Rate Processes

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Lecture No. # 27

Kinetics at Electrodes (Contd…)

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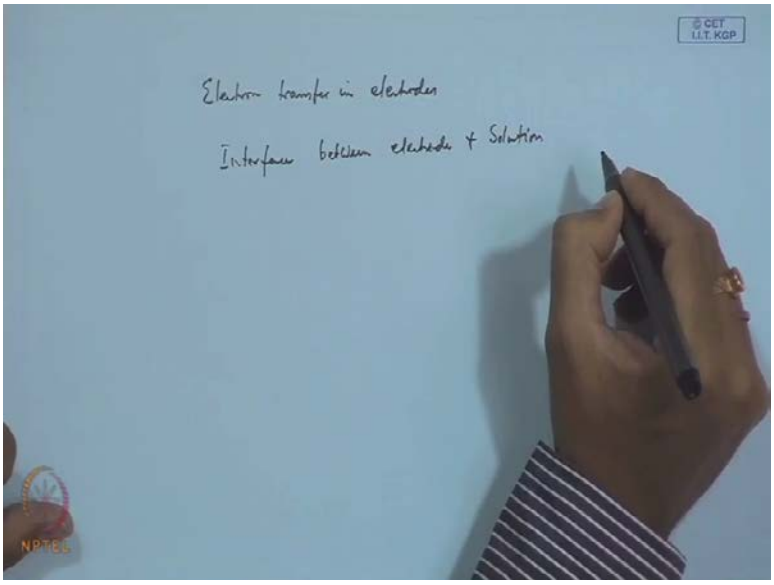

Electron transfer in electrodes

Interface between electrode + Solution

Good morning everybody. Friends, we are back here with rate processes. So, in our last lecture, in our last class we discussed electron transfer in electrodes, so and, so electron transfer in electrodes, in electrodes. So, there we talked about the interface of electrode and solution. So, interface we talked about, interface, and interface between electrode and solution. We discussed Helmholtz double layer, gouy-chapman layer and finally, we discussed stern layer, which is a, you know, mixture of these two. We also talked about interfacial potential, then you know, connection between galvanic and electrode potential rate of charge transfer. Then, we discussed also the free energy of activation, that is, electron transfer. When it is the case of electron transfer reaction, it must be associated with some, you know, free energy of activation. So, we discussed on that also. We came up with this butler-wullmer equation, then we discussed over potential and these things we discussed. So, today, you know, and also, you know, general arrangement of these rate measurements. We, you know, general, you know, experimental arrangement means, how to measure this, you know, rate, rate of electron transfer at the electrode. So, those we discussed in our, in our last lecture.

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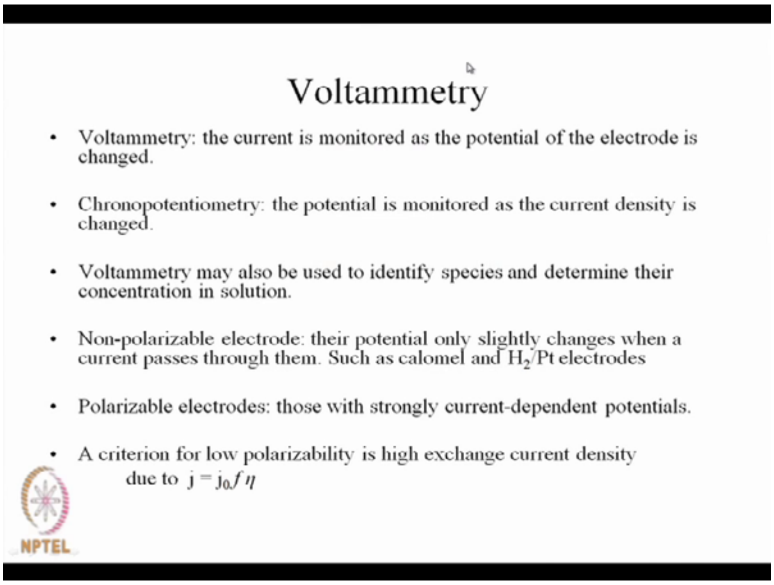

Voltammetry

- Voltammetry: the current is monitored as the potential of the electrode is changed.
- Chronopotentiometry: the potential is monitored as the current density is changed.
- Voltammetry may also be used to identify species and determine their concentration in solution.
- Non-polarizable electrode: their potential only slightly changes when a current passes through them. Such as calomel and H_2/Pt electrodes
- Polarizable electrodes: those with strongly current-dependent potentials.
- A criterion for low polarizability is high exchange current density due to $j = j_0 f \eta$

So, today, we will start with another topic, which is very important with you, you know, in connection with electron, in connection with kinetics at electrodes. So, it is Voltammetry, Voltammetry, Voltam, it is Voltammetry. So, in this case, current is monitored as the potential of electrode is changed. Now, Chronopotentiometry is, in that case, potential is monitored as the current density is altered. Now, in this case, what is the use of this voltammetry? This may be used to identify the species, which are present in the solution. So, it is a, it is a, you know, electrochemical means of identifying chemical species present in the solution. And of course, when it is the question of chemistry, the most important aspect is the, is the determination of concentration. So, using voltammetry, you can also find out concentration.

Electrodes like, there are various kinds of electrodes, like non-polarizable electrodes. Their potential only slightly changes when a current passes through them, as for example, as for example, calomel, standard hydrogen electrode H 2 Pt. And polarizable electrodes, you know, those with strongly current dependent having potential, which is having strongly dependent on, you know, on current. So, a criteria of low polarizability is high exchange current density due to, you know, j is equal to j 0 into f times eta, anyway. So, voltammetry is one of the techniques, which electrochemists employ to investigate electrolysis mechanism; there are numerous forms.

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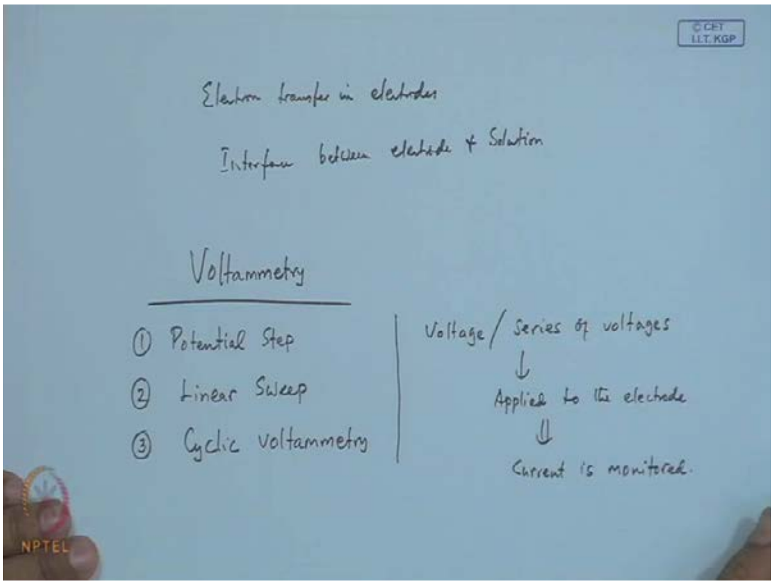

Electron transfer in electrodes

Interface between electrode & Solution

Voltammetry

① Potential Step
② Linear Sweep
③ Cyclic voltammetry

Voltage / Series of voltages
↓
Applied to the electrode
⇓
Current is monitored.

So, one is like a potential step, step; another is linear sweep, voltammetry, and 3rd is your cyclic voltammetry. Now, for each of these cases, a voltage or a series of voltage, voltage, so voltage or a series of voltages, voltages are applied to the electrode and the corresponding current, that flows, is monitored. So, voltages applied to the electrode and corresponding current that flows is monitored. Now, so current is monitored. Now, electrodes, generally, since you measure, you know, you apply some voltage and you measure current. So, naturally, question comes, you know, essential elements, that are used.

