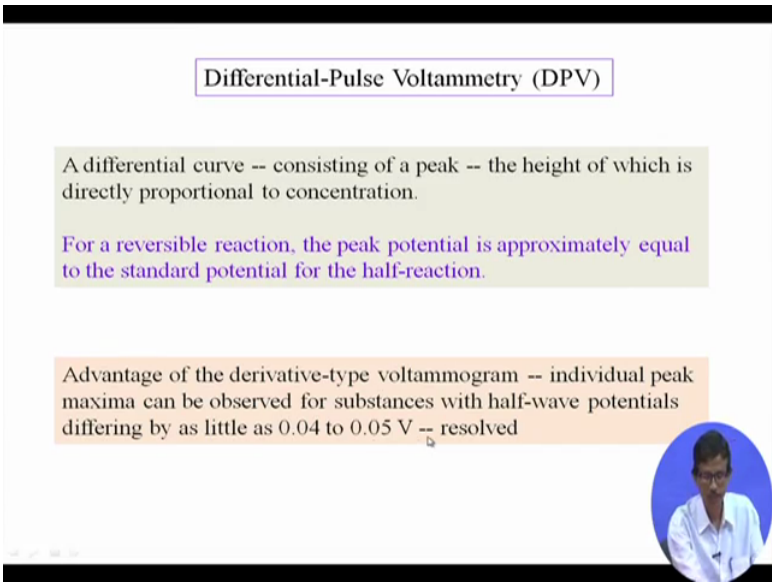
Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 11
Lecture No 55
Electrochemical Methods 3(Contd)

Hello and welcome back to this class where we are talking about the differential technique DPV. And as we had discussed that we can have the different types of modifications in terms of the electrode modification that we discuss just now and before that we can have the development from the electronics part to generate the pulses and the computers what you can have 2 records those pulses as well as to deliver those pulses to the electrodes.

(Refer Slide Time: 1:02)



So what are the basic advantages of this particular technique that we can see that in DPV we get a differential curve so is not that typical that a staircase like curve but we get typical like your absorption spectro photometric type of curve which the differential curve consisting of a peak. So if you have a maximum or if you have a peak, we can find the corresponding peak as the corresponding potential for electron transfer reaction and one more interesting thing is that is a very sharp peak and the height of which is directly proportional to the concentration.

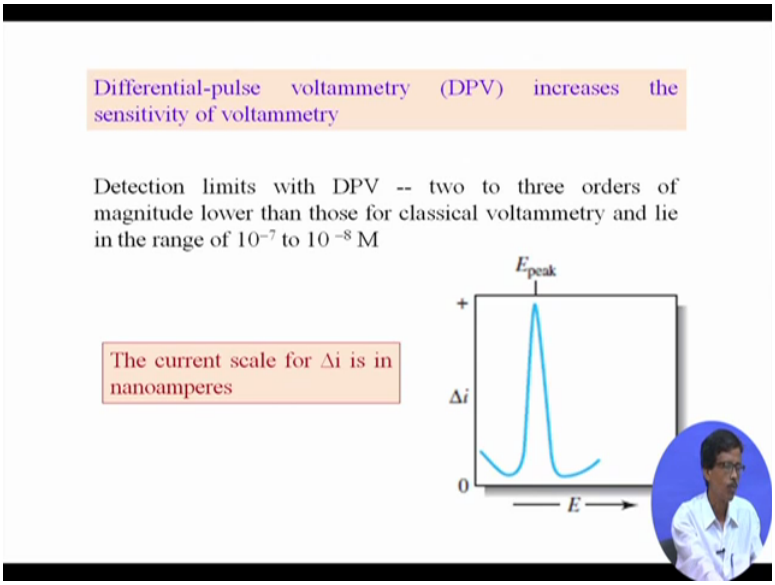
So if you know the concentration of the analyte in the electrochemical cell and the electrode is dipped in it and DPV technique is very much similar to that of your cyclic voltammetric technique because you do not need to require any kind of special arrangement for your electrode because the same electrode what you can use for your cyclic voltammetric

measurement can also be used for your differential pulse voltammetric measurements as well. So for a reversible reaction, the peak potential is approximately equal to the standard potential of the half reaction because in case of cyclic voltammetric measurements what we have seen that we can have 2 potential, one is EPA and another is EPC.

