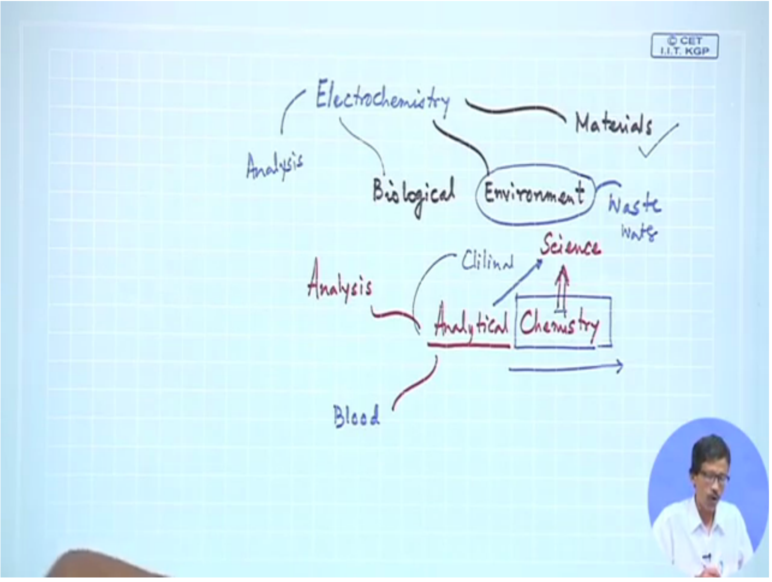
Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 12
Lecture No 58
Applications (Contd.)

(Refer Slide Time: 0:26)



Good morning everybody so as we are proceeding towards the end of this course uhh where we are now discussing in an elaborate fashion, the electrochemistry and how it is applicable to analysis or development of new techniques in analytical chemistry so analysis and also today we will see and we have also given you some examples for that that how this particular part that means the electrochemistry can be beneficial to handle biological samples such as proteins, metal enzymes et cetera as well as the environment and the materials.

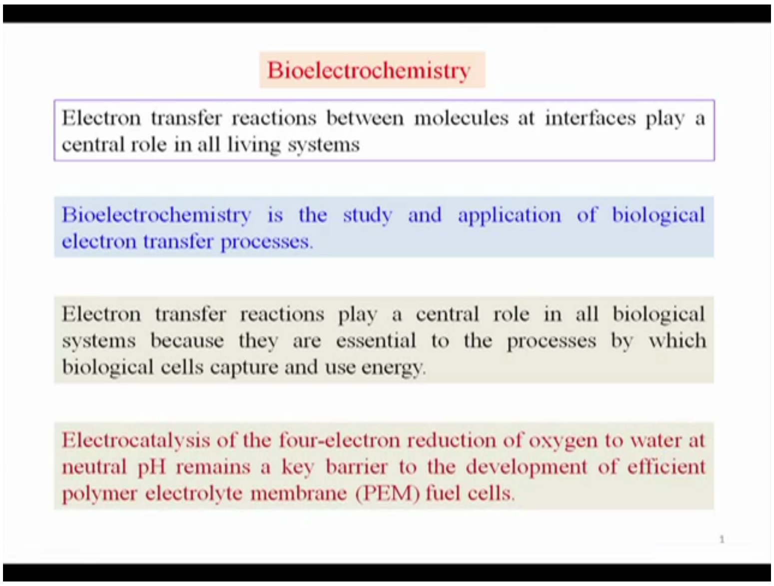
So in a sense that the whole (())(1:15) of analytical chemistry what we are talking so far and will be talking the next 3 classes is based on something where we talk that we are doing some analysis and is the methodology development or some analysis of some real-life samples that will probably discuss in our last class that how you tackle or handle the real samples, so the analytical chemistry what we can have and what we have discussed so far this particular part is very important because this when we attach for depending upon the sample basically when you go for say analysis of blood sample, what we put? We make this as the clinical one only.

When you go for these materials make is as the analytical chemistry (())(2:21) analyse the materials particularly with the development of any such films and all these things which are required for your electrochemical measurement can come under this category and as we are proceeding towards the end of this course you must have the typical realisation that in all cases chemistry is not playing the major role or the important role.

It is the thing can be developed which is based on, the basis, the fundamentals is on chemistry but slowly we can apply to all branches of science, all areas of science even history, geography, geology all these things. So slowly we are as we finish the course we will have the realisation that whatever you have studied in this particular course, the basics and the fundamentals we have started from the school level chemistry knowledge then we applied what are the analysis and what are the different analytical techniques we can have and now as we move towards the end of this course you can consider this as a typical analytical science.

