**Nanobio Technology Enabled Point-of-Care Devices**
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Lecture - 35
Tutorial - 02

Dear students, so today I will teach you some new topics and then we will try to complete this course slowly. So, today just let us take one more Tutorial and some new concept I will bring and based on some discussions of the questions, you can just try to remember all the stories and then try to make some new innovations for your thinking I mean you can make some new projects. So, just think today I will give you tutorials first that is very much useful for the various electrochemical sensors.

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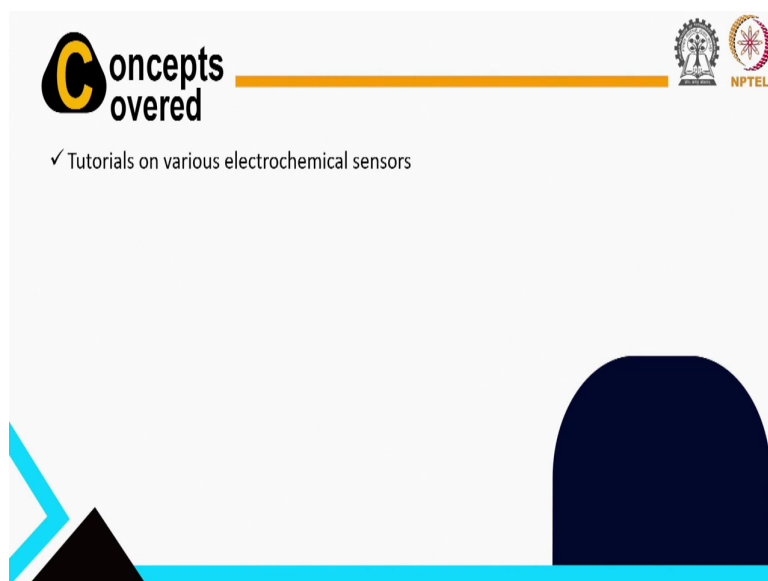
So, my plan today in this tutorial I will discuss some important electrochemical equations and then you can apply those equations for applications of the sensors ok. So, I already taught many electrochemistry, I already taught the characterization of the surface by the help of different like cyclic voltammetry, chronoamperometry right.

Cyclic voltammetry, chronoamperometry, chronocoulometry, those all the electrochemical technique you have learned and that is very much useful for biosensors, surface characterizations, detections, development of sensing device.

But sometimes you may need to explain those cyclic voltammetry with some equations. So, I just briefly just I will summarize few equations and you can use those equations for the explanations of the different different single outputs that you are getting that you can explain.

But let us I will cover little bit our three equations one is the Nernst equations, second is the Randles-Sevicik equations and third is the Cottrell equations. Do not worry they are not I am not going to teach you the all the mathematical details just try to understands how we can use those equation to predict the output that you are getting from the biosensor applications.

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So, first let us cover the Nernst equations. Before the Nernst equations so, I will try to explain you few things very basic things just you can remember those basic things you already know you I think you have you already learned during your 10th class 10th plus 2 class there is the what is the anode what is the cathode that you know right what is the anode? So, anode at with electrode where at the at this electrode oxidations happen right.

So, if some ion if M release 1 electron M from M plus it means oxidation this oxidations happen if this electrode that is called the anode and the elect so, the electrode that you know

this electrodes actually see you know the biosensors right your working electrode and sometimes you are applying some positive potential (Refer Time: 03:43) and applying the negative potential.

So, those the mean sometime there is maybe electro oxidations happen right sometime may be electrode reductions can happen means we are providing some electron so, you. So, you should have the basic concept you already know, but before covering this Nernst equation let us try to summarize. And what is the cathode? Cathode means at which the reductions occurs.

So, here means if M plus H takes 1 electron formed by M then it will become this is the reduction reactions and at which electrode it happens that is the cathode. So, the electrode that can the cations approach in this case and electrode that anion's approach that is the an anode case. So, here is the schematic the equations I plot here.