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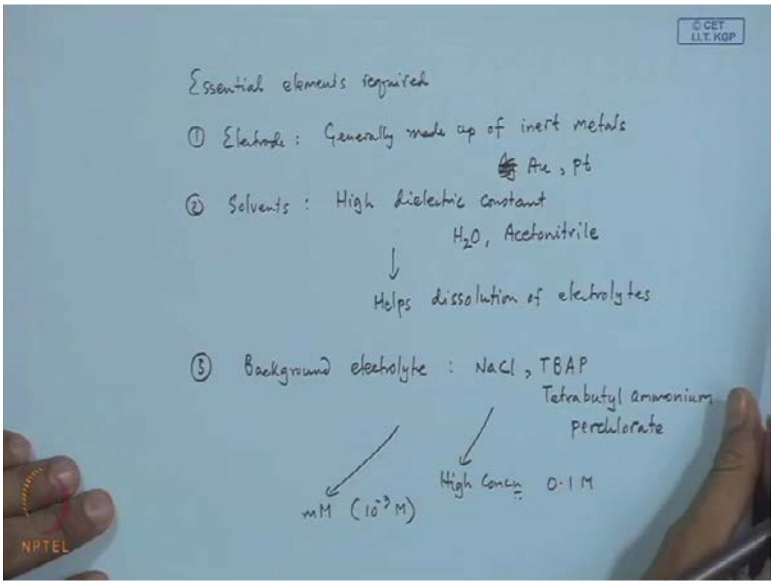

Essential elements required

① Electrode : Generally made up of inert metals

Au , Pt

② Solvents : High dielectric constant

H_2O, Acetonitrile

↓

Helps dissolution of electrolytes

③ Background electrolyte : NaCl , TBAP

Tetrabutyl ammonium perchlorate

High Concn. 0·1 M

mM (10^{-3} M)

So, essential elements, elements required: one is your electrode, of course, you need electrode, electrode, generally made up of inert metal, made up of, made up of inert metals, like you know, gold, sorry, Au, Pt, not silver; solvent, generally solvent like solvents of high dielectric constant, high dielectric constant, like you know, your water, acetonitrile, acetonitrile, these are used because these will enable your electrolytes to dissolve and help passage of current. So, this helps dissolution of electrolytes and naturally, which is required for the passage of current.

And generally, a background electrolyte, you know, background electrolyte, electrolyte is needed, maybe like NaCl, which are generally electrochemically inert, inert, salt like NaCl. Then, tetrabutyl, TBAP, tetrabutyl ammonium per chlorate, tetrabutyl ammonium per chlorate, these are generally used. And of course, it is generally added in, I mean, in high concentration, concentration of the order of say 0.1 molar. So, this will allow initially the current to pass through and you, your reactant, I mean, reactant, I mean, your reactive material, I mean, the substance on which you will carry out your experiment apart from this background electrolyte, that is used in low concentration, maybe in, you know, milli-molar concentration, milli-molar, that is, 10 to the power minus 3 molar. So, this is the, this, the, these are the essential elements used now in, you know, in your potential step voltammetry.

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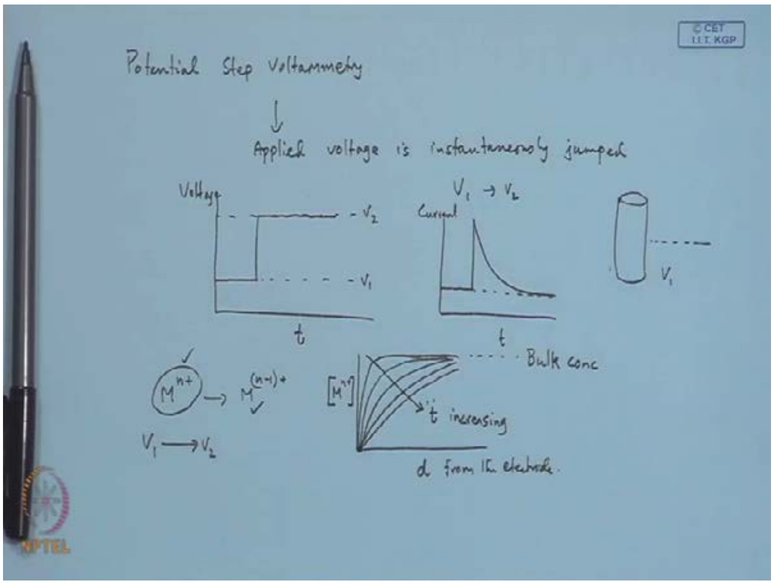

So, first one, potential step voltammetry, so potential step voltammetry, you know, this applied voltage, voltage is suddenly and you know, instantaneously, instantaneously jumped, you know, from one value to another, like say, from V 1 to V 2 and the resultant current is measured as a, as a function of time. Suddenly, it is jumped, instantaneously it is jumped and then, the resulting current is, is, is monitored as a function of time. So, it is basically a step potential function you are applying. So, basically, say from, this is your V, this V 1, say this is your V 2, what you do? Instantaneously, it is jumped, so from here to here and this is time and this is your voltage and you measure, and you measure, measure the current as a function of time, like initially, it was like this. The moment it is high, then current is high and then slowly, it decays to some value, maybe. So, and, and what is happening?

That, and ultimately, if you, if you monitor and concentration versus distance if you plot as a, as a function of, you know, distance. If you plot concentration of, say if you, suppose you have a reaction, say M n plus 2, say M n minus 1 plus. So, this reaction, what is happening, you, you can find out the concentration from the distance. So, with distance, I mean, this is your distance d and this is your concentration of say, M n plus as a function of, of time, you know, if you plot, what is happening, that maybe, it becomes something like this. So, this is your, at different times t, increasing t, increasing t, increasing and this is your, this is your bulk concentration and this is your distance d from the electrode. So, this will give you, you know, give you the idea of how this concentration is changing and you know, other like this, this maybe ultimately related to your rate of electron transfer. So, this is one way of, you know…

Usually, the voltage range is set, such that your reduction, reduction of M n plus, M n plus to M n minus 1 plus is thermodynamically, you know, thermodynamically unfavorable. And the 2nd voltage, you know, I mean initial voltage V 1, V 1 is set such that this is not happening and the 2nd voltage is selected. So, that, that, that the, that the ions, which are very close to the electrode, electrode is converted to the corresponding this from, so current response, you, this is the corresponding current response, so what is happening, that current. Therefore, since you change voltage from V 1 to V 2, your current response, I mean, when the time is very small, I mean, there is a, there is a huge change in concentration. There is a huge change in concentration due to, due to this reduction. Those ions, which are very close to the electrode, they are affected. That is why, there is a huge change in current and then, slowly it decays to, your, your starting value.

The current rises instantaneously after the change in voltage and then begins to drop as a function of time; you see it is as a function of time this occurs. Since the instant before the voltage step the surface of the, it is completely covered with reactant, this is your electrode. When it is at V 1, there was no reaction like this, so it is completely covered with your M n plus and you know, this throughout the solution, it has got a constant composition.

So, this is your electrode and this is the distance from the electrode. So, composition is almost closed and once the step occurs, what is happening, that your this reaction happens, I mean, this reaction occurs and a large current. Since this reaction occurs, electrons are required to, you know, reduce. So, large current is flowing, that is why, it is hugely up and the first layer, you know, of this metal is depleted. So, what is happening, that next layer of reactants should come through diffusion close to the electrode and then, reaction will take place.

So, and the reaction to continue, it is, there is a need for the supply of the fresh reactant and therefore, this happens in, in, in you know, this happens due to diffusion, therefore it requires time. So, the supply of fresh, you know, unconverted metal to the surface depends upon the diffusion, diffusion of the flask, and at short time, the diffusion flask is high as the current. I mean, as the change in concentration between the bulk value and the surface occurs over, you know, means at shorter time, the diffusion flask of this metal, I mean, this metal is high as the change in concentration between the bulk value and that at the surface occurs over a short distance.

