# Biological Inorganic Chemistry
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**Lecture 46**
# Redox catalysis by manganese ions

Hello, students. So, good morning, everybody. So, today we will just move to a new module, which is your module 10 and is basically a very compressed module because we do not have enough time left. So, we have reached module 10 then we will have 11 and 12 module. So, here we will be compressing three metal lines.

Those are not very vast, but still they have some important applications. So, today in lecture 46, we will go for the redox catalysis by manganese. So, out of these three metal ions the manganese one and half lecture, again another one and half for the cobalt, and finally, the two that way I thought to distribute the classes in that fashion.

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Concepts to be Covered

- $O_2$ production by photosynthetic plants, algae and cyanobacteria
- ATP production during photosynthetic ET
- The electrons are derived from water
- Mitochondrial Mn-SOD

So, why manganese? So, we will just start from the corresponding thing the biological world of plants, algae and cyanobacteria, because previously say around 2.5 billion years ago, the atmosphere was not oxidizing, because oxygen was not there is typically reducing. So, after that when the environment due to the cyanobacteria, plants and all started getting oxygen out of photosynthesis, then our entire world then we also came that our entire world is becoming oxidizing and we have much amount of oxygen in that environment.

So, today we will see why you need manganese and how the manganese is very much essential to get an environment where your oxygen will be the predominating gas which is there in our environment. So, during this particular process also we never forget it that we will have the right amount of ATP production during one very interesting type of electron transfer reactions we have seen electron transfer reactions.

The ET reactions based on copper, ET reactions based on iron, now we will see the manganese can also take part nicely for your many number of electron transfers and very simple example of your photosystem II will take. And where from we will get those electrons. Many number of electrons we will just derive it from water. So, that is why the water is your substrate for your photooxidation and will be releasing the oxygen molecule, and finally, we will just devote our classes to a microconidal manganese SOD.

So, already we know about the superoxide dismutase related to your by the bimetallic side the zinc and copper and there we know how copper is involved for your catalytic site for the corresponding disputation or disproportionation reaction of the superoxide ion. So, now, we will bring the manganese over there again.

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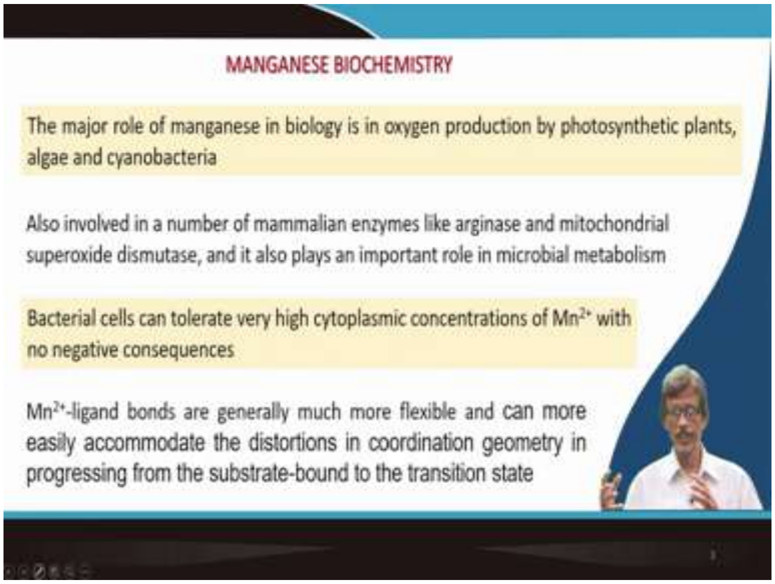

MANGANESE BIOCHEMISTRY

The major role of manganese in biology is in oxygen production by photosynthetic plants, algae and cyanobacteria

Also involved in a number of mammalian enzymes like arginase and mitochondrial superoxide dismutase, and it also plays an important role in microbial metabolism

Bacterial cells can tolerate very high cytoplasmic concentrations of $Mn^{2+}$ with no negative consequences

$Mn^{2+}$-ligand bonds are generally much more flexible and can more easily accommodate the distortions in coordination geometry in progressing from the substrate-bound to the transition state

So, what we see? So, little bit we definitely should know about the corresponding manganese based by inorganic chemistry, how the manganese can play some important role compared to the other metal ions. So, already we have traveled a lot, we have crossed many metal ions, and starting from say, if we consider that we have started from our journey, basic journey for the transgender lines like iron, then we have seen the copper and previously we just see that zinc.

So, side by side we will try to compare the corresponding manganese biochemistry with that of iron biochemistry, copper biochemistry and the zinc biochemistry. So, this is also very important. Not that I am asking you go and follow the typical bioinorganic chemistry book or biological inorganic chemistry book, you can go straightaway to any kind of biochemistry book also and try to find out whether they are dealing with these metal ions or not.

So, if they are dealing with manganese, go and stay to read. You will be able to enjoy a nicely about the perspective, the vision what a biochemist can see, because they are not seeing nicely around the manganese center or the metal ion center, but they will see differently. But in total, the total picture is basically based on manganese and the biological environment.

So, we have therefore the role which the manganese can play for the production of the O2 molecule in all these categories of systems that is the algae, cyanobacteria and photosynthetic plants. They are also involved in arginase. Maybe in tomorrow's class we will be talking about the arginase which is a non-redox system, then mitochondrial superoxide dismutase the SOD activity and finally also it can play about the microbial metabolism.

So, these are the very few examples where the manganese plays some important role. And is not the end of the story, you can have many number of manganese in the coming years also. People can discover many new sites where your manganese can play some important role. But historically all these discovery and all these identifications are very important and always you should carry these informations with you such that you can understand the new activity of the newly discovered molecule where you have the manganese 2 plus in your hand.