EPA is for anodic potential and EPC is the cathodic peak potential average of 2 which give you the corresponding standard potential for the half reaction if it is for any electron transfer for the complete cycle for oxidation as well as reduction. But why we should go for DPV compared to CV is that it has the advantage because the individual peak makes you can be observed and substances with halfway potential differing as little as 40 to 50 millivolt, the resolution is very important so just now what we are talking about that if we have these 2 plots in the cyclic voltammetric one particular way of scanning.

So when we go for so this is the one part basically reverse is also there so if it is for CV so DPV for that will give you from baseline very sharp and prominent one for these 2 electron transfer reactions because this separation it can be simply say 40 to 50 millivolt. So the resolution is very high and we can differentiate out these 2 in case of DPV so from CV we can go for DPV when we have the corresponding overlapping peaks in the range of 0.04 to 0.05 volts which can be resolved nicely.

(Refer Slide Time: 3:48)



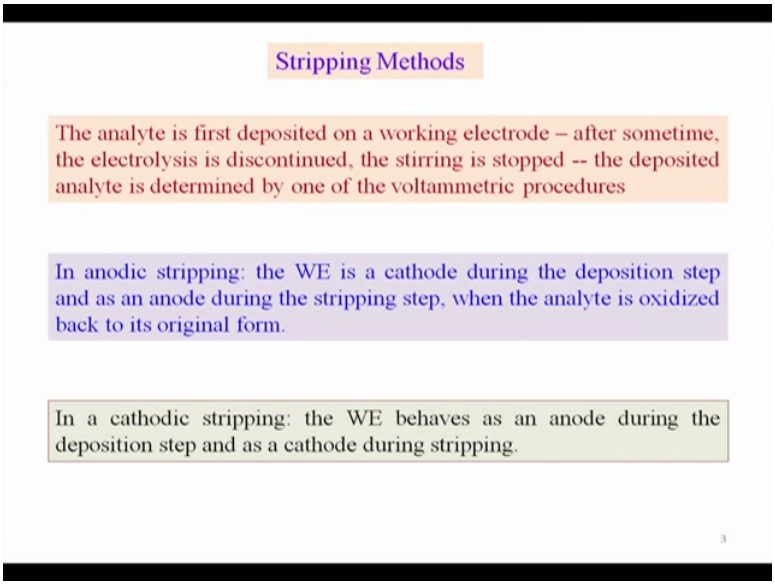
So it increases also the sensitivity of the voltammetry, so you have the linear scan voltammetry, you have polarography, you have then cyclic voltammetry but when it comes to the question of running DPV, it increases the sensitivity because it is sensitive and the current

height is also little bit bigger than that of your current height what we get for your cyclic voltammetric measurement. And what about the detection, since sensitivity is high detection limit is also very high so 2 to 3 orders of magnitude, you see when we mostly do for your cyclic voltammetric measurement, we start from 10 to the – 3 molar solution for the basic one, then we go down 10 times dilution to 10 to the – 4 to 10 to the – 5 molar solution.

But in case of DPV compared to the classical voltammetry that lies within the range of 10 to the – 7 to 10 to the – 8 so that basically gives a 2 to 3 order of magnitude compared to 10 to the – 5 molar concentration what we use routinely for our cyclic voltammetric measurement. So this just now what we have drawn so is taken from textbook also again the (())(5:02) book that book also shows that how you plot that is not your I it is Delta I that is why it is a differential technique so differential pulse voltammetric technique because you plot not i against E by Delta I against E. So this is the range from 0 to positive magnitude of this and you measure this as the peak and this peak is giving rise to the corresponding potential value for your electron transfer for any oxidation or reduction.

And the current scale is very less it is a nano ampere now, so what you see that you can remember that is also nicely that when we are handling a solution which is in the range of 10 to the – 7 to 10 to the – 8 molar solution but we can handle the current also which is in the nano ampere range so that is why the techniques will be very much useful for developing some sensors and biochemical sensors also and with certain kind of modifications in the electrodes.