As the electrolysis, you know, in this way, as the electrolysis continues, the material can diffuse further from electrode and therefore, concentration gradient is, you know, is dropped. As concentration gradient drops, so the supplies of this reactant to, you know, to surface and therefore, the current also decreases. I mean, since, you know, longer time is given, you see, that this is the initially, there was a huge concentration gradient, you know, as the distance is more. So, distance is more, so it is bulk. So, gradually what is happening, that your, this concentration gradient, you know, it becomes, you know, like having a, having, having a fixed value, I mean, concentration versus distance. Therefore, your, current, I mean, as time is increased, you know, concentration gradient is decreased.

So, you know, from this diffusion, coefficient can be obtained using, using some standard relation, you can find out, you know, the diffusion coefficient for the ion to the electrode. So, this is, this is called your potential step voltammetry. This is, basically you would change the potential and the moment you change the potential, the ions, which are close, they are initially consumed and then, next, next layer of electrodes, I mean, I mean, ions will diffuse. So, this will, this diffusion will continue at, at shorter time. This concentration gradient was large, but as you give more time, then diffusion occurs as a result of which, you know, this concentration gradient, concentration gradient decreases with time. So, this happens with, you know, this potential step voltammetry.

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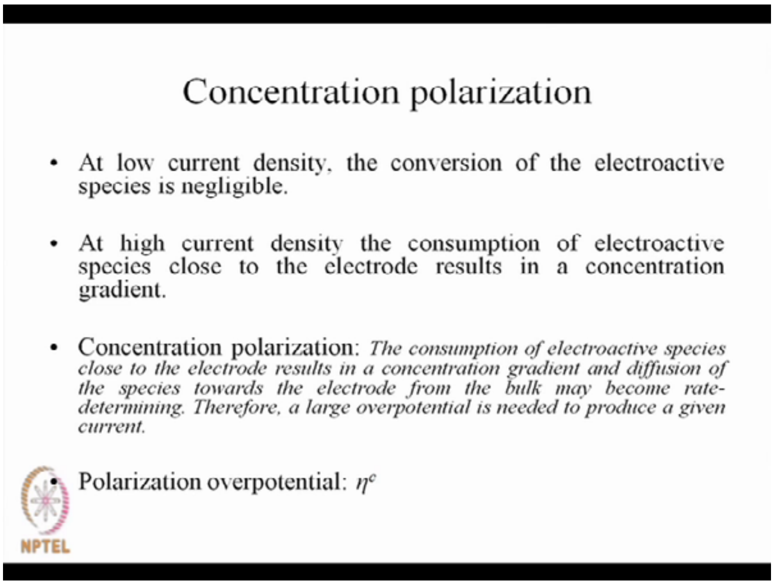

Concentration polarization

- At low current density, the conversion of the electroactive species is negligible.
- At high current density the consumption of electroactive species close to the electrode results in a concentration gradient.
- Concentration polarization: *The consumption of electroactive species close to the electrode results in a concentration gradient and diffusion of the species towards the electrode from the bulk may become rate-determining. Therefore, a large overpotential is needed to produce a given current.*
- Polarization overpotential: η^c

Now, next thing, we were, we were talking about another point, that we should mention that the concentration polarization. Now, you know, this is your one thing, another point, which we must think of is your concentration polarization, here we should look into. Now, when the current density is less, the conversion of electroactive species is negligible, but at high current density, the composition consumption of electroactive species close to the electrode results in concentration gradient. As I told you, that here, here, this is consumed, so therefore, there is a huge concentration gradient, gradient, which is, which is there when current density is quite high and so this results in concentration polarization.

That is, the consumption of electroactive species close to the electrode results in a concentration gradient and diffusion of species towards electrode from the bulk may become the rate limiting process. As I told you, that in potential step voltammetry, this I told you, that at the, at the very, you know, start of your in, you know, stepping of voltage, what is happening, that here it is consumed, all the ions close to this is consumed and then it starts to diffuse. So, it is not that instantly the, the other, I mean, the ions, which were at a further distance from the electrode, at a further position from the electrode, that will come instantly, it will, it will require some time and that will that is diffusion limited and that is why using some standard relation like current has got some, I mean, the, from, you know, using some equation, that is mass transport equation and that has relation to your current, that is absorbed. So, you can find out the diffusion coefficient.

So, anyway, therefore, a large over, overpotential is needed to produce a given current. In this case, since there is a, there is a, there is a, you know, concentration difference, there is a huge concentration gradient that is created now. Polarization therefore, a large overpotential is needed to produce a given current and that over potential may be regarded as the polarization overpotential.

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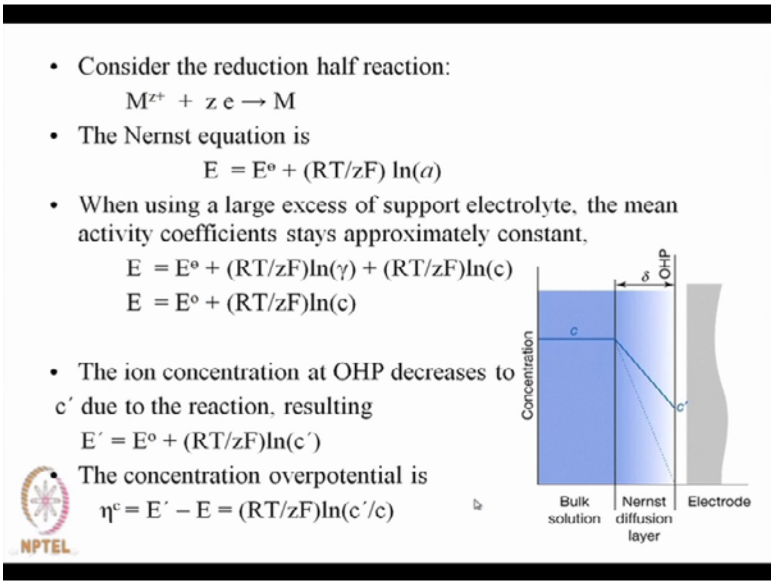

- Consider the reduction half reaction:

  $M^{z+} + z\,e \rightarrow M$

- The Nernst equation is

  $E = E^o + (RT/zF)\ln(a)$

- When using a large excess of support electrolyte, the mean activity coefficients stays approximately constant.

  $E = E^o + (RT/zF)\ln(\gamma) + (RT/zF)\ln(c)$

  $E = E^o + (RT/zF)\ln(c)$

- The ion concentration at OHP decreases to c' due to the reaction, resulting

  $E' = E^o + (RT/zF)\ln(c')$

- The concentration overpotential is

  $\eta^c = E' - E = (RT/zF)\ln(c'/c)$

Now, consider a, consider a simple reaction, consider a simple reaction, that is, M z plus giving, you know, after giving z electrons, it is giving out M. Now, this is your Nernst relation, E is equal to E 0 bar plus RT by zF ln a. So, when using a large excess of support electrolyte, as I told you, that you know, key ingredient for, you know, these experiments, you need, you know, that is, background electrolyte or support electrolyte. The mean activity coefficient stays, you know, approximately constant because your ionic strength is huge. Therefore, any little change in concentration of your reactant does not alter the, you know, ionic strength a lot and as a result of which, your, the mean activity coefficient of the ions involved in this reaction remains approximately constant. So, you can write this expression E is equal to E 0 bar RT by zF ln gamma, you know, gamma into concentration. So, you know, you can write in this way and if you, if you, if you write these 2 together, see you write, E 0 plus RT by zF ln c.

So, what is happening, that as I initially, initially, the ion concentration, I mean, the ion concentration at outer Helmholtz plane decreases to some value due to reaction. So, it was c, now it has decreased to some value c primed and due to the reaction, as I told you, as I, as I have shown to you, that like this with distance. So, this is your bulk concentration, this is your bulk concentration and this is your, maybe, concentration at the electrode because concentration at the electrode is always 0 because, you know, electrolysis is occurring, reaction is taking place at the electrode, therefore your E is now converted to E primed because of the change in concentration.