So, when high cytoplasmic concentrations you have in the bacterial cells, the manganese 2 plus with no negative consequences, that means unlike iron, we have seen that iron can very quickly activate the dioxygen molecule and can also go for the interaction with the water molecules for your corresponding precipitation as ferric hydroxide, but the manganese chemistry or the biochemistry in terms of its coordination will be little bit different.

So, these manage ligand bonds are generally much more flexible. So, the binding, so it is comparable to that of your magnesium binding, and more easily accommodate the distortions in the coordination geometry in progressing from the substrate bound to the transition state form. So, if you have a system or manages coordinating to your substrate, in your enzyme, we have seen earlier that you can have ES or E plus S enzyme, so is basically enzyme you call.

If it is E, so is binding the substrate. So, this is the pocket basically goes inside that is why the English letter E is also fine to tell you the example of an enzyme. So, then that is there. So, if the binding is so strong, it is very difficult to go for the transition state in this particular form or release of the product, because ES via TS to EP. So, the enzyme substrate assembly or aggregate to your transition state and then transition state to your enzyme product system.

So, if your binding is very strong, it would not be possible to release the product which is being formed over there to regenerate the active enzyme again. So, that is why the intermediate nature of binding or intermediate strength of the binding is important.

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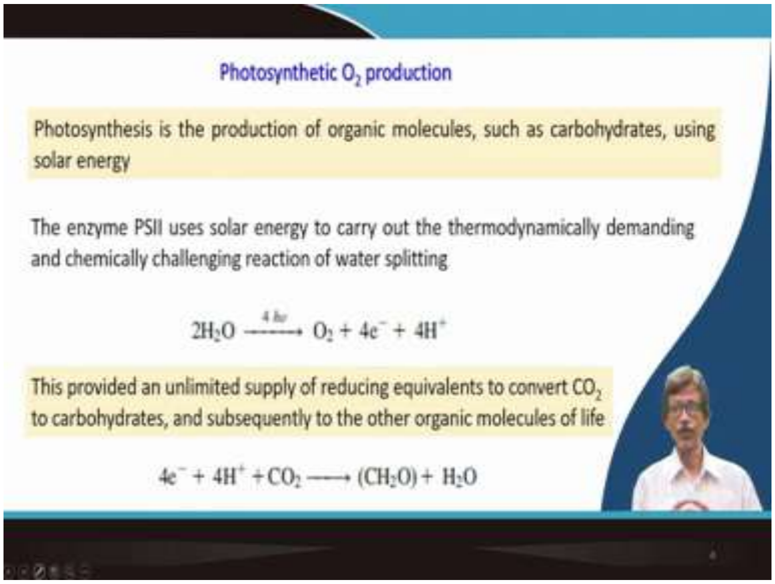

Photosynthetic $O_2$ production

Photosynthesis is the production of organic molecules, such as carbohydrates, using solar energy

The enzyme PSII uses solar energy to carry out the thermodynamically demanding and chemically challenging reaction of water splitting

$$2H_2O \xrightarrow{4\,h\nu} O_2 + 4e^- + 4H^+$$

This provided an unlimited supply of reducing equivalents to convert $CO_2$ to carbohydrates, and subsequently to the other organic molecules of life

$$4e^- + 4H^+ + CO_2 \longrightarrow (CH_2O) + H_2O$$

So, what we now see is that your photosynthetic autoproduction. How come it is related to your photosynthesis. So, if we focus our attention the last part maybe it is the autoproduction like your last step of electron transport to your water molecule when we burn our food molecule or the glucose molecule or the carbohydrate.

So, what do we do basically, because the photosynthesis mainly devoted to the production of the glucose molecule, which is nothing but your organic molecule, so it can be your carbohydrates also using solar energy. So, you require H nu. So, is a synthetic process where we will be utilizing H nu. So, how the light can help us?

But you can have two things, one is your photosystem I and another is your photosystem II. And photosystem I will be involving the corresponding thing what I learnt earlier in relation to magnesium. So, is magnesium bound chlorophyll, but in case of this photosystem II, we will get something else which is based on manganese.

So, basically, the solar energy is required or used up to carry out the thermodynamically demanding and chemically challenging reaction of water splitting. What does it mean basically, because we want to go for the splitting, that means your OH bond is not that simple OH bond removal and getting that particular O2 minus that means the oxide ion is not that is the water splitting.

But you have to go for new interaction between two oxygen centers such that you can have O type of interaction like your peroxide or superoxide then you can have the corresponding O2 formation that means O double bond O formation. So, O-O formation is important from the molecule which is your water. So, if you just consider the number of H nu also people calculated it all these things, because from your childhood also you are knowing that what is photosynthesis.

But we never thought of this particular thing. We are not asked to learn this also nicely about the production of oxygen. We are only interested to know about the formation of the hydrate of carbon. That is why it is carbohydrate. So, how you put, basically, we write it also the form in that way the C and H2O. But that is not the thing. But the molecular composition will be like that CH2O that is the hydrate of carbon and some number n.

But when you talk about the other thing, the more complicated one, the splitting of water molecule and the corresponding production of O-O based auto molecule, so we see that here again the reverse one basically when we take this $O_2$ to produce water we have seen during the burning of your food material, we did the reverse thing, that means we have consumed $O_2$ molecule for burning your food material and producing $H_2O$ molecules.

So, we do the reverse reaction. So, again is a particular step where you can have the involvement of four electron and four proton transfer reaction. So, that four proton, four electron transfer is important and there we find that is important to provide that particular reaction and if the reaction is pretty complicated for that four electron transport because always focus your attention when I am telling you that okay is four electron transfer at a single step.