So is a separate branch of science definitely we can consider where we can have the typical foundation uhh we can have because most important area what people are talking about the environment (())(3:46) to tackle the waste water problem or the effluent water from the industry, the river water, the seawater and on the lake water. So talking all these things so environmentalist also can think of this thing but without going for a very good or sound knowledge of chemistry they can tackle these problems by simply saying that okay whatever I am handling is based on your analytical science, okay.

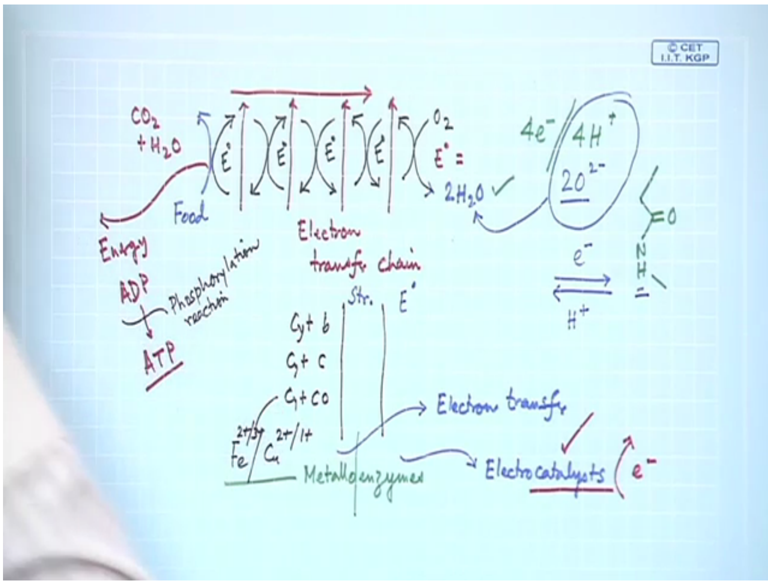
(Refer Slide Time: 4:24)



So what we will now go for is your biological part that how we can apply this for your bioelectrochemistry studies, so bioelectrochemistry studies will be definitely very important as we have seen that some part we have exposed also during the development of the sensors because these are very much interrelated that development of the sensors, that corresponding fabrication of the electrode and what are the solutions we basically handle.

So the basics and the fundamentals what makes your knowledge of analytical chemistry and the electrochemistry in particular and now the bioelectrochemistry is that, it should be very easy to understand if we consider something related to the reaction what we are thinking or what we are talking about the 2 electrodes the cathode and anode.

(Refer Slide Time: 5:23)



So for the molecules which are coming from the living systems and the electron transfer reaction basically as I told you that whatever you have that what we want to burn the food material what we consume so as a result this particular branch is also the cable to your food chemistry, agricultural chemistry also. So food we are trying to burn to get carbon dioxide and water with required amount of energy elimination.

Why we require that energy because we have to synthesize ATP molecules from ADP so this is basically known as the corresponding phosphorylation reaction but it has some energy (()) (6:05) definitely, so your phosphorylation reaction. So what we have seen for our electrode reactions that we can get these like this sort of thing what we all know now, these sort of things okay.

So these are basically thing what we can have then, then for your O2 because will be burning your food material with that of your O2 that we know that how you synthesize your carbohydrates and proteins and fats so and at one time you have to burn this, so O2 will go for 4 electron 4 proton reduction to give you 2 molecules of water, so this is the ultimate thing and in between what you can have you can have all these things are related to something what we call as electron transfer chain.

So we have the electron transfer chain so as we all know that this is also well-known to was where O2 can be reduced to water molecules and we all know the corresponding E0 value is 1.23 versus (())(7:37) and it sometimes the corresponding O2 if you want to measure by cyclic volumetric technique that also gave us some idea that with respect to your SCE or uhh the silver silver uhh electrodes it will come close to 0.8 volt.

So this magnitude so O2 is a very strong oxidising agent compared to the material life food what we are trying to oxidise, so during this electron transfer chain we can have certain mediators what we have discussed in considering the corresponding when you are considering rather that how we develop a particular electrode for the sensing mechanism of O2 or the sensing mechanism for your glucose.