So, this you see, this has changed and this is your outer Helmholtz plane, this is your bulk solution, this is your electrode. So, electrodes, this value has reduced to some value because of this reaction. Actually, it should be reduced to, you know, at the electrode, it should be 0, but suppose, if it is reduced to here, then, your, your, your E primed becomes, I mean, E becomes E primed. So, E primed is equal to E not plus RT by zF ln c primed. So, your corresponding potential is this.

So, what is the concentration over potential because of this concentration gradient that is set up, because of this reaction, you see. So, eta c, this is the concentration overpotential as I told you, because of this concentration polarization a large overpotential is needed to produce a given current. So, polarization overpotential is, it has c and that can be related this way, E primed minus E, which is nothing but, RT by zF ln c primed by c. So, so you know, therefore this is your, this is the overpotential that, that can be you know, that can be calculated in this way.

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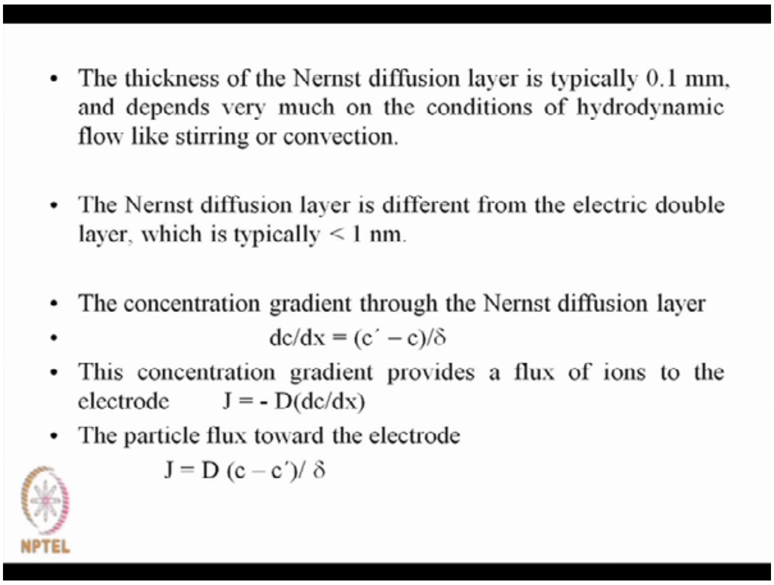

- The thickness of the Nernst diffusion layer is typically 0.1 mm, and depends very much on the conditions of hydrodynamic flow like stirring or convection.
- The Nernst diffusion layer is different from the electric double layer, which is typically < 1 nm.
- The concentration gradient through the Nernst diffusion layer
- $dc/dx = (c' - c)/\delta$
- This concentration gradient provides a flux of ions to the electrode $J = - D(dc/dx)$
- The particle flux toward the electrode

$$J = D\,(c - c')/\,\delta$$

Next is thickness of the Nernst diffusion layer. This is your Nernst diffusion layer, this is your bulk solution, this is your electrode. So, diffusion layer is typically of the order of 0.1 millimeter and depends very much on the condition of hydrodynamic flow, like starring and you know convection. So, these are the, means, if you star the solution, then its, this thickness will be different and this Nernst diffusion layer, it is not, it should not be, you know, confused with electrical double layer. Actually, electrical double layer is even less than a nanometer, if you know, if you, maybe, molecular, you know, atomic diameter thickness, I mean, I mean, less than a nanometer.

Now, the concentration gradient through the Nernst diffusion layer, your, this through the Nernst diffusion layer delta is the, delta is the thickness. So, your, your, this dc dx is the, is the concentration gradient, is nothing but the difference in concentration, that is, bulk minus that at the electrode divided by delta. This concentration gradient provides a flux of ions to the electrode through your, you know, j is proportional to this, this dc dx and of course, this is the diffusion coefficient. So, particle flux towards the electrode, towards the electrode is given by this, j is D into this, which I already have told, that this particle, particle flux will be dependent, dependent on how, means the process is rate limited by the diffusion of the of the substances. I mean, the diffusion of the ions and this particle flux can be, can be expressed in this way.

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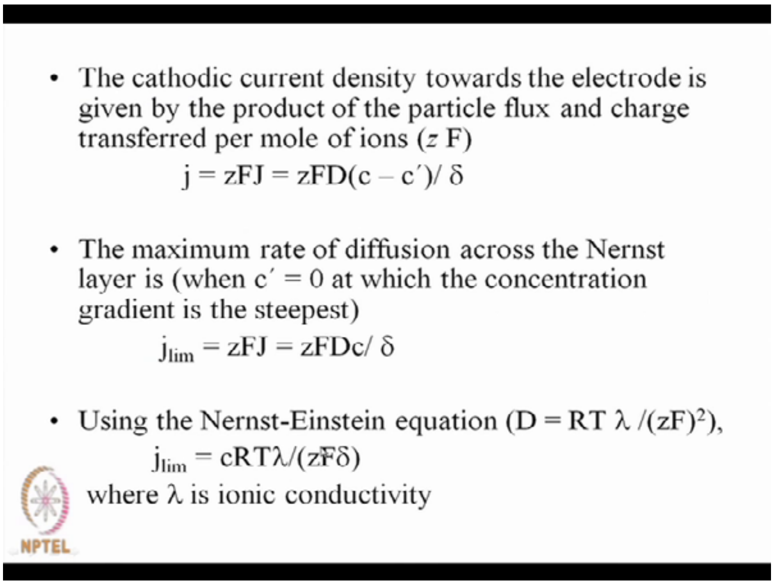

- The cathodic current density towards the electrode is given by the product of the particle flux and charge transferred per mole of ions (*z* F)

$$j = zFJ = zFD(c - c')/\delta$$

- The maximum rate of diffusion across the Nernst layer is (when c′ = 0 at which the concentration gradient is the steepest)

$$j_{\text{lim}} = zFJ = zFDc/\delta$$

- Using the Nernst-Einstein equation ($D = RT\lambda/(zF)^2$),

$$j_{\text{lim}} = cRT\lambda/(zF\delta)$$

where λ is ionic conductivity

Now, the cathodic current density towards the electrode is given by the by the product of particle flux and the charge transferred per mol of ion that is z into F.

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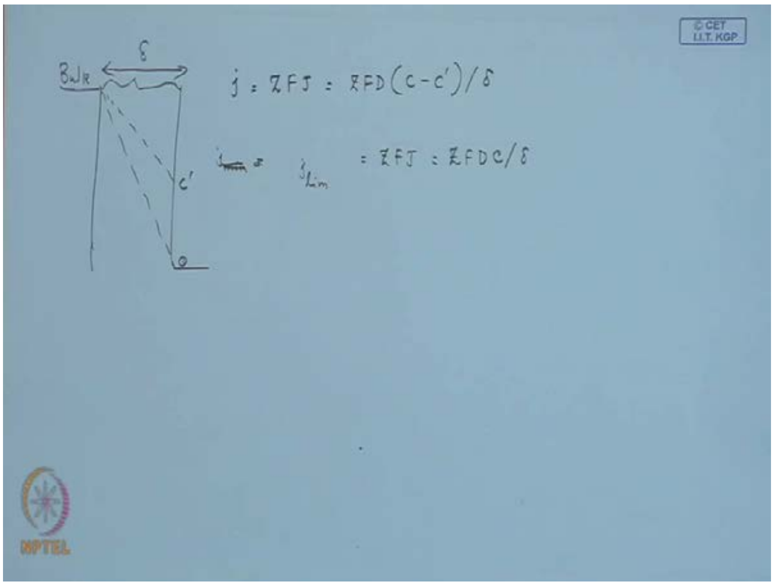

$$j = zFJ = zFD(c - c')/\delta$$

$$j_{Lim} = zFJ = zFDc/\delta$$

Therefore, cathodic current density, you know, it is given by j is equal to zFJ, J is this, J is this particle flux and the charge transferred is z into F. So, basically, it becomes zFD c minus c primed divided by delta.