So, earlier we have seen that corresponding case where you have the CCO cytochrome c oxidase reaction. There also you have the binding of the $O_2$, then you have the iron center and the copper centers were involved for the transfer of four electrons to the $O_2$ molecule. Similarly, when we go for the conversion of this particular $CO_2$ to the carbohydrates, we find that there will be some reactions where the other molecules also we can form.

So, basically, if you now take those four electrons and four protons and add it to the carbon dioxide so is a major concern for us also, again in terms of your environmental chemistry or the environment that the four electron and four proton transport can be done on the greenhouse gas carbon dioxide, which is a very notorious greenhouse gas.

So, this greenhouse gas $CO_2$ can be converted to $CH_2O$, the carbon and its water, that means hydrate of carbon, that is why it is carbohydrate, and with the elimination of one molecule of water over there and we go for this particular conversation.

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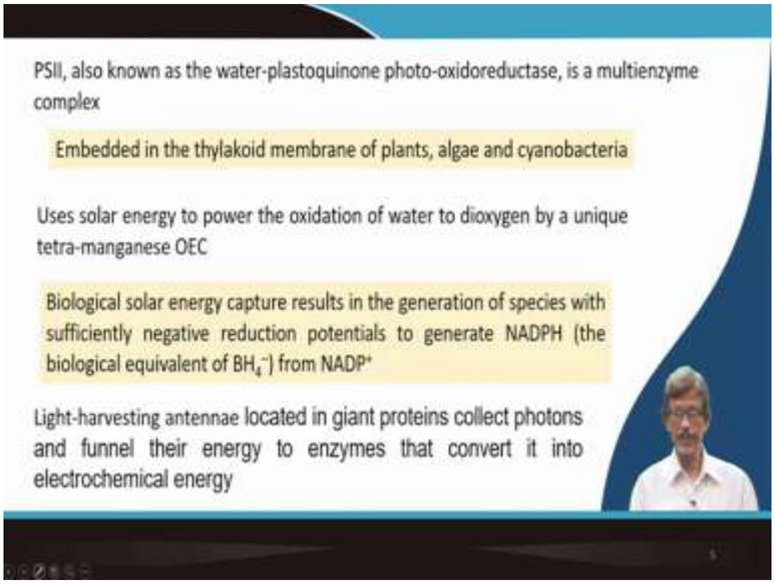

PSII, also known as the water-plastoquinone photo-oxidoreductase, is a multienzyme complex

Embedded in the thylakoid membrane of plants, algae and cyanobacteria

Uses solar energy to power the oxidation of water to dioxygen by a unique tetra-manganese OEC

Biological solar energy capture results in the generation of species with sufficiently negative reduction potentials to generate NADPH (the biological equivalent of $BH_4^-$) from $NADP^+$

Light-harvesting antennae located in giant proteins collect photons and funnel their energy to enzymes that convert it into electrochemical energy

So, PSI little bit we talked about when we were talking about the corresponding magnesium and chlorophyll, now we will talk about only PSII in this particular class, is nothing but a water-plastoquinone photo-oxidoreductase molecule. So, you require the involvement of water, involvement of the plastoquinone that means, the oxidized form of the quinol, and then the photon is required for your oxidation reduction reactions, and therefore, it is a multi-enzyme complex.

Earlier also you have seen your cytochrome c oxidase that many such species are their complex I, complex II, complex III and complex IV. Similarly, this can also be a multi-enzyme complex, but we will only focus on that particular manganese-based system or the manganese-based catalysts where we see something where you can explain or identify the corresponding intermediates for your O2 production.

So, this particular PSII is basically fixed or embedded in the thylakoid membrane of plants, algae and cyanobacteria. And you have to take H nu, that H nu is the energy source to power the oxidation of water to O2 a unique tetra-manganese center which we call as the oxygen evolving center or oxygen evaluating center or oxygen evolving center, anything you can say, oxygen evolution center. So, you have to take out oxygen and people were excited when they first discovered is as a tetra-manganese system like your tetra-iron ferredoxin oxygen molecule.

So, the system of tetra-iron ferredoxin is older one little bit, but this discovery of tetra-manganese OEC is a new one. So, now, we have immediately that answer in your hand that since we are having the four manganese centers and if we are able to change the oxidation stores of each manganese center by one unit, we will be getting four electrons and the removal of the corresponding hydrogens or the protons from the water molecule give you the four protons in number.

So, basically what the solar energy H nu at a particular frequency we all know that the, our green vegetables are green in color because the chlorophyll and any other related molecules the pigments, we call them as the plant pigments, plant pigments are too strong absorptions beyond the green region that means either blue region or the red region, so you have the absorption in the blue region and the red region that is why your plants and all these vegetations are green in color.

So, in that particular region if we get the corresponding h nu, because why it is green, because it is absorbing blue as well as it is absorbing red light. But longer wavelength is your red light. So, it can be red light activated thing.

Say around 700 nanometer if you utilize that particular energy to excite the system, what will you get, we will get something that where the generation of some species which are having the negative reaction potentials to generate the NADPH, already we know what is NADPH, and like us, like inorganic chemist, an inorganic chemists love to stay that way that it is the biological equivalent of borohydride coming from sodium borohydride NABH4.

So, it is very strongly reducing one. So, that way you get it from NADP plus. And NADP plus we have seen earlier that it can give you the NADPH. So, it is a valid thing also in learning about NADP and NADPH also. So, what we harvest? We basically harvesting light.

And that light at a particular wavelength say around 680 nanometers can be trapped by some antenna, we call the signal, like that the radiation absorption can be through the antenna located in the giant proteins called photons and collect the photons then and funnel their energy to enzyme to convert it to the electrochemical energy. So, that is why the photon energy h nu will be converting to a electrochemical gradient and that electrochemical energy is required for your conversion.

