Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 252 (2008) 231–232

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Preface

Keywords: Photosystem II; Manganese; Oxygen evolution; Water oxidation

One of the most important milestones in the Earth's history occurred when a photosynthetic organism figured out how to use water as a reductant in photosynthesis (Fig. 1). This marked the onset of oxygenic photosynthesis, and resulted in the transformation of the atmosphere from its primordial anoxygenic state to the present aerobic state. The biosphere was changed dramatically by this reaction. Among the many transformations was the evolution of aerobic respiration that enabled high-energy requiring organisms such as humans to exist. Oxygen released as a by-product of photosynthesis continues to sustain respiring organisms.

The conversion of solar energy into biomass by photosynthesis is the source of most of the energy available to life on Earth. This includes not only the on-going production of high-energy organic molecules by plants that supports the food chain, but also the excess production of biomass over the Earth's geologic history that has been buried in the form of coal, oil and gas. Most of our current energy comes from burning these fossil fuels. However, energy from fossil fuels is non-renewable. We need to develop renewable sources of energy in the near future. Photosynthesis provides a successful example of how solar energy can be converted into fuel.

A key step for the development of artificial photosynthetic processes for fuel production is extracting electrons from a sacrificial donor. Owing to its abundance, water is the obvious sacrificial donor, but water is very difficult to oxidize. Photosystem II (PSII) is the pigment–protein complex in oxygenic photosynthetic organisms that carries out the water-oxidation chemistry. If we can understand in detail how Nature has solved this problem, then we may be able to develop artificial photosynthetic processes for renewable solar energy utilization.

In the past 5 years, there has been dramatic progress in the structural characterization of photosystem II by X-ray crystallography (Fig. 2). Combined with a wealth of experimental data from biochemical work, site-directed mutagenesis, spectroscopic studies, computational modeling and inorganic model chemistry, our understanding of the structure and catalytic chemistry of the Mn_4Ca cluster in the O_2-evolving complex (OEC) of photosystem II is becoming increasingly clear. This volume provides an outstanding collection of reviews on the current status of research on the role of manganese in photosystem II. I am grateful to Barry Lever for his help to make this special issue possible and to all the authors and reviewers who have contributed to the high quality of the articles.

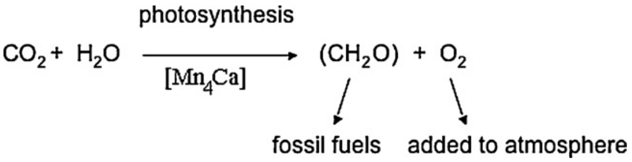

Fig. 1. Overall equation for oxygenic photosynthesis, showing the reduction of CO_2 to form carbohydrate (CH_2O) and the oxidation of water to form molecular oxygen.

This special issue covers a wide range of topics related to the OEC. **Barber** and **Murray** begin by describing the structure of the OEC as revealed by X-ray crystallography. However, with the current resolution of 3.0–3.5 Å, there are still uncertainties about the amino-acid residues that coordinate to the metal ions, and this can be clarified by spectroscopic studies of site-directed PSII mutants, as described by **Debus**. A photochemical charge separation in the PSII generates the very high-potential oxidant necessary to drive the water-oxidation chemistry. **Rappaport** and **Diner** describe the primary photochemistry leading to Mn oxidation. Note that the primary photochemistry generates only one oxidizing equivalent per charge separation, whereas the oxidation of water to O_2 is a four-electron reaction. **Dau** and **Haumann** describe the four-electron water-oxidation reaction cycle of the OEC.

A unique property of the OEC is that the redox chemistry requires the participation of both Ca^{2+} and Cl^-, as described by **Yocum**. Another complicating aspect of the OEC is that the substrate is also the solvent, which prevents standard enzyme kinetics to be used to interrogate the involvement of the substrate. Instead, **Hillier** and **Wydrzynski** have used time-resolved mass spectrometry experiments to study binding of the substrate

