General

The greatest challenge facing our global future is energy. Worldwide primary energy consumption in 2007 was $458 \times 10^{18}$ joules, which is an average energy consumption rate of 16.2 terrawatts (TW, one TW equals $10^{12}$ watts, or $10^{12}$ joules per second). Global energy need will roughly double by mid-century and triple by 2100. Much of this demand is driven by a growing world population, which is projected to increase from 6.2 billion in 2001 to approximately 9.4 billion by 2050. In addition to these 3 billion new inhabitants of the planet, 3 billion people in the non-legacy world seek a rising standard of living.

The need to provide 16 TW, even in light of unprecedented conservation, sounds simple? Well, consider the total amounts of possible energy from the following sources:

- From **biomass**, 7 - 10 TW: This is the maximum amount of biomass energy available from the entire agricultural land mass of the planet (excluding the area required to house a population of 9 billion people). This value requires that all crops be harvested exclusively for energy.
- From **nuclear**, 8 TW: To deliver this TW value with nuclear energy will require the construction of 8000 new nuclear power plants. Over the next 45 years, this would require the construction of one new nuclear power plant every two days.
- From **wind**, 2.1 TW: This energy is harvested by saturating the entire class 3 (the wind speed required for sustainable energy generation, 5.1 m/s at 10 m above the ground) and greater global land mass with wind mills.
- From **hydroelectric**, 0.7 - 2.0 TW: This energy is achieved by placing dams in all remaining rivers on the earth.

Under the untenable scenarios of the bulleted points listed above, an energy supply for 2050 is barely attained. The message is clear. The additional energy needed for 2050, over the current 16.2 TW energy base, is simply not attainable from long discussed sources – the global appetite for energy is simply too great.

There is one possible sustainable and renewable carbon-neutral energy sources, however, that can do the job. Sunlight. More solar energy strikes the Earth’s surface in one hour of each day than the energy used by all human activities in one year.
**Photosynthesis**

Photosynthesis has produced most of the energy that sustains life on our planet by using the sun to store solar energy in the rearranged bonds of water and carbon dioxide to produce oxygen and carbohydrate. Analysis of the energetics of the solar fuels conversion process shows that it is water splitting and not carbohydrate production that is at the heart of solar energy storage. The reversible potential for the water splitting reaction is,

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad V_{\text{rev}} = 1.23 \text{ V} \]

whereas the reversible potential for production of carbohydrate from water and CO\(_2\) is

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + (\text{H}_2 + \frac{1}{2}\text{O}_2) \rightarrow \frac{1}{6}\text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 \quad V_{\text{rev}} = 1.24 \text{ V} \]

Note, water splitting is subsumed by water splitting. On an electron equivalency basis, therefore, the production of the carbohydrate stores only 0.01 eV more energy than water splitting. Thus, the solar energy storage in photosynthesis is achieved by water splitting; the carbohydrate is nature’s method of simply storing the hydrogen released from the water splitting reaction (it does not store any energy, it only is a mechanism for storing the already energetic hydrogen).

In the process of water splitting, sunlight is stored in the re-arranged bonds of water to make chemical fuels, hydrogen and its accompanying byproduct, oxygen.

![Diagram of photosynthesis cycle](image)

Thus the sunlight is stored in hydrogen and oxygen. The hydrogen can then be combined with the oxygen in a fuel cell to give back water and energy. This is how the life energy process works. Photosynthesis stores sunlight to produce water and “hydrogen”. Natures form of hydrogen is NADPH (which effectively stores the 4 electrons and 4 protons of two molecules of hydrogen produced in water splitting). As we said above, the hydrogen is then combines with CO\(_2\) to produce carbohydrate as a “storage” mechanism of hydrogen (since it is difficult for Nature to store a gas).
The crystal structure of the photosynthetic membrane has recently been solved. So we know what all the “players” are in the solar water splitting process:

The Life Energy Cycle

How do you harness the stored solar energy? You eat the carbohydrate and you break it down back into CO₂, which you breathe out and release the stored as “hydrogen, i.e., 4 protons and 4 electrons.

\[
\frac{1}{6}C_6H_{12}O_6 + H_2O \rightarrow CO_2 + 4H^+ + 4e^- 
\]

At this point you have released no energy. The protons are then delivered to your mitochondria. You breathe oxygen, and hemoglobin (see last lecture), carries the O₂ to your mitochondria where it is combined by an enzyme called, cytochrome c oxidase (CcO), with the 4 protons and 4 electrons to produce water and release the stored energy from sunlight to your mitochondria (see first figure of the lecture, you release 58 kcal mol⁻¹ of energy) are delivered to your mitochondria.
Photosynthesis thus is the solar fuels producer, and CcO is the fuel cell that releases the energy from the solar fuels in your body. In the overall cycle, sunlight is released in your body to power you!