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Now, let us come the before covering the Nernst equation for Nernst that formula you know already this, please try to cover this slides also that is the electrode potentials right. So, what is the electrode potentials? So, potentials of an electrode for suppose some reactions happen know Fe 3 plus so, it can take one electron from the Fe 2 plus or a Fe 2 plus can release one electron from the Fe 3 plus.

So, this kind of reactions or very common reactions like copper you see here the copper 2 plus take 2 electron from the copper. So, this is in the cathode reactions right or zinc 2 plus takes the 2 electron from the zinc. So, in this case I mean if it is the opposite I mean here when we are representing any equations already always, we are mentioning the reduction reactions.

But any electrochemical cell one part is the cathode one part is the anode right. So, one part you can see copper another part is the zinc right you I think you are very much well known about this setup. So, if one is the cathode and one is the anode if zinc this reaction is the anode and copper this is the cathode, right. So, in this case what is the net potentials? So, that is called this is the cell right one cell. So, in this cell the E cell we say E cathode minus E anode this is the net potential.

So, the electrode potential are conventionally defined as the reductions potential like this, but actually reactions happen like zinc here oxidizing copper here reducing right this is the actual cell. And E cell I mean the net E I mean electrode potential net potential I mean of the cell E equals to E of the cathode minus E of the anode.

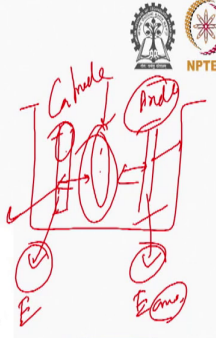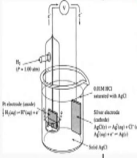Now, let us come to the representations slowly to the Nernst equations when we are determining the potentials right in a cell right here you have a electrode here anode and cathode, cathode and anode. So, you can remember I always told I mean this potential this I just we are measuring the potentials of this cathode potential of this anode, but you need one reference electrode, right.

So, compared to the reference based on this reference electrode we can say how much the potential depends that is the E of the cathode, the anode electrode how much potential depends if based compared to the reference electrode that is the E of the anode right. So, that is called the reference electrode. So, reference electrode always very much important. So, see I am just summarizing all the concept here.

So, I already taught you. So, we need always the reference electrode because otherwise (Refer Time: 07:54) it is very difficult to understand the potentials of one single electrode right. Generally, we are considering like silver silver chloride or hydrogen Standard Hydrogen Electrode SHE standard hydrogen electrode as the reference electrode or calomel electrode that is mercury based, they are the reference electrode.

Generally, the standard hydrogen electrode we are considering their potential is 0. So, 0 potential now we can compare then here I mean your copper electrode or your zinc electrode their potential compared to the standard hydrogen electrode. So, they are the reference electrode. So, this is the basic concept I already covered just I am summarizing please try to remember and use this concept while you are developing a electrochemical cell ok.

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Now, let us come to the Nernst equation. So, Nernst equation you can see these equations I think you already you learned this equations in your BSc or who are already in UG course maybe some of you already have learned in your 10 plus 2 level also. But just I am just summarizing here what is the Nernst equations.

See the values of the E cathode can also be calculated in the other concentrations or activities. So, generally we are considering first the half cell reactions. What is the half cell reactions? Means you have the cathode. So, this is the half cell reactions whatever so, here reductions happen or suppose here oxidizations happen.

So, this is the half cell reaction, this is the half cell reactions that is E of the cathode or E of the anode. So, we can represent suppose this is the reactions happening in the solutions. So, as I mentioned genenerally we are representing the reactions as a reduction reactions reduction reaction ok.

So, E electrode is equals to E is equals to E 0 minus RT by nF ln say a R of r means this reductions I mean this species by this species and we are considering activity of this all the species. So, where R is you know already gas constants and F is the Faraday constants ok.

So, E 0 so, what you can ask me sir what is the E 0? So, actually E 0 means actual potentials of the electrode that I will come the next slide. So, we are calculating the actual potentials of this electrodes that equal to E 0 I mean actual formal potentials E 0 that I am going to tell you again the what is the E 0. So, E cell generally we are representing like this equals to cathode minus equals to anode.