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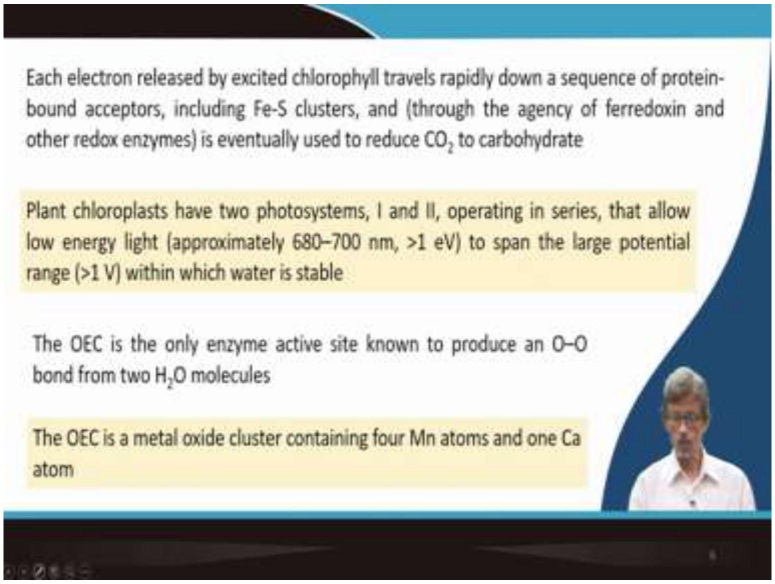

Each electron released by excited chlorophyll travels rapidly down a sequence of protein-bound acceptors, including Fe-S clusters, and (through the agency of ferredoxin and other redox enzymes) is eventually used to reduce $CO_2$ to carbohydrate

Plant chloroplasts have two photosystems, I and II, operating in series, that allow low energy light (approximately 680–700 nm, >1 eV) to span the large potential range (>1 V) within which water is stable

The OEC is the only enzyme active site known to produce an O–O bond from two $H_2O$ molecules

The OEC is a metal oxide cluster containing four Mn atoms and one Ca atom

So, when you have the excited chlorophyll, the photon is exciting your chlorophyll and it travels rapidly down a sequence of protein bound acceptors including your iron, sulfur protein, the ferredoxin molecules are involved. So, though are involved for electron transport chain only. So, through the involvement of your ferredoxin or any other redox enzyme and it eventually reaches to your CO2 molecule. That is what we can have.

We can have the plant chloroplasts, we have PSI and PSII, and they allow a low energy light that means the red light, the red light of approximately 680 to 700 nanometers of energy greater than one electron volt basically and that is why it is basically a span a potential of one volt. So, in electrochemical scale, basically, we know it is one volt versus NHE or versus saturated calomel electrode. So, we find that this particular window your water is terrible.

So, then how to break the water molecule? So, we required this OEC center is only enzyme active site known to produce an O-O bond from two water molecules. So, that is our primary goal that how we can attach these to oxygen and we get O-O molecule. So, if we can have metal ion oxido, not like that metal oxide is metal ion and oxido related cluster containing four manganese ions, but not only four manganese, but you have to distort the structures in such a way that our functional property is important, the reactivity is important, that is why it is not a very regular and symmetrical Mn4 system.

It is asymmetry because the calcium will come and will try to distort this Mn4 unit such that you require more distortion and more loosely bound interactions with those of manganese center, because the manganese center can go to a high oxidation state. And as you move to the high oxidation state, what happens that your interaction with that oxygen centers will be stronger and stronger. So, that way for the release of that particular O2 molecule will also be challenging in that particular point.

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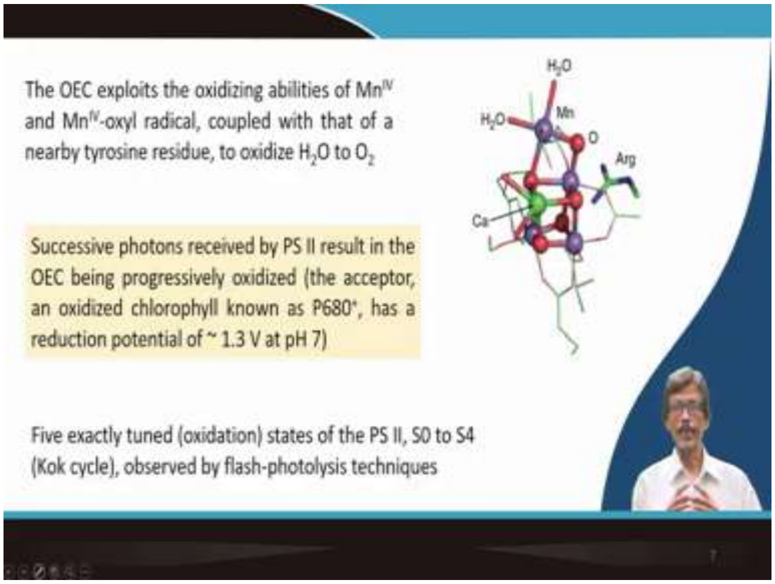

The OEC exploits the oxidizing abilities of $Mn^{IV}$ and $Mn^{IV}$-oxyl radical, coupled with that of a nearby tyrosine residue, to oxidize $H_2O$ to $O_2$

Successive photons received by PS II result in the OEC being progressively oxidized (the acceptor, an oxidized chlorophyll known as $P680^+$, has a reduction potential of ~ 1.3 V at pH 7)

Five exactly tuned (oxidation) states of the PS II, S0 to S4 (Kok cycle), observed by flash-photolysis techniques

So, if we allow them, now, let us see whether we can reach up to a oxidation state of tetravalent manganese or a manganese 5 state also, sometimes people are proposing that it can have the manganese 5 also, but is not that is the manganese 4 oxyl radical or some organic molecule like tyrosine can also happen to give you that extra electron through oxidation. So, is basically oxidized species. The four metal iron manganese along with one calcium, so it is Mn4Cs system.

