

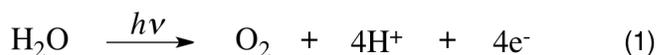
## Modeling the Oxygen Evolving Complex of Photosystem II

Olbelina A. Ulloa

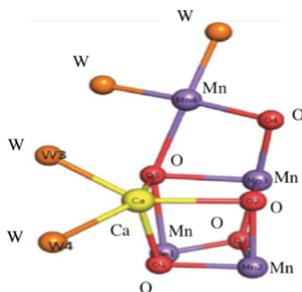
“Literature Seminar”

09/20/2011

Photosystems are chlorophyll-containing units of proteins that use light to conduct chemical reactions. Photosystems in the thylakoid membrane of plants and algae can produce oxygen for respiration, adenosine triphosphate (ATP) for energy, and hydrocarbons for food.<sup>1,2</sup> Photosystem II (PS II) is the only protein system in nature that performs the oxidation of water to produce molecular oxygen, protons, and electrons (eq 1).<sup>3</sup> The oxygen produced is given off by plants and algae and is used by other organism in mitochondrial respiration.<sup>1</sup> Protons are released into the thylakoid membrane, and create the gradient that drives ATP synthesis by ATPase. Finally, the electrons produced are transferred to Photosystem I, where NADPH is produced and used to synthesize hydrocarbons from carbon dioxide.<sup>1</sup>



The oxidation of water by PS II occurs at an active site known as the oxygen evolving complex (OEC). Recently Umena *et. al.* reported the crystal structure of the 350KDa system with a 1.9Å resolution. Revealing the previously elusive OEC structure consisting of a  $\text{Mn}_4\text{CaO}_5$  cluster (figure 1). The cluster is an asymmetric  $\text{Mn}_3\text{Ca}$  cubane with an additional dangling Mn, five bridging oxygen, and four terminal water molecules<sup>4,5</sup>. The mechanism of water oxidation by the OEC is still greatly debated;<sup>4</sup> however it is known to be initiated by four consecutive oxidations of the cluster.<sup>1,4,5</sup> It is suggested that this high oxidation state may form a Mn oxo intermediate with an electrophilic oxygen, which is susceptible to nucleophilic attack by a second water molecule<sup>3</sup>. This O-O bond-forming step is followed by release of molecular oxygen and regeneration of the low oxidation state cluster.<sup>2,4</sup> The OEC is able to produce oxygen with turnover numbers of 180,000 molecules of  $\text{O}_2$   $\text{cite}^{-1}$ .

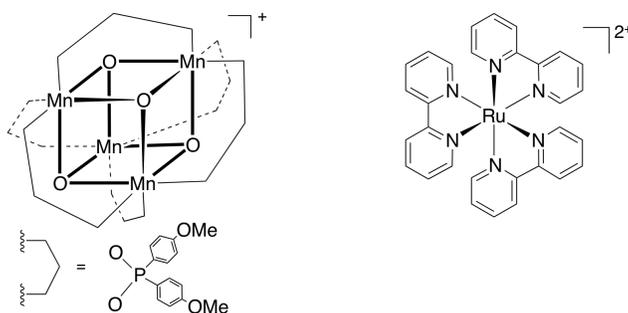


**Figure 1.** Structure of the oxygen evolving complex.<sup>4,5</sup>

The OEC is seen as a potential template for the anode of an electrochemical cell that uses water to produce protons and electrons<sup>2</sup>. At a cathode these products could be transformed into molecular hydrogen and be used as fuel.<sup>2</sup> This motivation has led to the

synthesis of many structural and functional models of the OEC <sup>6</sup> Some of the traits researchers aim to model are, the ability to absorb light and convert it into chemical potential, the use of chemical oxidants to oxidize water, the structural capability of storing two to four oxidizing equivalents, and the ability to form a reactive Mn oxo intermediates to aid in O-O bond formation<sup>3,7</sup>. In this presentation, two exemplary models have been chosen to explore some of the traits mentioned above.