So, how we can calculate the E equals to cathode, how we can calculate E equals to anode that is the Nernst equations from here we can calculate. So, we you have to I mean you should know the concentrations of your all the species here actually a means the activity you know the activity equals to some factor and concentration.

So, here we are representing all the your actual species concentration you have to know means activity a means the activity actually activity you should have the this information of your species that is they are involved in the reaction.

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See in this slide I just going to show you the E 0 values right that I told you know that what is the E 0. So, as I mentioned E equals to E 0 minus RT by nF then all the activity of this species you have to mentions here. So, what is the E 0? E 0 is the standard electrode potential. So, standard electrode potential is measured the electro potential when all the species solutions or gas has an activity is the 1 and it is also called the standard reductions potentials because we are representing the reductions way.

And we are see if you go back the equations here we are representing as the activity and here is the equations like activity equals to some gamma x is the activity coefficients of its analyte or whatever if a solute X then you need one coefficient and the concentrations. So, that is you can calculate. So, standard electrode potential E 0 mainly only we can get this one when your species and solution gas has an activity of 1 or that is in the ideal case not always possible the 1.

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And all the formal potential I just going to tell you the brief summary and I mentions here something that you can also try you can also search I already gave some reference book please try to read the books also. So, that you can understands very if you want to learn more then you can go through that book that I already put in the reference section.

So, but all the parameter I already mentioned during the biosensor development like what is the formal potential you have to then try to remember the cyclic voltammetry right. So, this is the cyclic voltammetry suppose this is Fe 2 plus from the Fe 3 plus when it release one electron then Fe 3 plus from the Fe 2 plus when it accept one electron right. So, here is the oxidations. So, in this case is the oxidation and here is the reduction right.

Now, I already mentioned right this is the peak potential, this is the peak potential of the oxidation reductions and say if this is the E 1 and if this is the E 2 then we generally we are calculating the formal potentials or E half value E half value E 1 plus E 2 divided by 2 means this potential right. So, this is actually formal potential that we can calculate from your cyclic voltammetry.

Nernst equation case that I already showed you here like actually your formal potential is 0 actual potential in this case activity should be 1. You can see here major electrode potential when all the species in the solution gas has an activity 1 then you get the standard electrode potential E 0. Please go through this few information's I already mentioned in the slide, but the main concept I already taught you last few classes like what is the E half value what is the formal potential how you can calculate those things ok.

So, this is the Nernst equations so, that you can get the electrode potential value. Now, some other equations also can help you to predict your output that you are getting during the cyclic voltammetry measurement during your chronoamperometry measurement or coulometry measurement.

So, another equation that is I am going to tell you is the Randles Sevcik equations. What is this? Randles Sevcik equations you can see this is just I am not going to derive you just try to remember what is the relations between the different factors no need to remember all the like a value just try to remember the relations of the different factors.

Suppose you get you receive you got one cyclic voltammetry something like this means you are getting cyclic when you are getting cyclic voltammetry. So, you are scanning in a within a

potential window and you are getting current right and within this potential within this potential window.

But there is so many other factors also can affect in the cyclic voltammogram like your current can be change your this E half also value also can be change there is a different factor see one factor is the concentration. What the concentration means what concentration concentrations of your the redox couple you are using suppose you are using Fe 3 plus Fe 2 plus right this redox couple you are using.

So, if we increase the concentrations of iron species then definitely you will get the higher and higher current. If we increase then you will get higher current again increase you will get the higher current. So, this is dependent on the concentrations more concentrations when you will get the more current not only the concentration there is another factor can affect that is the scan rate.

In how fast you are scanning within this potential window and you are getting the this cyclic voltammogram know. So, suppose you have the Fe 3 plus Fe 2 plus right this one in the solutions, but if you scan when I will show you during our laboratory means demonstrations, I will takes a laboratory demonstration that time I will show you.

In the instruments that is called the potentiostat in this instrument. If you apply slow scan rate to high scan rate during the cyclic voltammetry measurement your current high scan rate your current also will be increase because your this species can move very fast towards the surface.