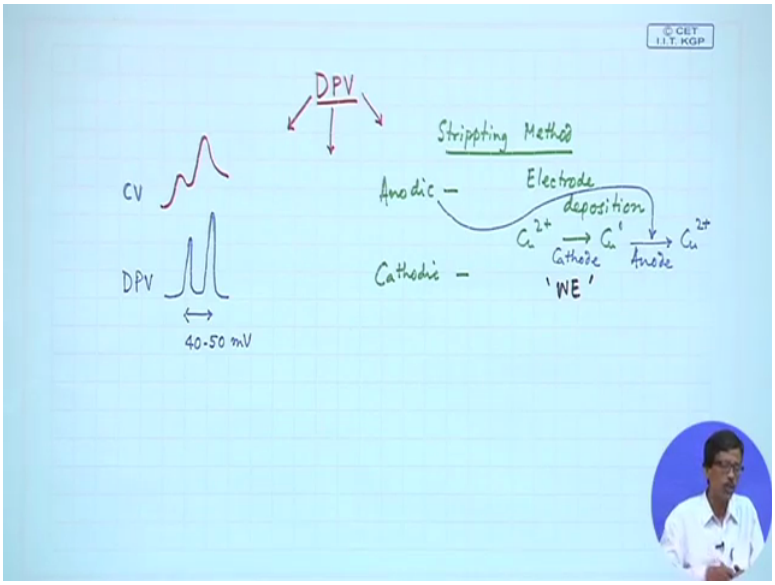
(Refer Slide Time: 6:39)



So what we find that before going to the modification of those electrodes another technique we briefly notice or briefly know that what is called the Stripping methods of electrochemical analysis. So the stripping method of electrochemical analysis the name itself tells us that you can go for some amount of electro deposition and that particular samples can be removed from that electrode surface by a method which is called stripping. So stripping method is that an analyte you having the solution so you take the analyte in the electrochemical cell and is deposited on a working electrode so basically we know that from the very beginning that when iron nail is inserted in a copper sulphate solution, copper is deposited on the electrode surface.

Now what you do that analyte can be allowed to go for deposition on the electrode surface by passing electricity, so if you allow sometime because that the position will take some time and after some time the electrolysis is discontinued. So you stop the electrolysis, once you pass the electricity for some time and allow that electrolyte to be deposited either through oxidation or reduction then you start and you stop so you stop the stirring and the deposited analyte is determined. So you know how much analyte is deposited to one of the voltammetric procedure what you have used so far.

(Refer Slide Time: 8:01)



So the first of this kind is your anodic stripping, so you will have definitely therefore the 2 types of stripping, what will be stripping method; one will be an anodic, other will be cathodic and is related to your electrode deposition so that electrode deposition will be useful for measuring this. When you go for anodic stripping, what we find here the working electrode is a cathode that is why we get the corresponding one so working electrode is the

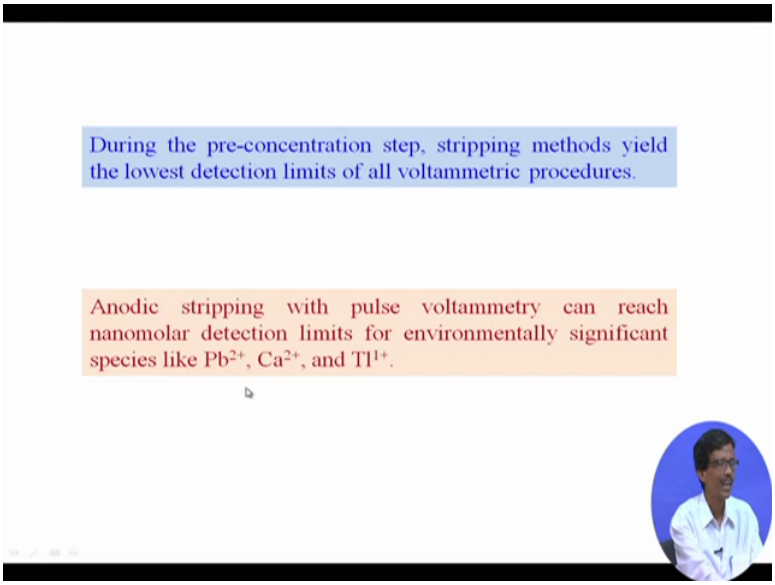
cathode during that deposition state and as an anode, so the nature of the working electrode we are changing. When you talk in terms of anodic stripping, so initially you see that once it is oxidised it is deposited say and what it is reduced this can be deposited so you have to go for the reverse process.