The minimum rate of diffusion across the Nernst layer, so minimum rate, j min, will be when c primed is, I mean, sorry, maximum, maximum rate, not the minimum because it is, it will be maximum, like if you think of this one, like it was c primed and it was, it is 0, therefore your gradient is more, this is your bulk. So, this gradient is less, this gradient is more, that is why, this limiting current, j limit, it is not the minimum, sorry. So, limiting current will be given by, you know, just you put c primed equal to 0. So, zFJ, which is equal to zFD into c divided by delta that is the limiting current, so maximum rate of diffusion across the Nernst layer, this layer delta.

Now, using the Nernst-Einstein equation, that is, D equal to RT lambda divided by zF square, your limiting current can be, you know, related, means, if you just plug in this over here and where, you know, lambda is the ionic conductivity. So, from the limiting current, I mean, limiting current can be, you know, ultimately related to the Nernst, you know, Einstein equation, I mean, you can replace D with this expression. So, this is the expression for the limiting expression for the, for the limiting current.

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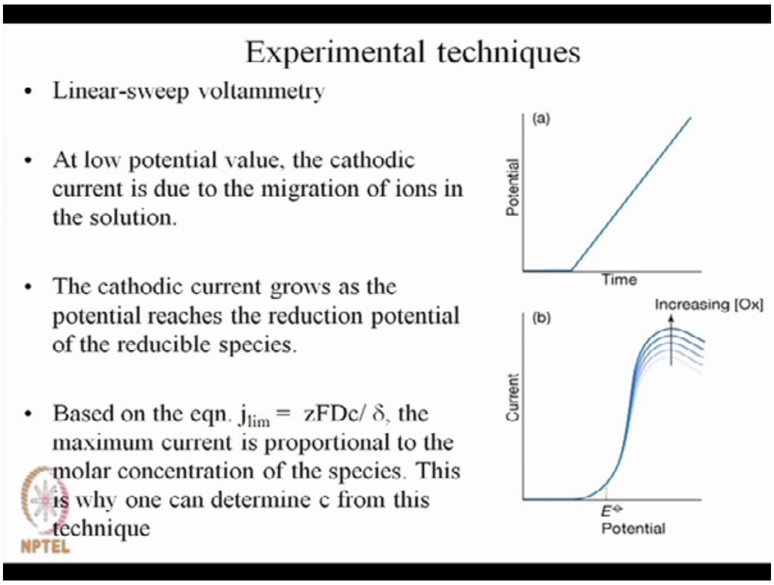

Experimental techniques

- Linear-sweep voltammetry
- At low potential value, the cathodic current is due to the migration of ions in the solution.
- The cathodic current grows as the potential reaches the reduction potential of the reducible species.
- Based on the eqn. $j_{lim} = zFDc/\delta$, the maximum current is proportional to the molar concentration of the species. This is why one can determine c from this technique

Now, as I told you, experimental technique, on, in which, I mean, I already have told talked about this potential step voltammetry, another method is your, another method is your LSV, linear sweep voltammetry. So, linear sweep voltammetry, it is, you know, at low potential value, the cathodic current is due to the migration of ions in the solution and cathodic current grows as the potential reaches the reduction potential of the reducible species.

And you know, as I told you, based on the, on the previous equation, limiting current is zFDC divided by delta, the maximum current is proportional to the molar concentration of the species. So, using this expression, use, using the linear, I mean, the limiting current, you can find out the concentration of the species. So, this is an application of this, this measurement. Now, in, in potential, you know, linear sweep voltammetry, you know, it is, your potential is linearly swept, linearly swept. I mean, it is, it is increased from not like just like your potential step like this, it is linearly swept. So, having some value, then it is linearly increased with, with, with time and you measure the current potential.

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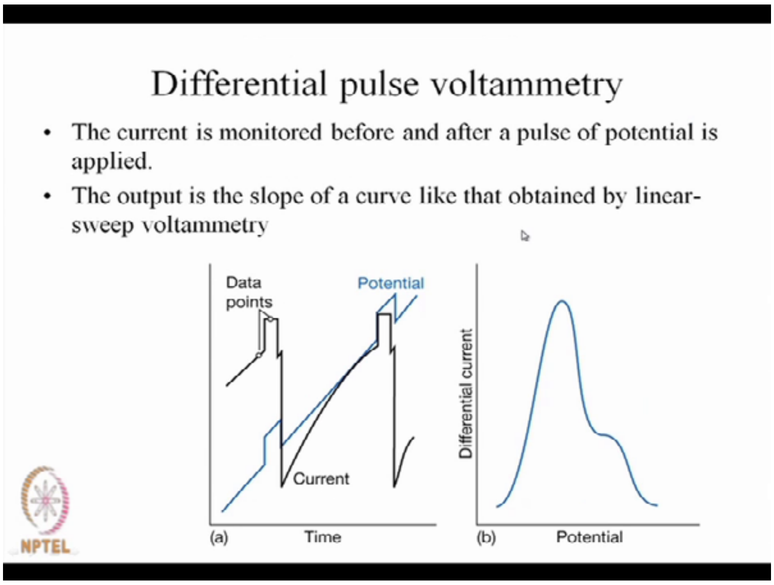

Differential pulse voltammetry

- The current is monitored before and after a pulse of potential is applied.
- The output is the slope of a curve like that obtained by linear-sweep voltammetry

Now, next is, there is another thing, which is called the differential pulse voltammetry. So, I, I, I will come to linear sweep voltammetry, but before that, let us have an idea of the differential pulse voltammetry. What is done here? The current is monitored before and after a pulse of potential is applied, a pulse of potential is applied, and you monitor the current. So, and the output is, output is the slope of a curve, like obtained by linear sweep voltammetry.

So, so, this is your basically potential versus time and this is your current as a function of time and differential current versus differential potential is, has got a plot like this. So, differential pulse voltammetry, in this case, current is monitored before and after a pulse or potential is applied and the curve, the curve is like this. So, now, let us come to linear sweep voltammetry. As I told you that, that voltage is linearly swept from one value to another for some interval of time, for some interval of time. So, let us see.

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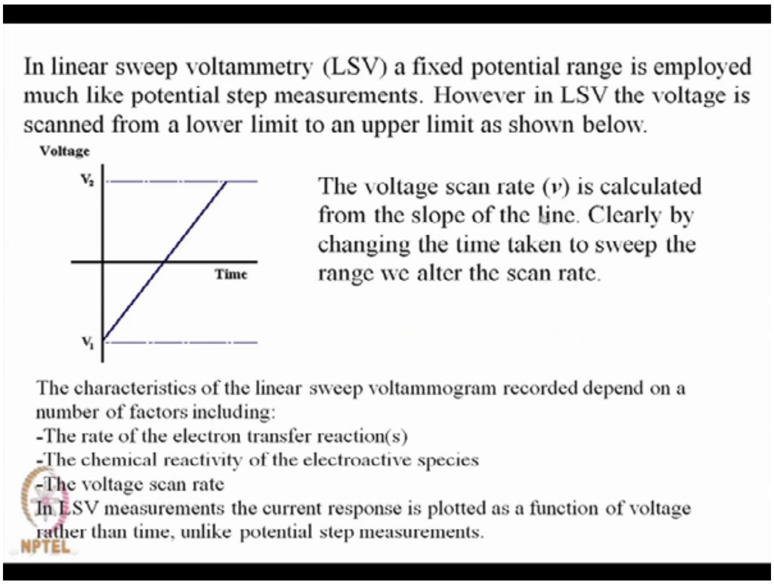

In linear sweep voltammetry (LSV) a fixed potential range is employed much like potential step measurements. However in LSV the voltage is scanned from a lower limit to an upper limit as shown below.

The voltage scan rate (ν) is calculated from the slope of the line. Clearly by changing the time taken to sweep the range we alter the scan rate.

The characteristics of the linear sweep voltammogram recorded depend on a number of factors including:
-The rate of the electron transfer reaction(s)
-The chemical reactivity of the electroactive species
-The voltage scan rate
In LSV measurements the current response is plotted as a function of voltage rather than time, unlike potential step measurements.