So, this Mn4Cs system is basically giving you a oxidized form and that oxidized form can be useful. If you have some tyrosine residue, you can oxidize the tyrosine residue also, because sometimes it is very difficult to identify the form, because you cannot get the access structure, because these are very fast thing happening within milliseconds or less than that time scale.

So, what you can have? The basic structure you should know. The entire thing is the protein entities are coming out. Then one residue which is nearby is also sowing as the arginine residue. So, this arginase amino acid is there. And then you see the manganese. So, one particular manganese, you can have the bound water molecules and others are fixed with either hydroxides or the oxide units.

So, successively you can have the transfer of these photons giving you a oxidized form where the acceptor and oxidized chlorophyll known as P680 plus that means it is oxidized already. So, that means, oxidized is the ligand peripheral part, the porphyrin part can be oxidized which is your, P is your porphyrin. So, that P can be oxidized. So, P680 means the 680 nanometer is utilized and is oxidized form.

But is strongly reducing when one is oxidized that means the oxidized form, so whether we will have a oxidized form of manganese in the trivalent or the tetravalent state or your oxidized chlorophyll can have more demand of electron that means they are oxidizing definitely so that is why they are attracting electron to take up.

And the potential, the thermodynamic electron transfer potential is important which is 1.3 volts is therefore a strongly reducing species at pH 7. Then if we find that your life is much more complicated, not only the four manganese but you can have five different states of oxidations. So, these five exactly tuned states has been identified. Is not the mixture of things and is not very well defined.

So, people have this particular informations from the long back when people first identified the Kok cycle they know that several steps are there and how much time is required to observe all this thing is also there. But the kinetic thing, a first kinetics is happening, potential we know, but the rate of electron transfer is important. We can go for a spectrophotometry based technique which is flash-photolysis technique. So, this flash-photolysis technique can tell you or identify the different steps which are involved over there and which are really taking part over there.

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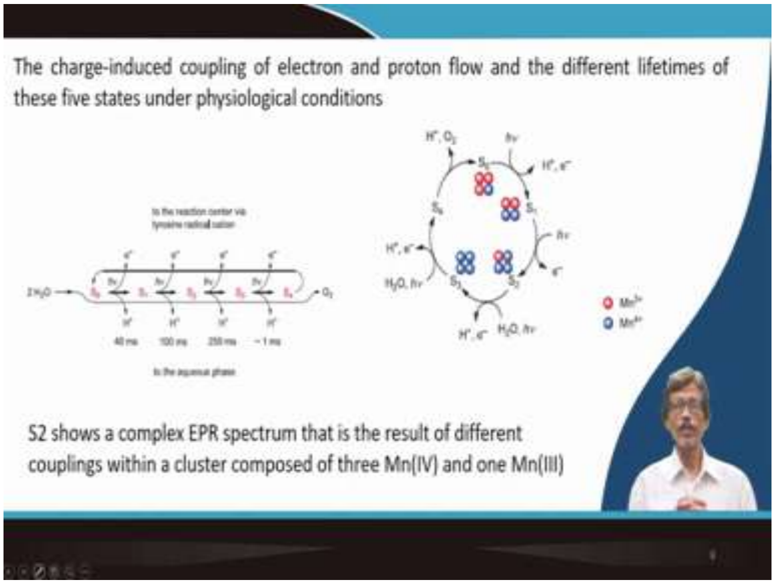

The charge-induced coupling of electron and proton flow and the different lifetimes of these five states under physiological conditions

S2 shows a complex EPR spectrum that is the result of different couplings within a cluster composed of three Mn(IV) and one Mn(III)

So, the charge induced coupling of electron and proton flow is important and you have the five states and the five physiological conditions you can have. So, water is entering and you can have 1, 2, 3, 4, S0 to S4, so these are the steps basically. And to the reaction center via tyrosine radical cation what you are transferring those electrons. So, you require four electrons. You see four intermediate steps when you are settling between S0 to S4 and you get four electrons and inside you enter the four protons and ultimately will be getting O2 molecule.

So, if you try to put now all these four metal ions together with manganese red in sphere is the trivalent manganese and tetravalent manganese is in blue in sphere. So, how much electron you can take up and how it is going from one particular point to the other that we get from there and that basically tells us that how easily or how nicely we can understand these things. So, what is S0, what is S1, what is S2 and what is S3, is well established people identified it.

Many spectroscopic techniques, the magnetic property, the model compounds all these have identified these particular steps. But S3 you are getting with the introduction of the water molecule, but S4 you are getting with the introduction of the second water molecule and then again you have the electron transfer, but finally, this S4 is the crucial pieces.

Out of all these you know the structure at one point, you can identify S2 spectroscopically, you can structurally we can determine one particular state. But what about S4, why S4 is important, because S4 you see the catalytic loop, you will find that the arrow, the related arrow one is reaching you to S0 and another is delivering something which is your H plus, plus O2.

That means the species S4 is important for the release of your O2 molecule and that is therefore the most important and the basic crucial thing where from we can get the O2 molecule nicely, because we all know we are dependent on oxygen. We are also surviving on oxygen, but how the plant is producing that particular oxygen.

So, spectroscopically we can identify the S4 state, which shows the characteristic EPR spectrum and these particular metal ion centers all of them are paramagnetic manganese 3, manganese 4, all of them are paramagnetic, but they are coupled together. So, they are either ferromagnetically or antiferromagnetically coupled to each other.