So when working electrode is cathode you get the deposition, when you change the potential to anode so when you go for its nature as the anode you get the corresponding stripping process. When the analyte is oxidised back to its original form so you can have the metal ion so suppose it is copper 2 + and copper 2 + can be deposit as copper 0 so what is that, so we know that the corresponding one is reduction so you require a cathode for that reduction then you change the nature of that electrode as anode this will go to copper 2 + once again.

So when it is the removal of these things, it is your anodic stripping so the process will therefore be known as your corresponding anodic stripping and the nature because we are talking so far we should also be very much careful forget about your reference electrode but you have the working electrode and the counter electrode. So your working electrode is the electrode on which all these things are happening. So then the other process, the other process is opposite to the first one so when we have the working electrode behaving as the anode, we get deposition so you get the particular deposition and it will be cathode during stripping.

So the process what is known as the cathodic stripping is because during it is coming out from the electrode surface it will be released from the electrode surface such that what we have seen that it will be released from as the copper 0 form the electrode surface because this deposition is there on the electrode surface as copper 0 and when it is oxidised as a part of your process known as anodic stripping process so the anodic stripping process will give rise to the corresponding generation of copper 2 + from copper 0 and it will be removed from the electrode, so the opposite one will be your Cathodic stripping method.

(Refer Slide Time: 11:22)



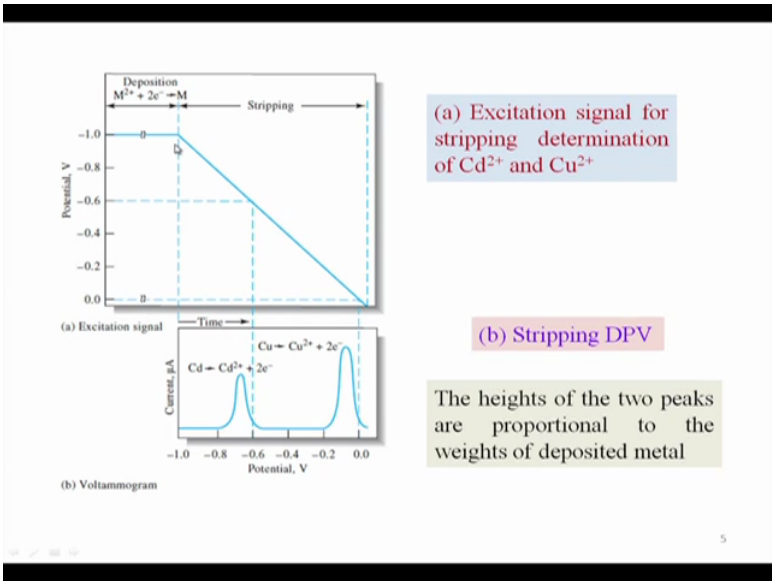
Then during the pre-concentrations step that means if we want to increase the concentration by certain step where we know that the analyte concentration is very less or very small say 10 to the – 5 molar or 10 to the – 7 molar, so if we want to increase the concentration of these things which is known as the pre-concentration step the stripping method is the lowest detection limits of all voltammetric procedures because from solution you go for deposition as a pure form of the material what you are going to get as deposited form of say 1 of the examples we call is your say copper 0.

So the anodic stripping with Pulse voltammetry so once you get this anodic stripping with Pulse voltammetry can reach to a nano molar detection limit because already we have seen that we can detect a nano ampere concentration in similarly, the nano molar detection is also possible with so many important metal ions which we know that are present environment from some of automobile exhaust or some other industrial exhaust or some other processes or activities what we mean are doing, so these 3 heavy metal ions say lead, bivalent lead, bivalent calcium and monovalent Thallium so they are very important in environment and the presence of those in environment is also very much problematic.

