Watanabe LAB.

[Molecular Mechanism of Photosynthesis]

International Research Centre for Sustainable Materials

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Biofunctional Chemistry

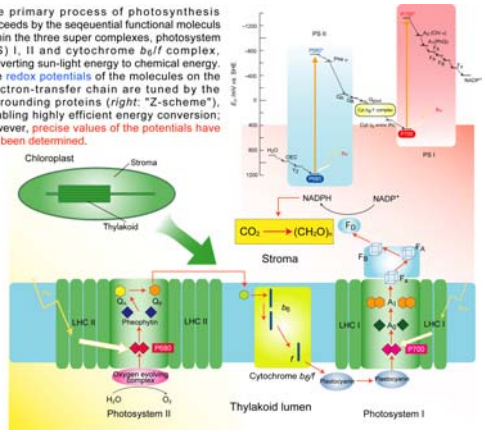
Department of Chemistry & Biotechnology

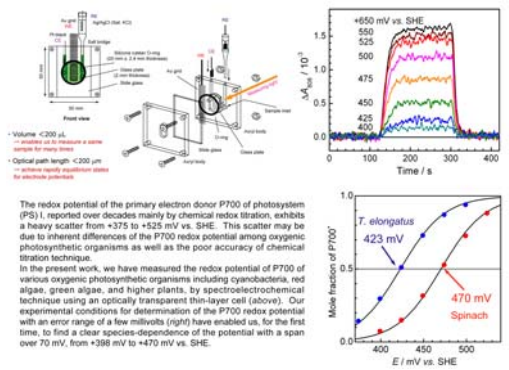
Molecular Mechanism of Photosynthesis

Photosynthesis is a energy-conversion system in nature from photon energy to chemical energy, resulting in all of foods and fossil fuels that are necessary for all living organisms including human. In spite of the high efficiency of it's energy conversion (quantum yield ca. 1), which will suggest design manuals for artificial photosynthesis, the mechanism of photosynthesis in molecular level is still unknown and to be elucidated. We are attempting to close in the principle of photosynthesis through the following studies.

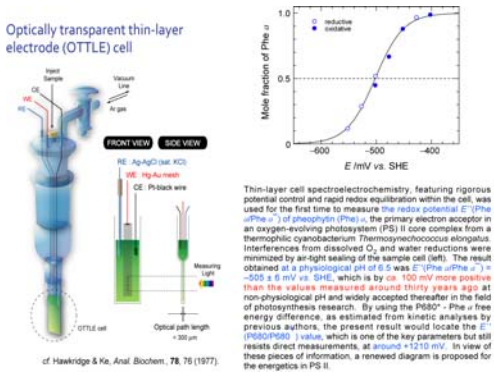
①Elucidation of the Molecular Assembly of Photosynthetic Machinery
②Characterization of the Physicochemical Properties of Photosynthetic Machinery
③Spectroelectrochemistry of the Functional Molecules in Photosystem II Reaction Center
③Light-induced Charge Separation in Photosystem I Sensitized by an Artificial Fluorescent Dye
④Analysis & Application of Photoelectrochemical Process

The primary process of photosynthesis proceeds by the seqeuential functional molecuils within the three super complexes, photosystem (PS) I, II and cytochrome b_6/f complex, converting sun-light energy to chemical energy. The redox potentials of the molecules on the electron-transfer chain are tuned by the surrounding proteins (*right*: "Z-scheme"), enabling highly efficient energy conversion; however, precise values of the potentials have not been determined.





The redox potential of the primary electron donor P700 of photosystem (PS) I, reported over decades mainly by chemical redox titration, exhibits a heavy scatter from +375 to +525 mV vs. SHE. This scatter may be due to inherent differences of the P700 redox potential among oxygenic photosynthetic organisms as well as the poor accuracy of chemical titration technique.
In the present work, we have measured the redox potential of P700 of various oxygenic photosynthetic organisms including cyanobacteria, red algae, green algae, and higher plants, by spectroelectrochemical technique using an optically transparent thin-layer cell (*above*). Our experimental conditions for determination of the P700 redox potential with an error range of a few millivolts (*right*) have enabled us, for the first time, to find a clear species-dependence of the potential with a span over 70 mV, from +398 mV to +470 mV vs. SHE.