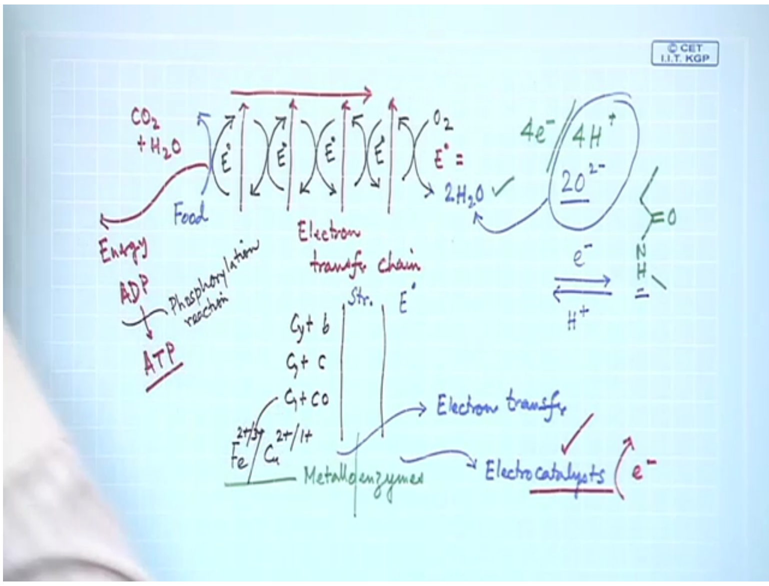
So your electron transfer chain is there and it slowly goes like this, so this is the reductant really which can be oxidise by this and at different steps of this in this electron transfer chain you have the corresponding amount of the corresponding E0 values for this couple because all these are attached with what? Your oxidant as well as the reductant, so is the pairwise so pairwise it can be a mediator, it can be an enzyme what we have seen that there are glucose oxidase is oxidised form and the reduced form when it accepts the electron.

So these things are there so these all are coupled with this E0 value so you will have for all this E0, so successively as we move from left to right the E0 values are increasing, so when we come to the left similarly your E0 value is very less that means your food material attached to this particular oxidising agent is not so exothermic in nature as a result we can say that your food is not getting burned.

So in a regular fashion in a very systematic manner we try to oxidise the food material in a step wise manner such that all these things particularly this are basically the different cytochrome, the cytochrome b, the cytochrome c and cytochrome c oxidase also CCO we call. So the at the end we have the cytochrome c oxidase so which is a very complex molecule for all this thing but in terms of this E0 values because this can be labelled depending upon one is the corresponding classification for these molecules as their structures.

So BC and CO that means cytochrome c oxidase in terms of the different structure as well as you can have the different E0 values. So we get the progressively your E0 values will increase ultimately it is reaching the corresponding dioxygen water couple, it reaches the dioxygen water couple so we can consider this as the good redox mediators, so these good redox mediator which are coupled nicely that required number of ATP are also synthesised during this transfer.

(Refer Slide Time: 10:59)



So what is this particular example what is told in terms of the corresponding uhh language that electron transfer between molecules so the molecules are now your mediators like cytochrome, the different cytochromes in the cytochrome electron transfer chain at interfaces, so when these are basically attached with this, so this is their so is there you have the corresponding one which is accepting that electron from that particular food material so uhh it is getting oxidised form and this is getting reduced form.

So reduced form is again attaching with that particular species which is getting oxidised, so oxidation reduction, oxidation reduction keep on going from left to right so is an interface a central role is playing for all living systems because you require the electron transfer, you require the energy development or the energy currency by burning of the food material such that we can have the required number of ATP molecules that particular process.

So when you talking terms of this electron transfer or definitely we can talk in terms of the bioelectrochemistry which can be a study and application of biological electrons transfer processes so it is a biological typically a biological electron transfer processes what we can have and is definitely a study how the electron transfer is taking these and how we can apply also.

Once we know that we can monitor this electron transfer in terms of your food material or oxygen reduction we can have some good application also and 2 very small applications we have seen for the development of the sensors, so all these different electrons transfer processes initially we can monitor for their thermodynamic electron transfer potential values means E half values are E0 values for their cell, what is formed between the cathode and the anode for that particular electron transfer reaction.

So when these are there so when they are playing some essential role in all (())(12:59) systems so when this that means uhh playing a central role in biological systems, it can be essential for the process is in which of biological cells captures and use energy, so how the energy is getting and how you use that energy equally from the burning of the food material or any other material which is typically a reductant or a reducing agent, so your food material is typically reducing agent your carbohydrate, your glucose is the typical reducing agent which can be used for reducing some other groups and then ultimately will be going for the reduction of your dioxygen molecule which is the ultimate oxidant.