So if we want to detect the concentration of these in very low concentration because in environment you do not get a molar concentration or decimolar concentration for minimolar concentration because it will go beyond micro molar solution mo resolution and it will reach to a nano molar concentration in the range of 10 to the power – 9 molar solution. So these things so these are all metal ions these stripping processes are very much useful for handling

metal ions like copper and I give you the example only thing you have to know the corresponding reduction potential values and it should be achievable through your cell as well as your electrode.

(Refer Slide Time: 13:29)



So what we find that if you have a mixture of those 2 also just now what we have seen for your copper so it can be a mixture of copper and cadmium also. So you have the corresponding time axis and when we go for this that means your excitation signal as we know that how much time we require so is the time axis you can have. So when we go for deposition so you get the deposition so you require some excitation signal so for this stripping process we consider these 2 as the corresponding excitation signal for stripping determination of cadmium 2 or copper 2. So what you find therefore you can analyse it also that this much time so this much time you have to spend because you have to wait for the electrolysis for your reduction.

So both bivalent cadmium and copper can be reduced so the potential of your choice is such that at this particular potential of – 1 volt both the 2 species that means both cadmium as well as copper can be reduced. So the exhaustive electrolysis for that particular purposes that the entire amount of copper or entire amount of cadmium will be deposited on the electrode surfaces when you apply a potential of – 1.0 volt.

So at this point that means if you sometime so after sometime because we have to definitely give sometime because as you switch on the potential to the electrode surface it will not that the all the solution will be deposited as the metal ion metal of 0 state of cadmium or copper

on the electrode surface because it is everything is diffusion control because that entire thing was that in the bulk that has to be moved on the electrode surface. So after giving some time for your reduction so you go for that so when you reach over there then if you go for that so this is the thing that means the potential you give and you allow for some time where all will be converted to M is not exactly we write it as M 0, it is a nicer way to write as M 0.

So this M is the metallic state, then you go for this one so if you go for because this was your cathode and then you go for the corresponding anode. So anode means that it will just go for the corresponding potential value that means you can scan the potential also because the corresponding thing what we are talking about this is your differential pulse technique so on the electrode surface you are getting stripping as well as you are trying to record the corresponding voltammogram due to the response of their oxidation of the species like cadmium 0 and copper 0 which are deposited on the electrode surface. So as you move from this is – 1 so again you move back – 1 to 0 will scan and in this particular case your electrode is now anode.

So the anodic electrode now go for your corresponding record of this voltammogram so you excite it then you recall that voltammogram after this time. So you allow this is a very quick process, you do not require much time to spend in so you get what that is again a decreasing plot but we now call it as a stripping decreasing because everything is stripped off from the electrode surface and what we are looking for is not a change between 2 oxidation states of copper 1 to copper 2 or iron 2 to iron 3 but it is from the state where you are talking about the metallic deposition of copper as well as the cadmium.

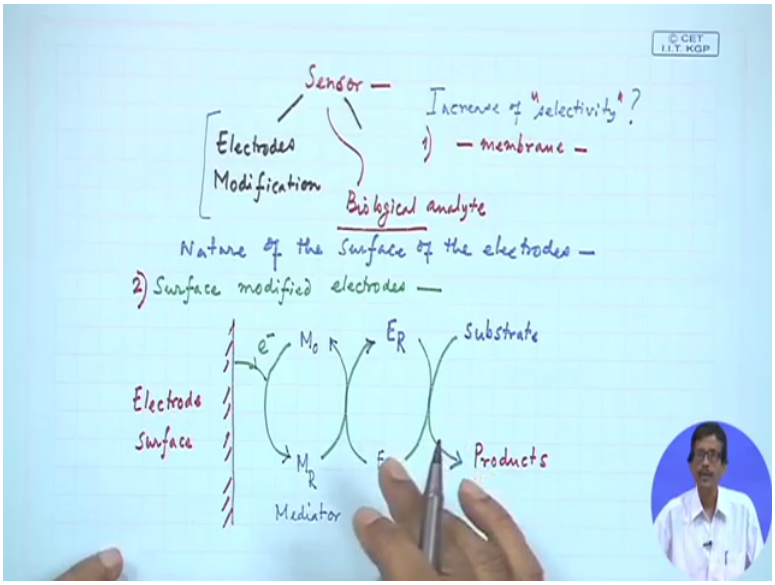
So these are the stripping DPV plot so the differential voltammogram plot will be the first, cadmium will be oxidised back to cadmium 2 because the potential for this is higher compared to your copper so copper will be in this particular range below – 0.2 volt you get the copper so with this very distinct and very well established potential values for the oxidation of these things. So if you have certain amount of impurity in the solution also that is also a very good technique because you do not bother about the corresponding impurities only, selectively the ions which are the bivalent copper as well as the bivalent cadmium will be deposited on the electrode surface.