In linear sweep voltammetry, a fixed potential range is employed. So, this is your potential range, say V 1 and V 2. In other case, that is, you know, pulse potential step voltammetry, that is, this one, it is a, it is just like a step function, but here, here, it, what is happening, that it is very steep, I mean, just like a vertical on this line, but here, it has got some slope, slowly it is increased. So, it is like a potential step measurement, but it is it is a slanting one.

Now, here in LSV, linear sweep voltammetry, the voltage is scanned from a lower limit to an upper limit, as shown here. So, you see, here lower limit and upper limit. So, V 1 to V 2 slowly increased, scanned, it is, it is a, voltage is scanned. The voltage scan rate V is calculated from the slope of the line because difference divided by time means, how much voltage it has, it has, you know, increased to, maybe, say 2 units and say, in 2 seconds. So, 2 by 2, it is 1, so scan rate is 1 volt per, say, minute. Clearly, by changing the time taken to sweep the, sweep the range will alter the scan rate.

So, there is an option, there is an option for changing, changing the scan rate and that scan rate may, may have some, you know, relation to the rate of electron transfer at the electrode. I mean if it is swept very fast, then one situation may happen or if it is swept very slowly. So, scan rate looks like, that scan rate should have some, you know, relation.

Now, thing is, the characteristics of linear sweep voltammogram recorded depends on a number of factors. So, you, you draw the current potential diagram, that is the voltammogram and that has got, you know, you know, characteristic is very much dependent on, on, on several factors. So, one is the rate of electron transfer, I mean, rate of electron transfer, I mean, you are, you are here, I mean, you are doing this experiment, that is, electron transfer at the electrode, you are looking at, you are, you are monitoring some electron transfer reaction. So, so, rate of electron transfer, voltammogram will depend on the rate of electron transfer.

Then, chemical reactivity of the electroactive species if it is a, it is a, if it is a highly reactive species. So, chemical reactivity is a factor on which this voltammogram, I mean LSV, LS voltammogram will depend and of course, the voltage scan rate. Now, in LSV, what you, what you plot, that is, current response is plotted as a function of voltage, rather than time, unlike potential step measurement. In potential step measurement, what you measure, you suddenly or instantaneously, you change the potential, voltage you change and then, you, you measure the current response with time; you measure the current response. But here, you do not do in that way, like you do not do any time, you know, you do not do any measurement as a function of time. What you do? You change the scan rate.

So, scan rate change means, you know, that has some dependence on time. So, you change scan rate, but, you, you plot the, you know, current response as a function, as a function of the voltage. So, you are changing the voltage. So, voltage change and then current response, you, you do it so, so, you know, in a in a linear sweep voltammetry you do that.

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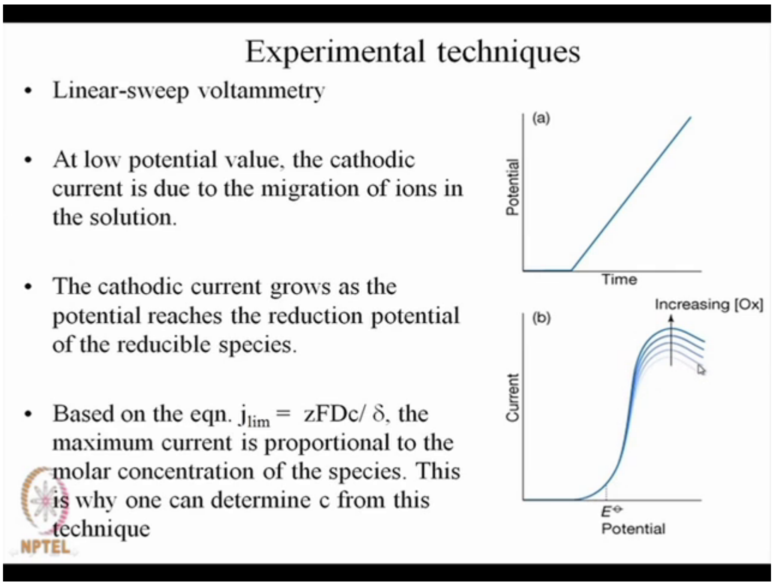

Experimental techniques

- Linear-sweep voltammetry
- At low potential value, the cathodic current is due to the migration of ions in the solution.
- The cathodic current grows as the potential reaches the reduction potential of the reducible species.
- Based on the eqn. $j_{lim} = zFDc/\delta$, the maximum current is proportional to the molar concentration of the species. This is why one can determine c from this technique

Now, now, typical plot is like this here, linear sweep voltammogram, you know, this is your potential versus time and it is your, you change the scan rate. So, potential, you know, you know, you, voltage increasing your scan rate, you do it. So, so, what is happening, that this is as a result of change of scan rate.

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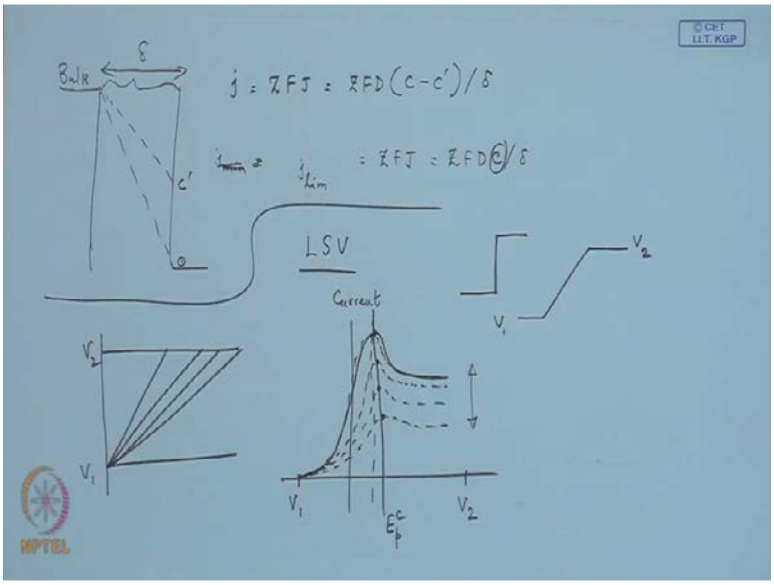

So, what is happening, that let us draw, like one thing you have got, say this V 1, V 2. So, you, you change like this; you change like this. So, accordingly; you will generate, you know, V 1 to V 2; say, your voltage here V 1, this is V 2; V 1, V 2; V 1, this is V 2.

So, something like this, then maybe like this, it is because of the scan rate changing. So, peak potential, actually this, this peak should not change, these peaks should, should not change. So, this is your peak potential E p c, cathodic peak potential. So, this peak potential change, but its position should not change. So, this is as a result of change of scan rate. You will get different, you know, response, current response; different current response. So, it depends on the, on the, so therefore, your profile, this current potential profile, current voltage profile, it depends very much. So, you see here, like changing, it is changing, so therefore, this is basically, you, what you get.

So, so, rate of electron transfer, transfer rate, I mean, electron transfer reactions and then, chemical reactivity of the electroactive species and of course, the voltage scan rate, anyway. Say, this is, this is pretty much, what is done in, in your linear sweep voltammetry. So, you keep on changing the scan rate and you get different, you know, response curve. So, and from this, you can cathode, you can get cathodic peak potential, cathodic peak potential you will be getting, that is, from this peak value. Next is, you know, now, next is in your linear sweep voltammetry, you know, next one question is remaining, that as I told you, that the profile is dependent on, profile is dependent on the rate of electron transfer reaction. I mean, how fast this electron transfer reaction is occurring and that is, it depends on the electron transfer rate.