So these things basically can be a keyword your electron transfer, your bioelectrochemistry and one thing is also there electrocatalytic thing because this cytochrome and all these are is we all know the sum of them are containing metal ion, so they are uhh metalloenzymes we call so this cytochrome C oxidase is also you have iron center and you have copper centre. So iron 2 plus is settling between 2 plus and 3 plus and this is between 2 plus and 1 plus.

So this basically goes for these things so what we can level this as typical metalloenzymes, so these metalloenzymes so will take out this part that means they are enzymes definitely by definition they will be enzymes and we can talk their nature in terms of the enzymes and these metal ions are responsible for electron transfer, electron transfer. And if this is a typical cycling process that means it is going to oxidised form and going coming back to the reduced form as we find by determining the cycling voltammetric pattern of the potential for these electron transfer reaction and it can go for an number of cycles in this particular process.

So you have enzymes, you have electron transfer, so it can be termed as electrocatalyst also. So our idea behind all these studies and knowing the corresponding applications is that how we can get a catalyst which can show some reversible electron transfer reaction, so we have to develop some catalyst is not some other catalyst we know that is not going through electron transfer reactions, so they are redox catalyst or the electrocatalytic because the development of all these things can solve so many problems related to electron transfer and we have to develop this good material as the catalyst.

So we get the idea from the biology so biological electrocatalyst we see little bit and if we can have some hybrid mechanism that you can get the material or the biological electrocatalyst from the biological or the living world you going to apply that to some synthetic mechanical thing that means some electrodes or the some cells we can develop in the laboratory.

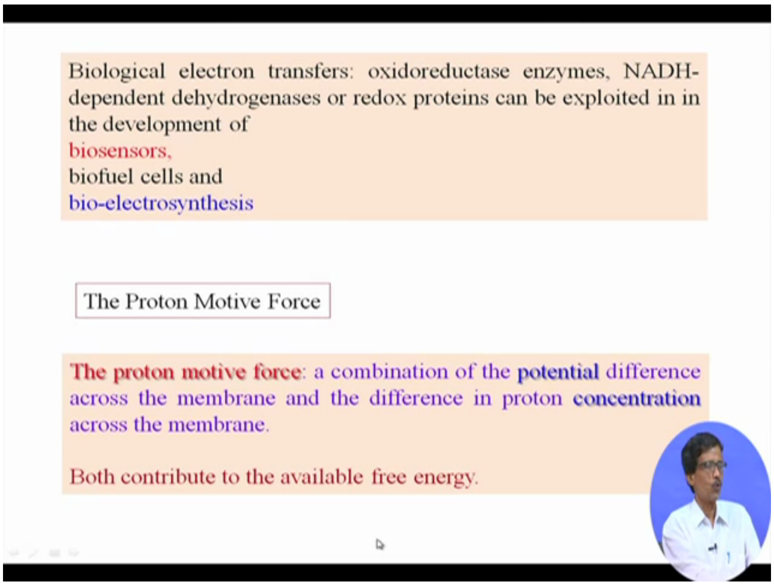
So one such example then again we are talking about the oxygen to water conversion that means the 4 electron 4 proton reduction of O2 to 2H2O we can see that for that electron catalyst is for the 4 electron reduction of oxygen to water at neutral pH remains the key barrier to the development of efficient polymer electrolyte membrane fuel cells.

So now we are talking in a single line so many important lines to be understood that if you have the idea that we are getting all these information from the biological world, the electro-catalyst is for very simple substrate like your sensing that go to molecule as your Clark oxygen sensor but at a neutral pH is not that it is driven by acidic pH or the basic pH it remains a key barrier for the development of efficient PEM fuel cells.

So we want to develop a fuel cell such that it can use that living system that means the biological molecules as the corresponding fuel for the cells and a polymer electrolyte membrane because membrane we already know now how we can use the membrane on the electrodes surface which can allow preferentially some to go and some should not so the development of this PEM based fuel cells can be a immediate target of those things where the pH is a neutral pH.

So is definitely we have the target we have the problem in our hand how we can develop all these things because definitely you have to try for a system for end number of times then only you get you achieve something where we can go for a very useful membrane type of fuel cell which can be used for generation of your electricity, the future electricity.