And you one thing that is also known as your pre-concentration because the pure form of cadmium and copper are deposited on the electrode surface and when you get those pure forms in some solutions it can be your polluted water sample, it can be any other industrial

effluent sample so those things are known as the corresponding pure amount of copper and cadmium present in that solution because you are showing some electro activity on the deposited pure form of copper as well as cadmium.

So the height of these 2 peaks as we discussed earlier in case of only DPV that the heights of these 2 peaks are proportional to the weights of the deposited metal because it is related to the concentration and that concentration is directly proportional to the amount of deposition during the Cathodic cycle.

(Refer Slide Time: 19:14)



So now we will just simply move to development of some sensors and these are the typical thoughts where we talk about the applications of your electrochemical methods of analysis. So 2 things are there that means when we try to develop a sensor so the development of the sensor will have something that means you can have the corresponding thing that means the electrodes so you can go for the modification of the electrodes so we get that as the electrodes and their modifications therefore, so modification and this thing how we can develop those thing that means some amount of modification covering and some other types of activities what you can do on the electrode surface.

So once we change the surface or the nature of the surface so nature of the surface of the electrodes, so we basically change those and as a result we consider some electrodes which is a very common terminology for those are known as your surface modified electrodes so you get surface modified electrodes. So pictorially we can identify these because what are the things we should do that we should do something on the electrodes for their modification and

selectivity what we can enclose, so if we try to increase the selectivity so increase of selectivity how we can do that how we can increase the selectivity of these species.

So this we can do by attaching some membrane you know that why we use membrane because membrane is some kind of filtration process, so membrane will allow only some species of our choice of our importance will pass and will reach to the electrode so you increase the corresponding sensitivity. So membrane is one so membrane is one part and 2 is your modification of the surface so if you have sometimes you find that you can have the very overlapping peaks and we have very close form of potentials so having some different electrode kinetics and you also some absorption.

So how increase this particular specificity because if we want to sense now something which is biological in nature so you have the biological analyte so how we handle those biological analyte that we will see. So this biological analyte means it should have some good selectivity in terms of its corresponding reaction with that of your electrode. So once we get that modification and that modification is your other electrode surface, so if this is your electrode so what is this, this is your electrode surface which will be in contact with the solution containing those analyte.

And suppose this gives you the corresponding electron that means it is responsible for reduction of something then we can have something how we can go for these modifications and these cyclic processes all you know now that will also be very easy to explain with respect to those because these are all known as your corresponding reversible thing, two species will be their X and Y and they are interconnected through electron transfer reaction so the reversibility of these things are also important because we get this sort of loop for electron transfer reaction as well as in different kinetic cycles. So to grow, to develop, to establish some electro kinetic processes also will be dependent on these sorts of modifications.

So in the first step on the electrode surface you can have the mediator some simple metal complexes with organic ligands can be a very good mediator which can immediately be attached or some other materials like carbon rod or carbon tube or carbon other carbon-based materials like that of your electrode which may or may not be your graphite electrode. So carbon tube can be there or some graphite sheet can be there so these mediators so once this electrode is going for that so you get the corresponding mediator in the reduced form and this can settle between these that means this mediator when it is going for the oxidised form is MO.