It means your current means i p that is why I am going to say that i p means your current your maximum currents that is you are getting that i p is proportional to actually your scan rate how fast you are measuring the cyclic voltammetry with some are measuring slow some are measuring fast.

So, that is why when you are going to publish your work you have to mention which scan rate you are using. There is a relations i p and the relation is proportional to scan rate to the power

half means it is saying (Refer Time: 18:46) root there is a relations ok. So, if you increase the scan rate and accordingly you will your current of a cyclic voltammetry also will increase.

So, this is the relations no need to remember just try to you can correlate or you can explain your output data based on the scan rate that is the main my goal to tell you the Randles Sevcik equation. So, while you are developing the biosensor surface. Sometime you may scan fast or something you may scan slow and you are getting different different current that you can explain it.

Because of this relationship that is my main motive to tell you the this equations. And all the factors like this is the number of electrons in this how many number of electron is flowing like Fe 3 plus Fe 2 plus and then here number of electron is the 1 because only 1 electron.

So, 3 plus 2 plus is reducing like 1 electron is taking right if n equals to 1 and A is the electrode surface area. So, see this electrode surface area also is very much affecting on your current. So, suppose your working area A 1 and if working area increase to A 2 definitely you will get the very much high current because of the high surface area because of the higher surface area you will get the higher current. So, your current is very much dependent on the surface area also.

So, here two very important things I am just telling you can explain your output of your cyclic voltammogram that is it will effect one is the scan rate and one is the surface area and another thing the diffusion coefficient D these are diffusion coefficient that is depends on in your I mean which solutions you are using based on your redox couple. So, different different redox couple in the solution they have the different different different diffusion coefficient, ok.

So, if you fix like same solution in this case the diffusion coefficient is constant and if you fix the area of the electrode and working electrode then the area also constant. But if you increase the scan rate then you will get the higher and higher and higher current right. So, this is the one important information's for you while you are when you will characterize the biosensor surface. So, you can try ok.

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Next thing is the Cottrell equation. This is again the very simple things I am (Refer Time: 21:35) want to derive the equations that I want to tell you the Cottrell equations actually is described the change in electric current with respect to time. Suppose you are measuring the different chrono-amperometry (Refer Time: 21:50) right.

So, here you are applying a fixed potential and you are getting the output of the current. So, current with respect to time that you are calculating or you are measuring while you have a chrono-amperometry. So, there can be some effect change of current can happen with respect to time and that you can explain with the help of Cottrell equations. So, this is the Cottrell equations. What is this?

So, the Cottrell actually is described this one. Specifically describe the current response when potentials we are applying in a measurement. The current measure depends on the depends

the rate that the analyte diffuses to the electrode and current. Suppose see you have the electrode surface some analyte actually diffusing right to the solution to your electrode so, from bulk solution through bulk solution towards the electrode surface ok. So, when material diffusing from bulk to electrode surface.

So, there is different different parameter different different conditions can affect your current with respect to time. Means, generally we are expecting one like with respect to time you are measuring current and the chrono-amperometry. So, this current will be always constant, but sometime maybe there is some different diffusion.

So, that is called diffusion control means if your analyte that analyte is diffusing towards the surface. So, somehow its affect then you will get the different. Now, with respect to time your current also can be change. So, that things actually written here the how the current can be changed. What is the factor?

So, i is the current and n is then as I said n is the number of the electrons, F is the Faraday constants, A is the area of the surface and C 0 here that is initial concentration of the reducible analyte and D the diffusion and t the time. So, this is the relations and from here you can I mean think about the change if there is any problems of the current change that you can explain with this equation.

One important things that I am going to tell you here in the Cottrell equation like is a planar sometime it can be different different surface. See it can be like see this line the Cottrell equation describe the case for an electrode that is planar, but it also can be derived from spherical, cylindrical, rectangular, geometry. Means if your surface is different or there is some different kind of reactions happen that everything can be explained through this reactions and there is a possibility of change of the current.