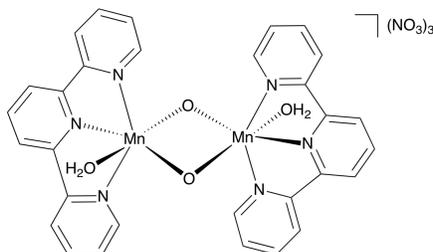
Dismukes and coworkers developed the first featured catalyst, a  $[\text{Mn}_4\text{O}_4\text{L}_6]^+$  cubium (figure 2) which is capable of electro-oxidizing water at 1.00V (vs. Ag/AgCl) when illuminated by UV-visible light<sup>8</sup>. The catalyst is suspended in a proton-conducting membrane called a nafion that is coated onto a conductive electrode<sup>8</sup> The proposed mechanism proceeds by dissociation of a ligand, and release of  $\text{O}_2$  to form a “butterfly” intermediate. The intermediate is able to oxidize two water molecules, and regenerates the cubium by association of a ligand.<sup>8</sup> Catalytic turnover frequencies of up to 270 molecules of  $\text{O}_2 \text{ hr}^{-1} \text{ catalyst}^{-1}$  and  $>1000$  molecules  $\text{O}_2 \text{ catalyst}^{-1}$  have been observed for this catalyst under mild conditions.<sup>9</sup> To overcome the need for applied potential Dismukes and coworkers designed a molecular based photoelectrochemical cell that employs nafion-cubium system. A  $\text{TiO}_2$ -supported  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy: 2,2'-bipyridine) photosensitizers (figure 2) is used to extract electrons from the catalyst providing the potential to oxidize water without the need of an external voltage. This photoelectrochemical cell can produce  $\text{O}_2$  with turnover frequencies of  $47 \pm 10 \text{ O}_2 \text{ molecules hr}^{-1} \text{ catalyst}^{-1}$  under mild conditions.<sup>9</sup>



**Figure 2.**  $[\text{Mn}_4\text{O}_4\text{L}_6]^+$  cubium as a functional and structural model of the OEC (left).  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer (right).

Another model for the OEC,  $\text{Mn}_2(\mu\text{-O})_2(\text{terpy})_2(\text{H}_2\text{O})_2^{3+}$  (terpy: 2,2';6',2"-terpyridine) (figure 3), is a dinuclear Mn complex synthesized by Limburg and coworkers. It is shown to form a Mn oxo intermediate, and catalytically produce  $\text{O}_2$  with the help of chemical oxidants.<sup>7</sup> The proposed mechanism begins with the oxidation of a  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu\text{-O})_2(\text{terpy})_2(\text{H}_2\text{O})_2^{3+}$  by a chemical oxidant. This is followed by formation of a Mn oxo intermediate, and nucleophilic attack by a second water molecule to form an O-O bond<sup>7</sup>. Elimination of  $\text{O}_2$  and oxidation regenerates the  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu\text{-O})_2(\text{terpy})_2(\text{H}_2\text{O})_2^{3+}$  species. The origin of the oxygen in this catalytic system has been questioned due to the possible oxidation of water by some oxygen-containing chemical oxidants<sup>3</sup> Kinetic experiments demonstrated a first order dependence on the oxidants, which cannot account for the mechanism where the oxidant is the only source of oxygen.<sup>7</sup>

Complementary  $^{18}\text{O}$  labeling<sup>7</sup> and electrochemical studies<sup>10</sup> with oxone suggest that water is in fact a source of one oxygen, but a chemical oxidant is required to produce  $\text{O}_2$ . The similarities between the OEC and this catalyst make it an important model for the study of high oxidation intermediates.



**Figure 3.** Dimeric model  $[\text{Mn}_2(\text{O})_2(\text{terpy})_2(\text{H}_2\text{O})_2]^{3+}$  related to the OEC

Models of the OEC have targeted oxidation states, structure, and formation of proposed intermediates.<sup>3</sup> Recent findings by Umena and coworkers on the structure of the OEC will likely inspire additional work on models.<sup>4,5</sup> The importance of other cofactor such as  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and the hydrogen-bonding network of the system are becoming more clearly understood, which may also prove beneficial to future biomimetic structures.<sup>5</sup>

## References

- (1) Bertini, I. G.; H. B.; Stiefel, E. I.; Valentine, J. S. *Biological Inorganic Chemistry: Structure and Reactivity*; University Science Books, 2007.
- (2) Lubitz, W.; Reijerse, E. J.; Messinger, J. *Energy Environ. Sci.* **2008**, *1*, 15.
- (3) Herrero, C.; Quaranta, A.; Leibl, W.; Rutherford, A. W.; Aukauloo, A. *Energy Environ. Sci.* **2011**, *4*, 2353.
- (4) Najafpour, M. M.; Govindjee *Dalton Trans.* **2011**, *40*, 9076.
- (5) Umena, Y.; Kawakami, K.; Shen, J.-R.; Kamiya, N. *Nature* **2011**, *473*, 55.
- (6) Kanady, J. S.; Tsui, E. Y.; Day, M. W.; Agapie, T. *Science* **2011**, *333*, 733.
- (7) Limburg, J.; Vrettos, J. S.; Chen, H.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 423.
- (8) Brimblecombe, R.; Kolling, D. R. J.; Bond, A. M.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *Inorg. Chem.* **2009**, *48*, 7269.
- (9) Brimblecombe, R.; Koo, A.; Dismukes, G. C.; Swiegers, G. F.; Spiccia, L. *J. Am. Chem. Soc.* **2010**, *132*, 2892.
- (10) Baffert, C.; Romain, S.; Richardot, A.; Lepretre, J.-C.; Lefebvre, B.; Deronzier, A.; Collomb, M.-N. *J. Am. Chem. Soc.* **2005**, *127*, 13694.