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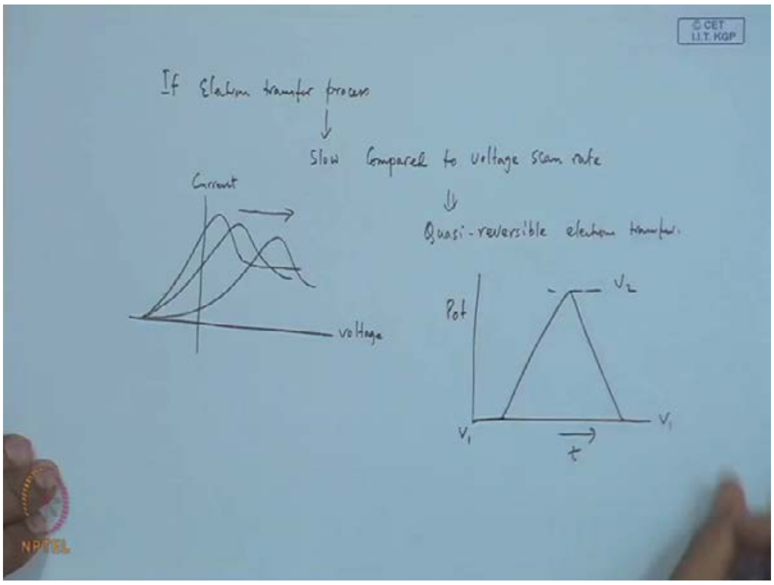

If Electron transfer process

↓

Slow Compared to voltage scan rate

⇓

Quasi-reversible electron transfer.

So, one question is still remaining, that if electron transfer, transfer, I mean, transfer processes are slow, I mean, slow in comparison to your voltage scan rate, slow compared to voltage scan, voltage scan rate and in that case, this is termed as quasi-reversible, quasi-reversible or maybe, it is termed as irreversible, maybe irreversible electron transfer, quasi-reversible electron transfer. So, in that case, if it is slow compared to the voltage scan rate, so let us have a plot, have a representative plot, you know. One case it is like this, maybe in another case it is like this or maybe, in still another case, it is like this. So, in this way, so slower and slower, so it is current, current and voltage. So, this is you know, electron transfer; you know, the electron transfer process is slower, then it is it is shifting this way. So, that means, it will give you the, give you the idea of, of whether the process is reversible or irreversible, I mean quasi-reversible.

So, you change the scan rate and if you, if you, if you get a curve like, like this one, which you know, if you get a curve like this one, no change in one case. This peak potential is not changing in this case; your peak potential is changing. So, that will give you the idea of, idea of whether it is a, you know, your electron transfer process is slower than your voltage scan rate, that is, it is a, whether it is a quasi-reversible or irreversible electron transfer.

So, a slight modification of this has been done with cyclic voltammetry. In linear sweep voltammetry, voltage is swept, you know, from say, V 1 to V 2 and it is kept, it is kept for, I mean, I mean, the value from V 1 to V 2 it is just done like that. But now, if you do an arrangement, such that, you know, you can change the voltage sweep, like from here to this value and then it is coming back to its original value. So, cyclically, cyclically change from say V 1 to V 2 and then, V 2 to again V 1, so this is your potential value and this is your time. So, in that case, what do you expect, you expect, you know, reversal of, you know, things, I mean, reverse curve.

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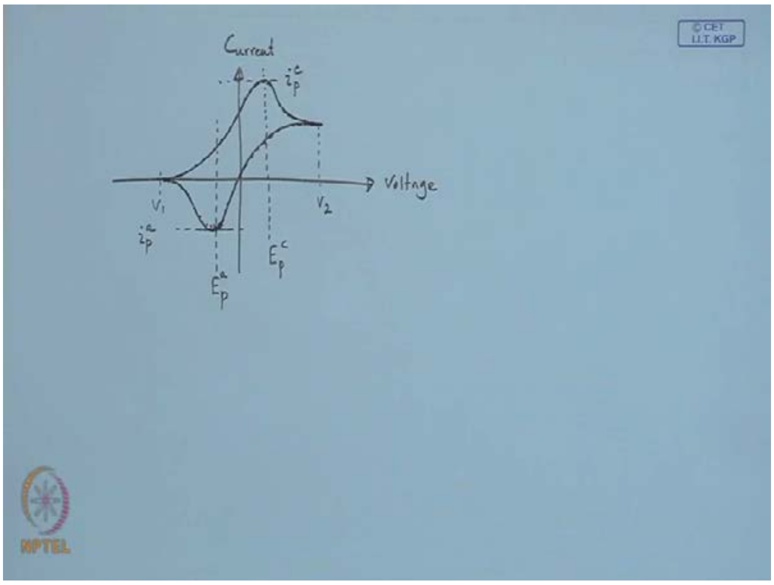

So, what is, what is the typical graph? For this a typical graph could be like, you know, this is your current potential diagram, so maybe, something like this. So, this maybe the curve if you join by a line; so, this is your current and voltage. So, this is your cathodic E p c and this is E p a, E p a, I mean, E value corresponding to the peek position. And i, this is your i p c and this is your i p a. These are the characteristic things, that you know, you, you can think of. So, this is your V 2, say this is your V 1. So, so, means, what is the usefulness of such a plot?

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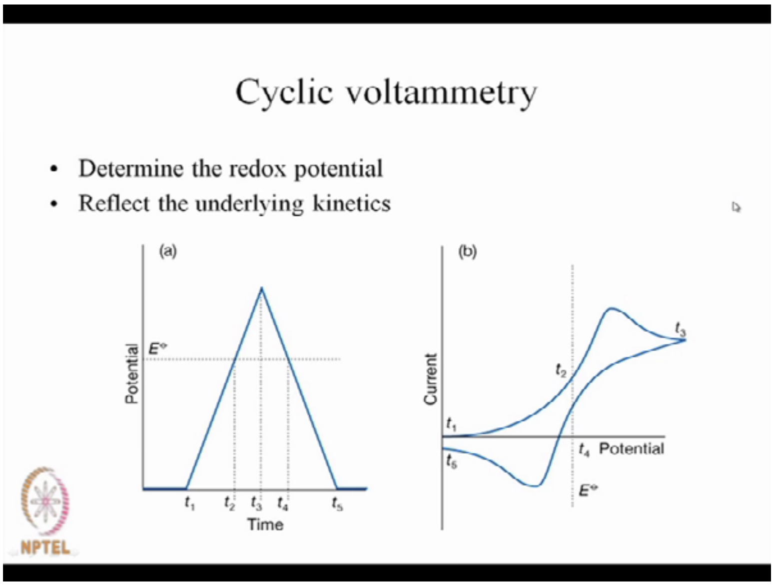

Cyclic voltammetry

- Determine the redox potential
- Reflect the underlying kinetics

Now, next, the important thing is, that we can determine the redox potential of a, of an electroactive substance of a, of a redox couple and it reflects the underlying kinetics. As I told you, in linear sweep voltammetry, you know, changing of your, of your scan rate gives you an idea of whether an electron transfer reaction is slow or fast**.**

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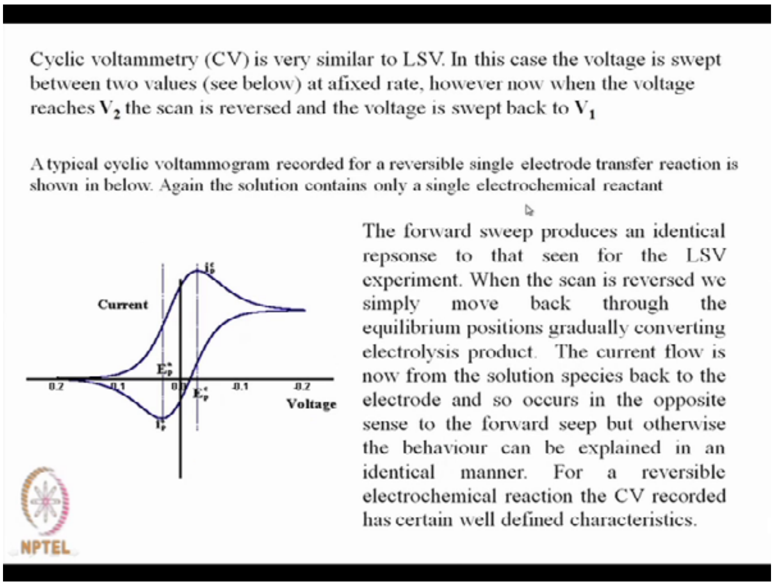

Cyclic voltammetry (CV) is very similar to LSV. In this case the voltage is swept between two values (see below) at afixed rate, however now when the voltage reaches V_2 the scan is reversed and the voltage is swept back to V_1

A typical cyclic voltammogram recorded for a reversible single electrode transfer reaction is shown in below. Again the solution contains only a single electrochemical reactant

The forward sweep produces an identical repsonse to that seen for the LSV experiment. When the scan is reversed we simply move back through the equilibrium positions gradually converting electrolysis product. The current flow is now from the solution species back to the electrode and so occurs in the opposite sense to the forward seep but otherwise the behaviour can be explained in an identical manner. For a reversible electrochemical reaction the CV recorded has certain well defined characteristics.

