial process (Chang). The oxygen gas produced is vital to aerobic life, and the potential for artificially photosynthesizing, capturing, and storing the energy produced as (for instance) clean-burning hydrogen or hydrogen peroxide fuel provides a sustainable potential solution to reducing greenhouse gas emissions (El-Khouly 38). The challenge of uncovering the complete intricate process of PSII is theorized to greatly relieved if the molecular structure of the oxygen-evolving center (OEC) could be accurately observed and recreated (Yamaguchi 138).

Past efforts to view the structure and determine precise distances between the functional atoms involved proved inconclusive as the magnification capabilities of the equipment used was not sufficient to view the oxygen bridges between inorganic atoms, nor the difference in distances between said atoms. Recent advances in magnification technology have allowed scientists to view and identify a cluster of four manganese and one calcium ions bridged by at least five oxygen ions at the active site of the OEC. With this knowledge of composition, a series of experiments was performed on artificially constructed $CaMn_4O_5$ structures as well as similar Mn_5O_5 and $Ca_2Mn_3O_5$ structures. The aim of these experiments was to determine the most stable and viable chemical series for an artificial water oxidation process, in an effort to further the progress of a new artificial photosynthetic design (Yamaguchi 138, 139).



The Optimal Geometry of Catalytic Site in the $CaMn_4O_5$ Cluster

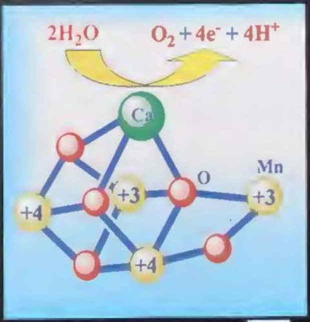
There are three possible structures for the catalytic site within the $CaMn_4O_5$ cluster: right-elongated, left-elongated, and central. The name of each refers to the distance between the catalytic site and a manganese ion on either side. None of the geometries within the optimal cluster proved to be superior, and all indicated that the natural structure of PSII contained labile bonds between the manganese ions and oxygen atoms, which is crucial for the oxygen-evolving process to take place (Yamaguchi 139, 147).

The geometry of the structure's catalytic site also plays a large role in overall stability. All three structures were investigated, and it was found that the Mn_5O_5 cluster was instable due to excessive distortion. When the calcium ion replaced on of the five manganese in the $CaMn_4O_5$ cluster and created two pairs of like-charged manganese ions, the distortion was reduced, and stability increased. The further substitution of another manganese ion with a calcium ion did not create a more favorable geometry (Yamaguchi 147).

The Need for Calcium in the Manganese Cluster

Manganese ions have variable charges, which can even change throughout one single cycle of oxidizing (removing electrons from) water. It is rare, however, to find a calcium ion that does *not* have a 2+ charge consistently. The three variations of manganese clusters were monitored throughout the oxidation process, and it was found that the most stable of the three was the $CaMn_4O_5$ cluster (Yamaguchi 139).

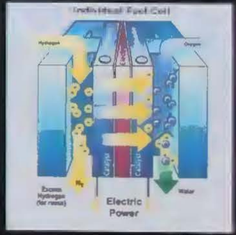
In the Mn_5O_5 cluster, there were three different charges between the five separate manganese ions (two 2+, one 3+, and two 4+). When one of the Mn^{2+} ions was replaced with the Ca^{2+} ion, the other Mn^{2+} ion's charge changed to 3+, creating two [illegible] When [illegible] it forces one of the [illegible] final [illegible] is present [illegible] natural [illegible]hi 139, 145).



Previous lab-created models of manganese clusters used for water oxidation were often destroyed during the high-energy cycle, so the presence of the stabilizing calcium ion indicates a more promising design for a functional model. Nonetheless, the variable and reactive quality of the clusters is an important aspect of the natural OECs, and it would appear that more than one calcium ion replacing a manganese ion within the cluster sacrifices its overall stability, as well (Yamaguchi 144).

Applications of Water Oxidation

[illegible] safely breathe it in and rely on it to survive. The other product, however, is very appealing for our future: hydrogen gas. Hydrogen gas (H_2) and hydrogen peroxide (H_2O_2) are both high-energy potential products of artificial photosynthesis. Hydrogen gas is already used as a fuel in place of fossil fuels in some applications, including hydrogen-powered cars. The biggest benefit of these hydrogen fuels is that the byproducts of burning such a fuel would be water, oxygen, and heat—no greenhouse gases—and better yet, any water will work in this process, even seawater. The search for a sustainable energy source with minimal environmental impact has been the focus of a lot of research in the last couple decades, and harnessing the power of water and the sun in a method that [illegible] win [illegible] ecological [illegible] 44, 77-79).



Works Cited

Alias, Abd Karim. "How Plant Make Food." *Storify*, 2016, https://storify.com/ProfKarim/how-plant-make-food. Accessed Mar. 23 2018.

[illegible]

[illegible] Accessed 02 Feb. [illegible]

El-Khouly, Mohamed E., Eithar El-Mohsnawy, Shunichi Fukuzumi. "Solar energy conversion: From natural to artificial photosynthesis." *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 31, 2017, Pages 36-83, http://www.sciencedirect.com/science/article/pii/S1389556716300727. Accessed 12 Mar. 2018.

HyGen. *How a Hydrogen Fuel Cell Works*. 2018, https://www.hygen.com/wp-content/uploads/2013/09/fuelcell.jpg. Accessed Mar. 23 2018.

OpenStax. *The Light-Dependent Reactions of Photosynthesis*. OpenStax CNX, 13 Mar. 2015, [illegible] Accessed 02 Mar. 2018.

Tatters, Avery O., Meredith D. A. Howard, Carey Nagoda, David A. Caron. "Multiple Stressors at the Land-Sea Interface: Cyanotoxins at the Land-Sea Interface in the Southern California Bight." *ResearchGate*, March 2017, [illegible] Accessed 23 Mar. 2018.

The Mellow Fellow. "Hydrogen-Powered Cars – The Future of Clean Energy." *Sites at Penn State*, March 2014, [illegible] Accessed 23 Mar. 2018.

Vidyasagar, Aparna. "What is Photosynthesis?" *Live Science*, July 31, 2015 [illegible] Mar. 2018.

[illegible]