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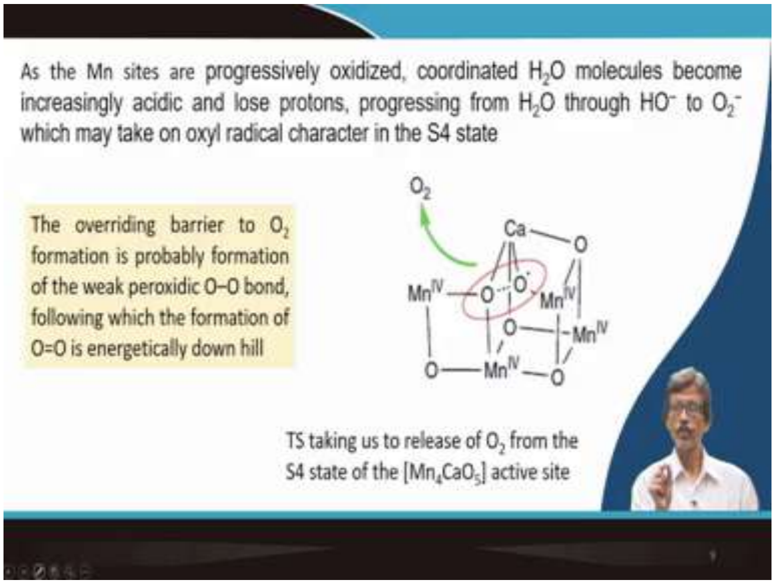

As the Mn sites are progressively oxidized, coordinated $H_2O$ molecules become increasingly acidic and lose protons, progressing from $H_2O$ through $HO^-$ to $O_2^-$ which may take on oxyl radical character in the S4 state

The overriding barrier to $O_2$ formation is probably formation of the weak peroxidic O–O bond, following which the formation of O=O is energetically down hill

TS taking us to release of $O_2$ from the S4 state of the $[Mn_4CaO_5]$ active site

So, as we are moving, as we are going for these oxidation reactions, the O2 molecules are giving you the hydroxide ion, as well as the oxido ion. So, either you can have this not is O2 minus is O2 minus the oxide ion, there is a mistake there, just correct it, that not HO minus 2, O2 minus and then you can have the oxyl radical character. Basically, you have to find out the character like the superoxide character we have established in case of your myoglobin and hemoglobin.

So, what is the character which is bound to your S4 state such that the formation of your O2 is there and O bond formation is taking place following which basically what we get that energetic any downhill thing can form and that basically taking something where we get that your transition state taking us to release your $O_2$ from the S4 state of the $Mn_4CaO_5$ system or the active site, because you require five oxygen atoms or oxygen ions as oxide ions to sustain that particular aggregate.

Now, this is the whole structure what we have started our journey, where from we have started our journey is the assembly of all these things. Now, you see where your thing is happening that you require the involvement of calcium, you require the involvement of all other four manganese centers which are tetravalent in nature.

Now, when thing is under control of all these things, so your one of the oxide iron is there, then you have to put another one which is coming from say water molecule also or it can be broken from some other place that means you can have the interaction. So, OE was connected earlier. Now, you have the $O_2$ is inside. So, that formation of the bond and the breaking of the bond can take place in a different way that OE is coming there taking the control of one oxygen which, where under control of so many metal lines.

Now, when the release is taking place, this O-O bond is stronger now. So, your $O_2$ molecule is forming. You can have the super peroxide initially single bond, then superoxide 1.5 bond and then your dioxygen, molecule which is a double bond. So, if your O bond is strong, it will just try to release from the system. So, your $O_2$ will be released from the system as dioxygen molecule.

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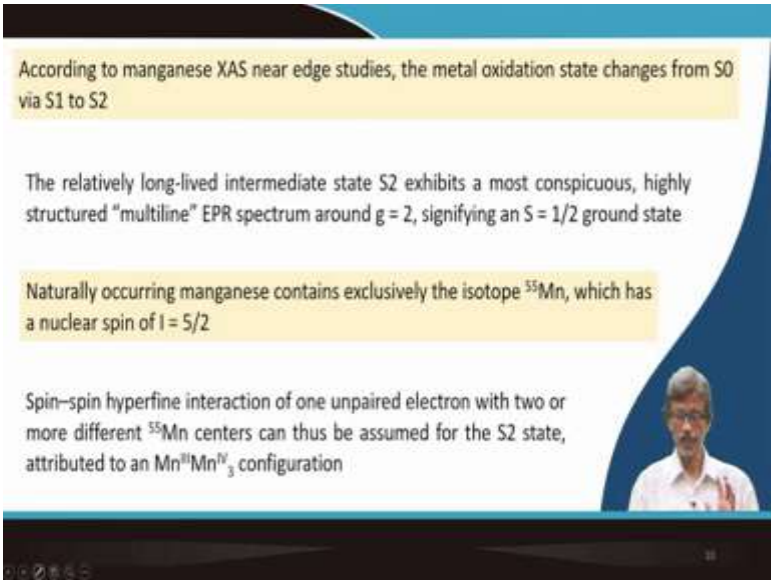

According to manganese XAS near edge studies, the metal oxidation state changes from S0 via S1 to S2

The relatively long-lived intermediate state S2 exhibits a most conspicuous, highly structured "multiline" EPR spectrum around g = 2, signifying an S = 1/2 ground state

Naturally occurring manganese contains exclusively the isotope $^{55}$Mn, which has a nuclear spin of I = 5/2

Spin–spin hyperfine interaction of one unpaired electron with two or more different $^{55}$Mn centers can thus be assumed for the S2 state, attributed to an $Mn^{III}Mn^{IV}_3$ configuration

So, you have many spectroscopic evidences like x-ray absorption near edge spectroscopy to find out all other features, EPR is also there which can identify all these things and the manganese 55 EPR is also very much characteristic, because you have I is equal to 5 by 2. You already know about copper. How many signals you get for your hyperfine spinning that also you can calculate out and find it out.