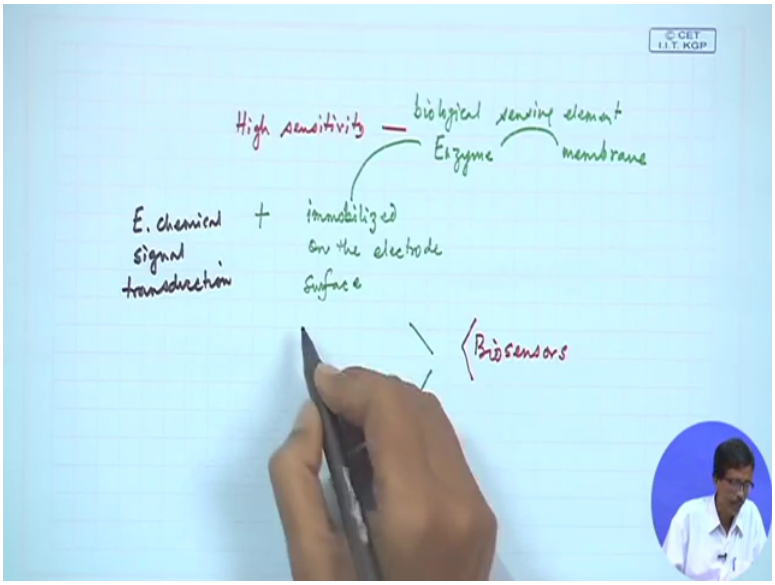
Why it is going for your oxidised form because your enzyme is also attached to that so the mediator is then attached to your enzyme in the oxidised form. That means your oxidised enzyme will oxidise your reduce mediator but reduce mediator we obtain from electron transfer from the electrode surface. So this will go so this electrode surface will go like this so it is reaction with this MR so E 0 + MR will produce M0 + ER your enzyme in the reduced form, so adorable what we get the enzyme in the reduced form so that is required. So enzyme in the reduced form so what is that is not in the oxidised form but enzyme in the reduced form will be utilised to take up your substrate.

And when it is reacting with your substrate we get the corresponding products, so these electron transfer reactions are therefore very much important to know because these electron transfer can directly go to your reaction with that of your substrate to product conversion or it can have some idea that it can be mediated by some enzyme so that is why we will be handling the biological system.

So some very selective enzymes we can use also, some enzyme can be anchored and can be put on the surface of the electrode, so without the presence of this mediator you may not have the mediator over here only that time as well as this thing so one thing you can know nicely that that electrode is fine to go for electron transfer reaction for getting substrate or product, if it is not then you bring the enzyme if it is not active in that way for electron transfer directly from the electrode because this enzyme what we are looking for a reduction from the mediator oxidised to the mediator radius is not that it can go for the electron for the enzyme directly that means oxidised enzyme may not be reduced to the reduced enzyme directly by attaching it to the electrode surface so that is why you use some mediator.

That is why we know there are large number of mediators are available in biological system suppose we know that in some cytochromes, the cytochrome C oxidise we know, there are large number of mediators are available and for each and every mediator we have sequentially the corresponding difference in the corresponding electrode potential values, so one place you have the corresponding food material which will be oxidised by O2 on the other side. So in between we have large number of mediators that means electron transfer mediators are available and in some steps only we get the corresponding synthesis of ATP molecules from the ADB molecules if the Delta E value rather the corresponding potential difference values that corresponding change in the potential values for these 2 coupled things are sufficient to go for your synthesis of the ATP molecule from the ATP molecule.

(Refer Slide Time: 29:06)



So these mediators are very common thing for all these types of development of the sensors particularly we will be discussing two sensors in our next class, one is your oxygen sensor, another is the glucose sensor. So we can have this that you can bring high sensitivity therefore, high sensitivity for the corresponding reaction that means you have to have some biological sensing element and what we bring, we bring the corresponding enzyme and this enzyme we can put within the membrane or it can be immobilised on the electrode surface . So what we get this biological sensing agent so you have the corresponding thing how we can measure the sensitivity, so you have this high sensitivity we can achieve by putting biological sensing element.

So that biological sensing element is important to know which can sense the biological molecules so it can be mobilised on the electrode surface so electrochemical signal what we can get that we have to monitor either current or the differential current so electro chemical signal transduction should be there. I will tell you record I or Delta I for those things and we can develop in that way the biosensors, so the electrode for this sort of measurements for making or handling the biosensors oxygen can be there in the biological sample, glucose can be there in the biological sample so when we talk in terms of the corresponding current plot with that of your potential and these are of 2 types, one can be your amperometric biosensors, the other can be your voltammetric biosensors okay.

So all these things we will develop next day and we will discuss once again all these things for your convenience okay, thank you very much.