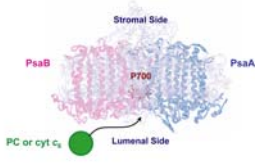
Thin-layer cell spectroelectrochemistry, featuring rigorous potential control and rapid redox equilibration within the cell, was used for the first time to measure the redox potential $E^{\circ\prime}$(Phe *a*/Phe *a*$^{\cdot-}$) of pheophytin (Phe) *a*, the primary electron acceptor in an oxygen-evolving photosystem (PS) II core complex from a thermophilic cyanobacterium Thermosynechococcus elongatus. Interferences from dissolved O_2 and water reductions were minimized by air-tight sealing of the sample cell (left). The result obtained at a physiological pH of 6.5 was $E^{\circ\prime}$(Phe *a*/Phe *a*$^{\cdot-}$) = −505 ± 6 mV vs. SHE, which is by *ca.* 100 mV more positive than the values measured around thirty years ago at non-physiological pH and widely accepted thereafter in the field of photosynthesis research. By using the P680$^+$ - Phe *a* free energy difference, as estimated from kinetic analyses by previous authors, the present result would locate the $E^{\circ\prime}$ (P680$^+$/P680) value, which is one of the key parameters but still resists direct measurements, at around +1210 mV. In view of these pieces of information, a renewed diagram is proposed for the energetics in PS II.

cf. Hawkridge & Ke, *Anal. Biochem.*, **78**, 76 (1977).

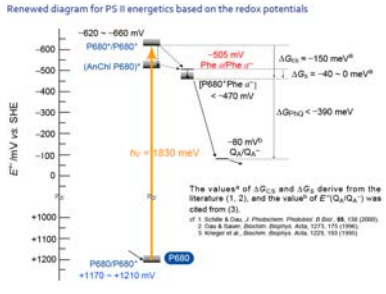
Species	$E^{\circ\prime}$ (mV vs. SHE)	Classification	Electron Donor
Gloeobacter violaceus	+398 ± 4	Cyanobacterium	Cyt c_6, Pc
Spirulina platensis	+414 ± 1	Cyanobacterium	Cyt c_6
Thermosynechococcus elongatus	+423 ± 2	Cyanobacterium	Cyt c_6
Cyanidium caldarium	+430 ± 3	Red alga	Cyt c_6
Porphyridium purpureum	+431 ± 1	Red alga	Cyt c_6
Tolypothrix tenuis	+438 ± 2	Cyanobacterium	Cyt c_6
Fischerella muscicola	+439 ± 3	Cyanobacterium	Cyt c_6
Anabaena variabilis	+441 ± 1	Cyanobacterium	Cyt c_6, Pc
Synechococcus PCC6301	+452 ± 1	Cyanobacterium	Cyt c_6, Pc
Synechocystis PCC6803	+455 ± 4	Cyanobacterium	Cyt c_6, Pc
Chlorella vulgaris	+458 ± 3	Green alga	Cyt c_6, Pc
Chlamydomonas reinhardtii	+468 ± 1	Green alga	Cyt c_6, Pc
Spinach	+470 ± 2	Higher plant	Pc
Phytolacca americana	+470 ± 2	Higher plant	Pc

* Pc : Plastocyanin Cyt c_6 : Cytochrome c_6

- A species-dependence of the P700 redox potential with a span over 70 mV was found.
- The order of the P700 redox potentials: cyanobacteria < red algae < green algae < higher plants
  → *The P700 redox potential appears to reflect the path of evolution of the photosynthetic organisms.*



- In organisms, oxidized P700 is re-reduced by electron donor proteins. → *The properties of the proteins may influence the P700 redox potential?*



The values[a] of ΔG_{CS} and ΔG_S derive from the literature (1, 2), and the value[b] of $E^{\circ\prime}(Q_A/Q_A^{\cdot-})$ was cited from (3).

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