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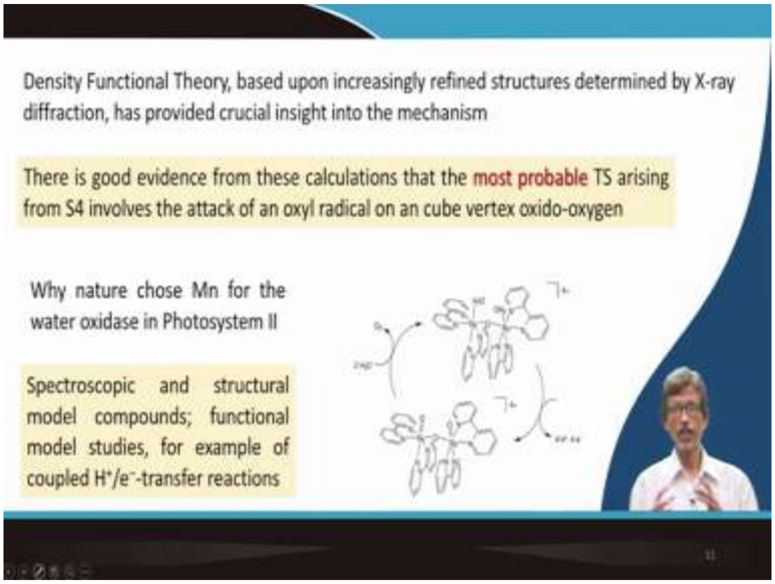

Density Functional Theory, based upon increasingly refined structures determined by X-ray diffraction, has provided crucial insight into the mechanism

There is good evidence from these calculations that the most probable TS arising from S4 involves the attack of an oxyl radical on an cube vertex oxido-oxygen

Why nature chose Mn for the water oxidase in Photosystem II

Spectroscopic and structural model compounds; functional model studies, for example of coupled $H^+/e^-$-transfer reactions

So, lastly, we just go before that you can have the theoretical establishment that DFT can also establish the corresponding mechanism and where you can have the involvement of the S4 which is the most probable one and which is giving you the transition state. And we can also ask that why manganese is being chosen only and why the manganese taking place over there. You go for the model reaction. So, take a ruthenium compound and where that particular ruthenium compound can also release O2 molecule from the water molecule that also people have identified and established nicely.

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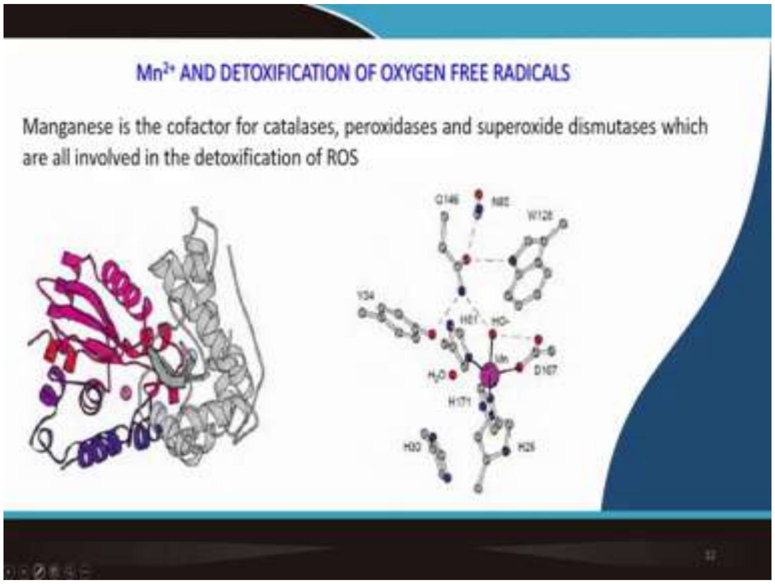

$Mn^{2+}$ AND DETOXIFICATION OF OXYGEN FREE RADICALS

Manganese is the cofactor for catalases, peroxidases and superoxide dismutases which are all involved in the detoxification of ROS

Then quickly we will see the last part that means the detoxification of the reactive oxygen species ROS by Mn2 plus. So, you have this. How the superoxide dismutase can work, like your iron SOD is the manganese SOD and that manganese SOD can very much useful, because the mononuclear side and the two step reaction. So, the environment you now find that you have the carboxyl environment and you have the imidazole environment also and then you have the water bound condition also for one particular monodentate coordination.

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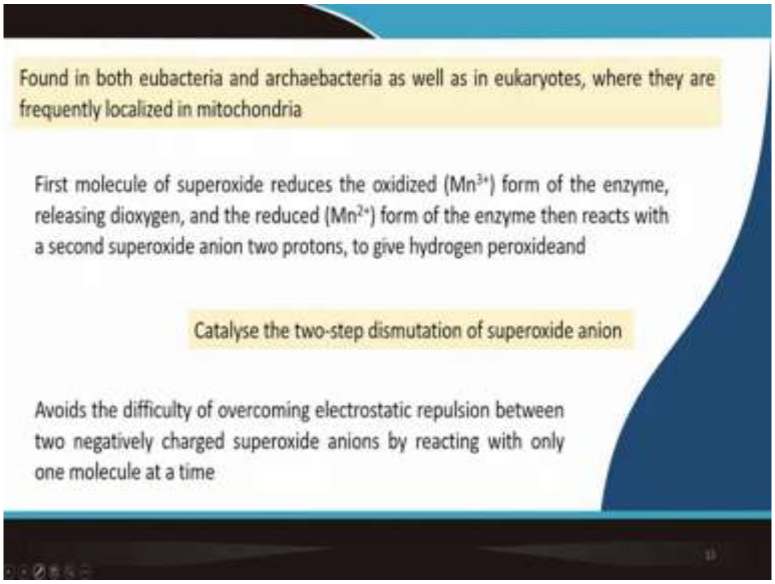