(Refer Slide Time: 18:13)



So biological electron transfer that is why we are pushing it to a biological system, a biological electron transfer reactions are very important and already we have seen in the development of biosensors. Now we will talk little bit about the bio fuel cells and if possible if time permits definitely you can have what it is you should know at this point that can have some synthesis as you know in the chemistry terminology that when we make a molecule we go for a plus b the target is c and sometimes some other part is also like water molecule like carbon dioxide is coming out as d or e molecule.

So synthesis is there but if it is going for electron transfer only then electron transfer can take place and then bio electrosynthesis is the biological molecules can be modified by electron transfer reaction to get some useful synthetic molecule which can have application as medicine or some other good purposes. So this biological electron transfer can be tackled by something where we see that one particular terminology he should be able to understand that nicotinamide added in dinucleotide that reduced form NADH we call.

So these are basically the co-factors the biological (())(19:30). So this dinucleotide in the reduced form can shows some reactions where it is independent, so oxidoreductase enzymes, so you have the oxidation reduction reactions so both are coupled together instead of saying them as redox enzymes we call them oxidoreductant enzyme, so these redox enzymes are NADH dependent dehydrogenases or redox proteins can be exploited in the development not in in, in the development of all these things.

So like your glucose oxidase your NADH is some other molecule and if it is in the reduced form definitely should know that this is the reducing agent in the (())(20:15) the corresponding mediator business and one important mechanism or one important characteristic will be useful there when we talk in terms of the electron transfer reaction now at the same time if electron moves in one direction, in the opposite direction you get the proton moment that is why the corresponding reduction of this O2 molecule what we are talking here is that if we see that is a 4 electron transfer reaction. Only is not that we should also have the 4 proton transfer as the result you get to a water molecule from your O2.

Is not that you only go for your O2 to 2O2 minus, you have to take this for proton to get this 2 water molecule, so so these 2 are coupled together and if you find that in one end you have the transfer of electron in one direction you have the transfer of protons the other direction, so electron in this direction and proton in this particular direction and most of the cases you have this a coupled one because if you have the very simple functionality as we all know that CO NH function is the backbone of all these things what we are talking here in terms of the corresponding protein polypeptides and all these.

So these are all your peptide bonds so if you have the peptide bonds and if you are able to go for the electron transfer reaction on the peptide bond itself or it is bound to some other species like metal ion. What we see there that during that particular reaction you can go for that means the O is there so that means you have this O and if it is in the oxidised form so that means you take out the electron, you have to take out the proton also because this can also go for the loss of proton also and sometimes it can also show that there is (())(22:12) protons in the charged form and that the charged form can go for your electron transfer reaction.

So whenever there is available proton it can go for proton loss or it can go for proton acceptance during the electron transfer reaction so like electromotive force we all know the E0 value and E half values we all know that the electron transfer potential or the electron transfer sensitivity for a particular system and how the driving force is there, so it is a force basically so proton can also have some kind of that kind of force so we define it as the proton motive force and now we can have something where we bring because earlier we get the exposure for your membrane, membrane which is very close to your electron also.

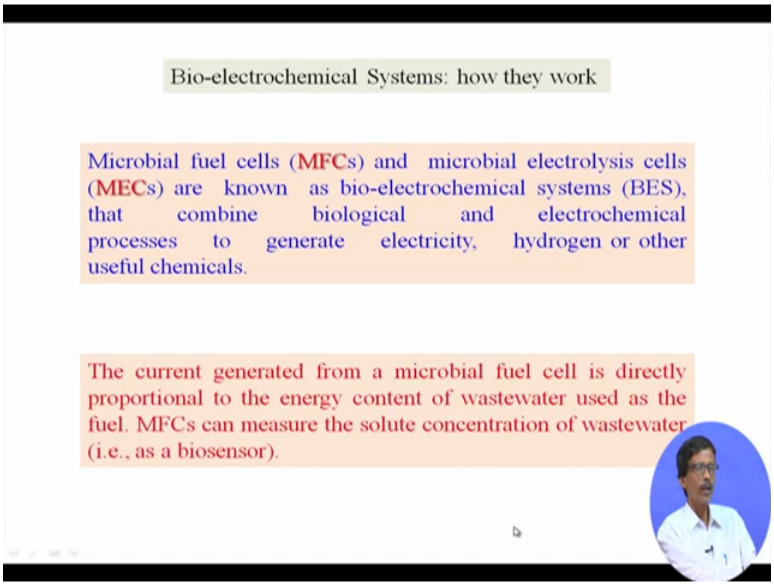
So where we get this proton motive force, the proton motive force is a very complex one and a combined form of a potential difference you should have a potential difference from one side to the other like that of your metallic rod dipped into the solution we have a potential difference, so the across the membrane and the difference in proton concentration across the membrane, so all biological membrane we all know that your ATP (())(23:27) they are then the potassium ion, sodium my and all these are enclosed in some membrane.