I think one thing I just want to mentions you very clearly when as you are the end of this course when we are getting different different current or charge or different shape of the

cyclic voltammetry definitely you have to explain properly and for this explanations you can use these three equations.

So, one is the Nernst equation you can use from here you can measure the potentials also you should have the information of the formal potential. So, this information sometime you can include while you are writing a manuscript you should have this information's or based on this information's you can predict some uncertainty or the if there is any problem on your biosensors surface that also you can predict.

And this Randles Sevcik equation thus I just mentioned this is very simple like just changing the scan rate and how your measurement can be affected right. And then Cottrell equation this is mainly telling you that the current can be change with respect to time with these equations and so many uncertainty if this happened that you can predict.

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So, mainly I wanted to mentions here in this tutorial this is just few equations I just described on a Nernst, Randles and Cottrell. Not only these three equations you can think some your independent way and you can try to explain some different different factors as I told some many uncertainty can happen during the fabrications of your biosensors.

And you have to think you have to explain why you are getting different different shape, why you are maybe you are not getting your expected result, why you are not getting that you can explain by existing equation or you can model something new also. Now, with the help of your if you have some computational knowledge, you can try some simulations then you can develop some new equations also that is my main motive for this tutorial.

See as I mentioned suppose like chrono amperometry right let us explain this I can ask you this question right why at the very beginning it is very high current you are getting right? Current versus time when you are measuring chrono amperometry at the beginning you are getting the very high current then slowly it is coming to the where equilibrium form why? Then you can explain because your electrode surface you are using suppose Fe 2 plus.

So, at the very beginning your surface very near to the surface the electrochemistry mainly here is the surface reactions right it is the surface reaction. So, at the near surface you have lots of Fe 2 plus right and here you are applying oxidation potential. So, Fe 2 become the Fe 3 plus right 1 electron it will release Fe 2 plus because at the very beginning you have lots of Fe 2 plus that is why you are getting very high current.

Now Fe 2 plus Fe 3 will means that slowly the Fe 3 plus concentration will increase and in the near surface not only the Fe 2 plus there will be a Fe 3 plus also that is why your current will be slowly decrease because the concentration Fe 2 plus very near surface will decrease.

Then slowly there will be equilibrium of the Fe 2 plus and Fe 3 plus and we will get the thing equilibrium current. So, like this way you can explain. So, this is the like Fe 2 plus is diffusing towards the surface and then Fe 3 plus form then again it will come to the far from the surface then slowly there will be equilibrium. Like this way you can explain. So, this is

called a diffusional effect mass transfer effect and how mass is transferring towards the electrode that also you can explain.

And the shape see like shape of the cyclic voltammetry voltammogram if this oxidation speed reduction speed they are very close means it is kind of the what it is a reversible your reaction if it is reversible. Then your oxidation peak and reduction peak will be very close because they can easily oxidize easily reduce right means Fe 3 plus goes to Fe 2 plus easy and then Fe 3 2 plus Fe 3 plus it is also very easier.

So, you will get the very good shape, but if the oxidation reductions peak is very far right like this here oxidation here reductions means in this case it is kind of irreversible process in that case they will go very far from each other. So, like this way you can explain also many things.

So, you can characterize your biosensor surface mainly if your sensor surface electrode transfer rate is very fast easily electrode can transfer then you will get very reversible phenomena, but if there is a hindrance of the electrode transfer then you will get the irreversible phenomena, ok. So, like this way just try to explain your all the data the next class again I will show you some other important topic some based on my tutorial lecture and then slowly I will complete the all the descriptions of this course.

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So, please try to read this reference book that I mentioned know the Cottrell equation, Randles Sevcik equation, Nernst equation there is very much were written in this book that Electrochemical Methods Fundamentals and Applications by Allen J. Bard and R Faulkner is the 2nd edition book please try to remember and try to read this book also.

So, that is all for today's this tutorial and next tutorial I will cover some again some basic biosensor part. So, that you can try to you can remember all the things that I taught in this class ok.

Thank you very much.