Now, in cyclic voltammetry is very similar to LSV, as I told you. In this case, voltage is swept between 2 values, so from one value to another at fixed rate and however, now, when voltage reaches V 2 here, V 2, then again it is, it is reversed, that is, scan is reversed to V 1 and the voltage is swept back to V 1 value. A typical voltammogram recorded for, you know, reversible single electrode transfer reaction is here, it is shown here. Again, the solution contains only 1 electrochemical reactant, that is, that is very important.

Now, your forward sweep produces an identical response to that, that is seen in linear sweep voltammetry because from V 1 to V 2 is basically your linear sweep, you, you are drawing a linear sweep voltammogram. So, if you, if you just forget about this part, you just forget about this, it looks like a linear sweep voltammogram. So, when the scan is reversed, we simply move back through the equilibrium position, gradually converting the electrolysis product. So, whatever reaction has taken place, in this reaction it is reversed through the equilibrium position, gradually converting electrolysis products. The current flow is now from the solution species back to the electrode, so here, electrode to solution; now, now here, solution to the electrode, back to the electrode. So, occurs the opposite sense of, sense to the forward sweep, but otherwise behavior can be explained in an identical manner, so it is just the reverse. For a reversible electrochemical reaction, the CV, you know, when it is recorded, we have well defined characteristics. As I told you, that for a perfect reversible one, you know, from the discussion of your linear sweep voltammetry, as I told you, the sweep position is changing if it is not a reversible one, if it is quasi-reversible, but if it is reversible, then you, you should expect something like this.

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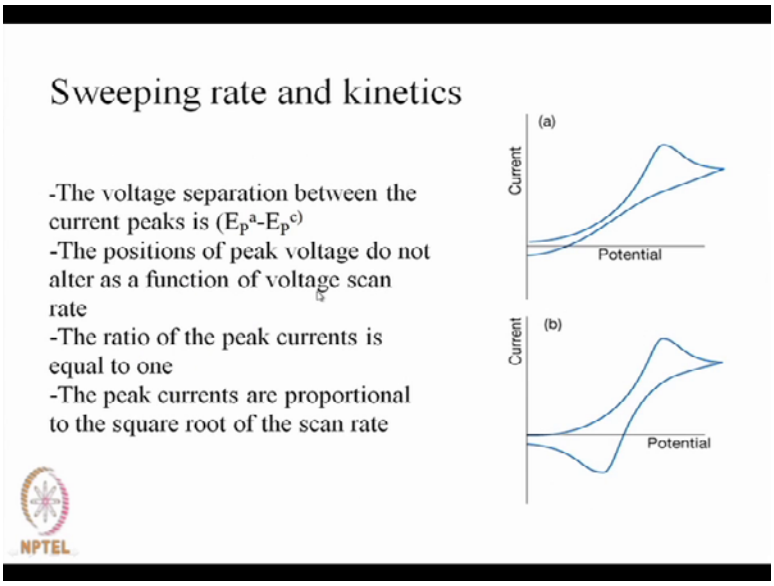

Sweeping rate and kinetics

-The voltage separation between the current peaks is $(E_p^a - E_p^c)$

-The positions of peak voltage do not alter as a function of voltage scan rate

-The ratio of the peak currents is equal to one

-The peak currents are proportional to the square root of the scan rate

Now, what are those characteristics? Characteristics are like the voltage separation between the current peaks E p a and E p c, this one, the position of the peak, these are the characteristics. So, position of the peak voltage does not alter as a function of voltage scan rate for, for, you know this perfectly reversible one. The ratio of the peak current is equal to 1, equal to 1, this peak current, this peak current and you know that peak current. So, this ratio is 1, I mean, this peak current i p c and i a c, these are equal to 1. The peak currents are proportional to the square root of the scan rate. So, so, these are, you know, important characteristics of your, your… So, so, and the voltage separation, you know, is given by E p a and E p c now and the ratio of the peak current is equal to 1. The peak currents are proportional, square root of scan rate. So, so, this peak currents are proportional, I mean, this peak current is proportional to the square root the scan rate. So, when scan rate is more, your peak current is more like that, but of course, it is in a square root fashion.

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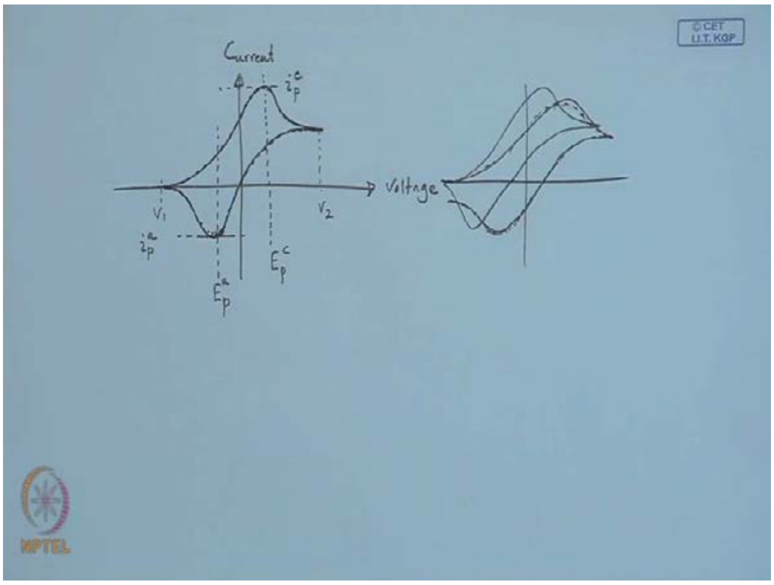

But one point, which I should tell you, that if it is, it is a quasi-reversible situation, then your cyclic voltammogram, I mean, if you change, do like this, then your this voltammogram will change, something like this and it may not look, may not, may not end up like this. Here, you see this, it is just like a perfect hysteresis kind of thing, but thus, that may not be observed. So, that is a signature of your reversibility. So, these are the points, that, that one should carefully look into while considering your, this current potential diagram for this voltammetric studies.

So, so what we have learnt out of this discussion? I mean, this, you know, kinetics, about the kinetics of electrode. Now, we have, here in this particular piece of lecture, we talked about mainly this voltammetry, various techniques, various voltammetric techniques, like you know, potential step voltammetry, LSV and cyclic voltammetry. Now, in, in potential step voltammetry, you can find out, of course, the diffusion coefficient of, of the ions to the electrode. So, and, and you know, it is diffusion limited, I mean, sometime you know, when, when you know, you know, 1st layer of reactants are used up or 2nd layer, then the, you know, reactants are to be, are to be taken from a distance place to, towards the electrode. So, that is limited by the diffusion.

Now, now, this voltammetry has got advantages, like you can, you can find out the, you can find out the concentration, you can find out the, like electrode potential and also, you can find out, I mean, you can, you can know about, you can, you can, you know, get information about the reversibility of the process. I mean, whether this electron transfer rate is reversible or not by changing the, your, scan rate and this characteristic cathodic peak potential, anodic peak potential and also peak current. These are very characteristic of, of some electroactive substance. So, so, from this I mean, you can know more about the electron transfer process, that is, I mean electron transfer process, that is, occurring at the electrode, I mean, electroactive substances, you can find out concentration. So, these are the, you know, these are the advantages or applications, I mean, with respect to using your, your voltammetric determinations. So, that is all for today's discussion. So, thank you for your patience.