doi:10.1016/j.ccr.2007.08.028

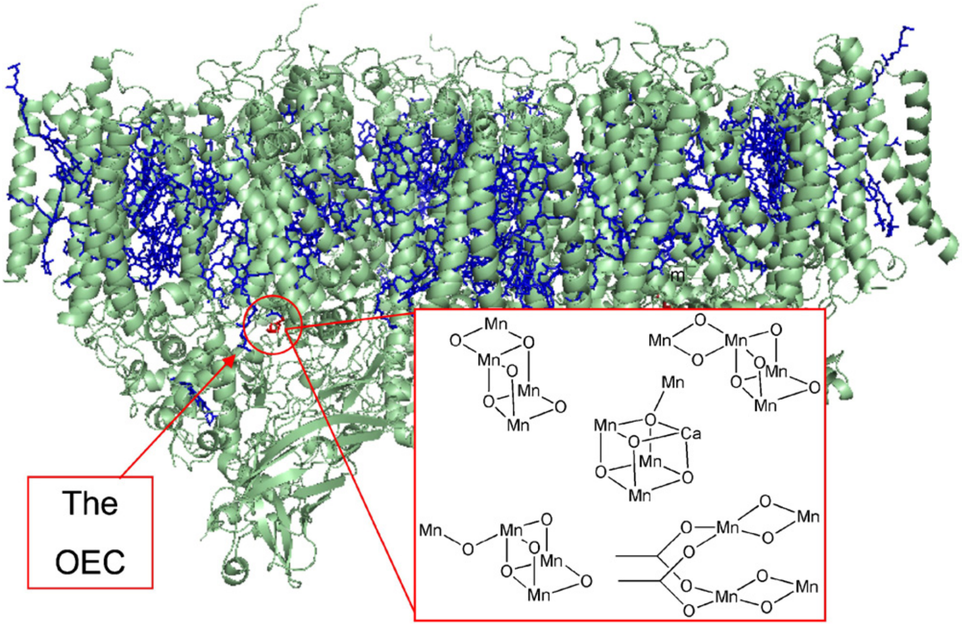

Fig. 2. Photosystem II crystal structure (pdb accession number 1S5L) showing the location of the O_2-evolving complex (OEC) and potential structures of the tetramanganese cluster that catalyzes the four-electron oxidation of water.

water molecules to the OEC. X-ray spectroscopy (**Sauer**, **Yano** and **Yachandra**) and Fourier transform infrared spectroscopy (**Noguchi**) have provided high-resolution information on the structure and properties of the OEC.

The oxidation of water requires formation of extremely reactive intermediates that damage the PSII complex. In order to maintain a steady-state population of active centers, PSII is constantly degraded and reassembled. **Dasgupta**, **Ananyev** and **Dismukes** describe the process of assembly of the OEC, and photodamage is described by **Tyystjärvi**.

One of the ongoing mysteries of the OEC is how PSII could have evolved the ability to use water as an electron donor. It would seem that a number of changes, such as formation of a very high-potential oxidant in the charge-separation reaction and incorporation of a four-electron water-oxidation catalyst, would have had to occur simultaneously in order to convert a non-oxygenic photosynthetic reaction center into PSII. **Raymond** and **Blankenship** discuss the origin of the OEC.

Computational chemistry is becoming an increasingly powerful approach to define the structure and function of the OEC. **Hammes-Schiffer**, **Hatcher**, **Ishikita**, **Skone** and **Soudackov** describe theoretical studies of proton-coupled electron-transfer reactions relevant to the OEC and **Sproviero**, **Gascon**, **McEvoy**, **Brudvig** and **Batista** present QM/MM studies of the OEC.

Inorganic model chemistry has played an important and synergistic role in studies of the OEC by defining potential structures and properties of well-characterized high-valent manganese coordination complexes. **Mullins** and **Pecoraro** describe manganese model complexes that mimic the OEC. Of particular interest are those functional model complexes that can catalyze the oxidation of water, as described by **Cady**, **Crabtree** and **Brudvig**. Finally, the goal for future renewable solar energy utilization is to develop artificial photosynthetic systems that can use solar energy for fuel production. Progress toward this goal is described by **Herrero**, **Lassalle-Kaiser**, **Leibl**, **Rutherford** and **Aukauloo**.

Gary W. Brudvig
Department of Chemistry, Yale University, P.O. Box 208107,
New Haven, CT 06520-8107, USA

E-mail address: gary.brudvig@yale.edu

28 August 2007