Found in both eubacteria and archaebacteria as well as in eukaryotes, where they are frequently localized in mitochondria

First molecule of superoxide reduces the oxidized ($Mn^{3+}$) form of the enzyme, releasing dioxygen, and the reduced ($Mn^{2+}$) form of the enzyme then reacts with a second superoxide anion two protons, to give hydrogen peroxideand

Catalyse the two-step dismutation of superoxide anion

Avoids the difficulty of overcoming electrostatic repulsion between two negatively charged superoxide anions by reacting with only one molecule at a time

So, eubacteria to archaebacteria everywhere there. You can have also in the eukaryotes. So, they are in the mitochondria and manganese like copper. There we have seen that copper can settle between cuprous and cupric, manganese can settle between manganese 2 and manganese 3 plus you should know what we have the understanding about that E0 value for the copper system and E0 value for the manganese system, whether that is matching for the disproportionation reaction of the superoxide what we have learned in case of your copper zinc SOD.

So, you just simply use that particular information what you have learnt over there and apply it over here to identify this thing. So, this particular thing can avoid the electrostatic repulsion between the two negatively charged superoxide molecules.

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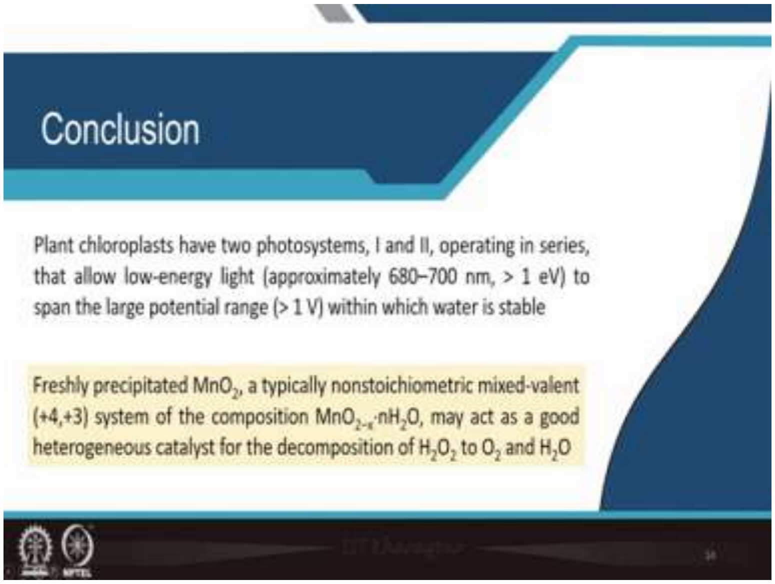

## Conclusion

Plant chloroplasts have two photosystems, I and II, operating in series, that allow low-energy light (approximately 680–700 nm, > 1 eV) to span the large potential range (> 1 V) within which water is stable

Freshly precipitated $MnO_2$, a typically nonstoichiometric mixed-valent (+4,+3) system of the composition $MnO_{2-x} \cdot nH_2O$, may act as a good heterogeneous catalyst for the decomposition of $H_2O_2$ to $O_2$ and $H_2O$

So, we have seen so far that your plant chloroplasts is important. Both PSI and PSII is involved in a particular wavelength region with a particular potential for your water oxidation. And then we have seen also some example whether the simple, our laboratory understanding, the laboratory knowledge of formation of immediately precipitated manganese dioxide can go for some decomposition reaction of hydrogen peroxide that is well known.

But that activity is very much different activity what we have seen for the SOD, but is related it is the relation the model activity of this particular species for your catalyst activity. So, the reactive manage can give you so many important information relative to is the activity point of view.

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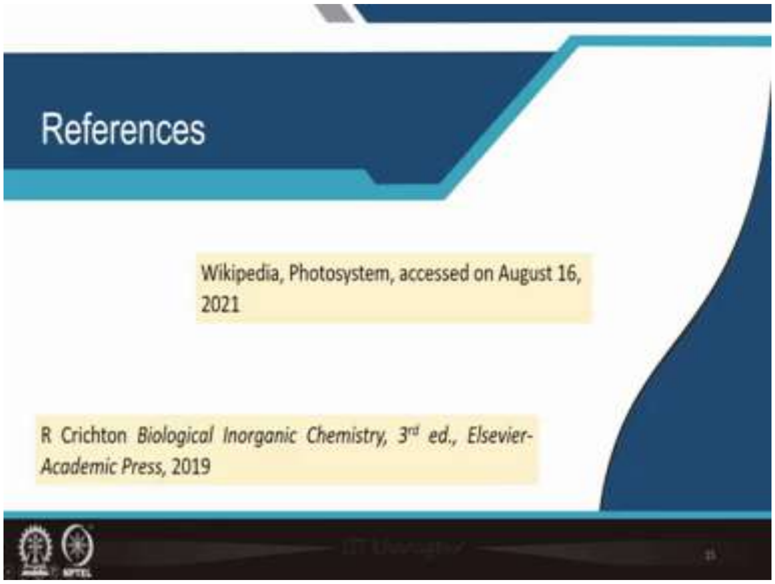

## References

Wikipedia, Photosystem, accessed on August 16, 2021

R Crichton *Biological Inorganic Chemistry*, 3rd *ed., Elsevier-Academic Press*, 2019

So, you go again, start from your study with the Wikipedia page on photosystem, then the manganese and the presence of manganese in the biochemistry also, and finally, the book of Crichton. So, thank you very much for your kind attention.