So lipid layers are there and the membrane are there and if the proton concentration on one side of the membrane to the other is different, so if there is a difference in proton concentration for this is across the membrane what we get definitely we will get a proton motive force, so that is the corresponding idea behind defining this proton motive force so definitely you have a different in proton concentration like that.

When you talk about the electron transfer reactions and the electromotive force or the EMF basically the electromotive force we talk that means we know that that is some way either from the downhill all from downhill to the uphill electron can be moved, so the electron can be transferred so when the membrane is available and if you have 2 different proton concentration from left to right, so proton will allow that particular proton to traverse or move from one part to the other such that we reached to a equilibrium because on all these cases whatever we are talking about is a non-equilibrium condition, so that non-equilibrium condition we have to establish in terms of either a EMF value or a PMF value.

So both these things means both contributes that means the potential difference across the membrane you must have a potential difference across the membrane and electrodes when it is there, those electrodes can also contribute to that particular potential difference and your difference in proton concentration both can contribute to the available free energy change or available free energy for a particular type of reaction to go.

(Refer Slide Time: 25:13)



So these bio electrochemical systems thus we have in our hand and we should know now how they work? So it is bio electrochemical systems if they go for electron transfer reactions, they can give rise to because already we told you that you can have the bio fuels cell, so what are those bio fuels cells? So when you go for little bit of elaboration those things that means we can have microbes are available so these these microbes are available for generating electricity we get the fuel cells.

(())(25:46) like battery you have the fuel cell we can generate the corresponding electricity for you, so the microbes are utilised to generate this fuel as the corresponding electricity so this will be microbial fuel cells. Then another one is the opposite one where we can go for electrolysis, so when you go for the electrolysis because these 2 are combined at if we go for the fuel cell somewhere you can have the electrodes is also otherwise you cannot get this thing like that of your electrolysis of water molecules.

Water molecule when it is electrolysed we know that we can get oxygen and hydrogen over there but when we go for the fuel cell based on hydrogen we know that hydrogen can be burned in presence of oxygen because hydrogen needs the fuel because the we do not have the natural supply of hydrogen but oxygen is there in air there are plenty supply of oxygen so this is hydrogen will be your fuel and we can go for the corresponding hydrogen based fuel cell but we should not uhh very much bother about the thing that where from we get the hydrogen.

If there is a good source of this hydrogen we can have the hydrogen-based fuel cell and if microbes utilised, so those microbes will be there generate the required amount of hydrogen for yourself. So these are known bio electrochemical cell, so once you are asked that what is your bio electrochemical cell, you can have the idea at okay race electron transfer reaction and the electrolysis cell or a fuel cell and outcome of the 2 combine thing that means one is the biological part and another is the electrochemical part.

So 2 processes can go side-by-side to generate electricity, to generate hydrogen or other value-added chemicals which we need for other purposes so value-added chemicals are some useful chemicals as we get chemicals from petroleum we call them as the petrochemicals. So it is microbial or the microbes can be useful for giving you the required amount of all these chemicals including your hydrogen.

So 2 such cells we can abbreviate that MFCs and MECs (())(28:01) the cell and microbes only one is fuel, F is fuel and E is the electrolysis, so the current what we can generate from a microbial fuel cell so uhh with a hope that we can generate electricity from there is directly proportional to the energy content of the waste water. Not only microbes now we are co-relating to something we consider as the waste water.

So it is a concern for the environmentalist, is a concern for the water treatment how you get pure water at the same time how you get the energy, so this waste water used as the fuel, so there is no need to think of that where from we get that particular fuel, so if you have the waste water you know that the organic matters are plenty in that waste water, only thing that we have to choose the right microbes which can degrade those organic matter and these fuel cells and measure indirectly the corresponding solid situation of the waste water.

So in terms of its bio sensing capability and use this to determine the waste water concentration of the solute in terms of your O2, you can detect the glucose you can detect some other species also, so the bio sensing part is over now you know that some good amount of material is there which can be used as a fuel for generating electricity, so those thing can come to give you the corresponding development of microbial-based fuel cells, okay. Thank you very much and we will continue this for our course uhh for your next class, okay. Thank you.