**Inorganic Chemistry of the Life Energy Cycle**

So where does inorganic chemistry come into the picture? The overall water-splitting reaction is a *multielectron* process, involving a total of 4 electrons and 4 protons. Solar light collection and conversion by photosynthesis is a one-electron, one photon process. Thus *inorganic catalysts* are needed to connect the 1 electron solar collection/conversion process to the multielectron chemistry of water splitting. And the reverse reaction, the fuel cell reaction performed by CcO is the same multielectron reaction run backwards. Here a catalyst is needed too.

As you can see from the figures above, the water splitting catalyst in photosynthesis, called the oxygen evolving complex is a Mn₄O₄Ca cluster. The catalyst in CcO is a bimetallic cofactor comprising a Fe heme (see last lecture) and a mononuclear Cu center. Though the cofactors are different in a plant and in you, the chemistry they perform is very similar, simply in reverse:

![Photosystem II](image1) ![Cytochrome c Oxidase](image2)

Note in PSII, a water (or hydroxide) attacks a terminal metal-oxo to produce a peroxo intermediate, which then is oxidized by two more electrons to produce O₂. In CcO, the reverse occurs—O₂ binds the Fe²⁺/Cu⁺ site to make a Fe³⁺/Cu²⁺ peroxo, which is then reduced by 2 more electrons to make water.
In some photosynthetic organisms, like algae, the $4H^+$ and $4e^-$, are not translated to a carbohydrate, but they produce $H_2$ directly. They do this using an enzyme called hydrogenase. There are many families of hydrogenases:

\[
H_2 \xrightarrow{\text{Methanogenic}} 2H^+ + 2e^-
\]

The active sites of typical hydrogenases are bimetallic FeFe or FeNi centers. In the most recent discovery of a new hydrogenase, it is a mononuclear Fe center:

The proposed mechanism for the active site is a $2e^-$ process to make a hydride, which is then protonated off as hydrogen:
Artificial Photosynthesis

If photosynthesis could be duplicated with catalysts outside of the leaf, then one could duplicate the energy life cycle and go a long way to solving the global energy problem. So just how much energy can you store in water splitting? Remember those astronomical numbers needed for future energy? Well consider this.

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad \text{Energy of formation} = 237 \text{ kJ/mol} \]

Thus 237 kJ/mol of energy is released upon combining H₂ and O₂ to make water. Therefore in 1 liter of water, you can store 13 million J/L (13 MJ/L). The MIT swimming pool,

Has 3.2 million liters of water in it. If inorganic chemists can make catalysts that convert the MIT swimming pool to H₂ and O₂ per second, then there will be an
energy system that delivers **43 TW** of carbon-neutral energy to the world. Note, you will do this globally. So everybody will have their little bottle of water that adds up to a swimming pool. And the swimming pool of water is not used up because this is a cyclic process. Sunlight splits water and the hydrogen and oxygen is stored for when the sun doesn’t shine. When the H₂ and O₂ are burned to produce energy (usually in a fuel cell – that is what a fuel cell does, combines H₂ and O₂ to produce electricity), the byproduct is water again. Thus water is simply the energy carrier for the sun, just as it is in the energy life cycle.

**Do You Want to Save the World? Then Become an Inorganic Chemist**

So the job of the inorganic chemist is to figure out how to do artificial photosynthesis outside of a leaf. A model is as follows:

![Diagram of artificial photosynthesis model]

- The device uses a semiconductor (SC) to capture and convert absorbed light into *wireless* charge-separated holes and electrons.
- Holes of the wireless current are captured by catalyst to produce O₂.
- Electrons of the wireless current are captured by a catalyst to produce H₂.

It is intrinsically the job of the inorganic chemist because:

1. The light harvesting and conversion to a wireless current can be accomplished in semiconducting materials. These are all inorganic materials (e.g., Si, CdTe, CdS, WO₃... and lots of other oxides).
2. The solar photon is converted to 1 electron and 1 hole. If a “hydrogenase”-like catalyst is interfaced to one side of the semiconductor and a “OEC”-like catalyst is interfaced to the other side, then they can collect the holes and electrons. When a total of 4 is attained, water splitting can occur.
3. Oxygen evolving catalysts are metal oxides.
4. Hydrogen evolving catalysts are metal hydrides.