Electrochemical Impedance Spectroscopy
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Lecture - 25
E-EAR Reaction, Negative Resistance (1 of 2)

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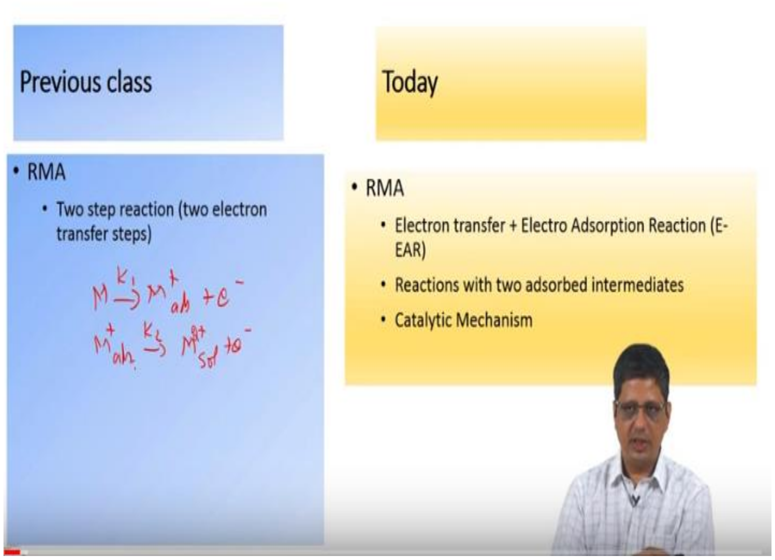

Previous class

- RMA
  - Two step reaction (two electron transfer steps)

$$M \xrightarrow{k_1} M^{+}_{ab} + e^{-}$$
$$M^{+}_{ab} \xrightarrow{k_2} M^{2+}_{sol} + e^{-}$$

Today

- RMA
  - Electron transfer + Electro Adsorption Reaction (E-EAR)
  - Reactions with two adsorbed intermediates
  - Catalytic Mechanism

In the last class we saw an example, where we had two step in a reaction first step is the electro chemical reaction and the second step is also an electrochemical reaction. And then we started with another example where we have one reaction which is electron transfer reaction which is a simple reaction, another reaction where there is an adsorption. So, I want to go through that and if term permits I want to go through a reaction with two adsorbed intermediates. I want to go through another reaction called catalytic reaction. I do not think we will go through all of them probably today in the next two or three classes. I would like you to actually go through underived the expressions we will take you step by step you also become more familiar with how to handle these mechanisms and propose a mechanism, derive the expression for it, and then get to expression for the impedance.

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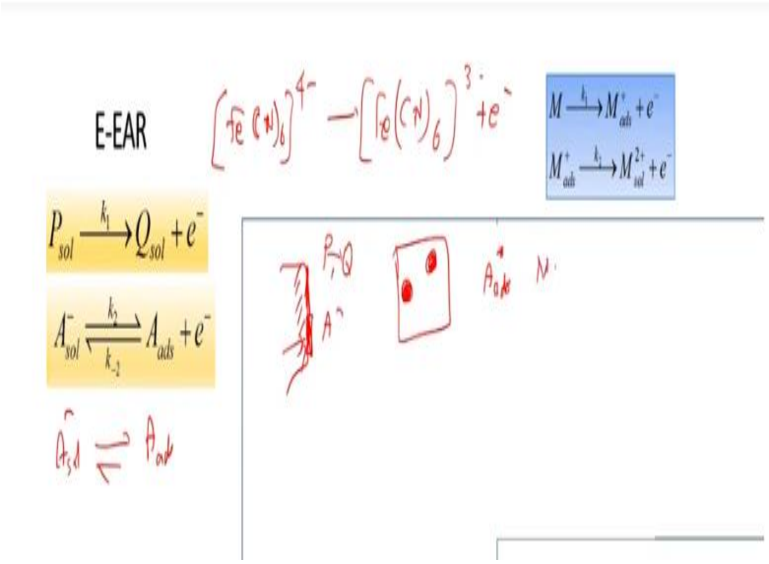

E-EAR

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$A^-_{sol} \rightleftharpoons A_{ad}$

So, what we saw in the last class it is given them the top right what we are going to see today is given on the left side on the top we have a reaction P going to Q. P could be for example, an electronic transfer reaction between ferrocyanide and ferricyanide redox couple right, then we have another material; anion is given by capital A it is in solution phase so it is A^- in the solution phase, it sits on the surface since it is blocking the surface.

Let us say this is the electrode we have P in solution, Q in solution; we have A^- here it can absorb on the surface and release an electrons it can also take up an electron and come out into the solution. This P going to Q we are going to assume right now that is just one directional we can also take the reversible reaction just going to be a little more complex than this and this can occur only on the free surface that means any surface where A is adsorbed. It is not going to catalyse this reaction of P going to Q only the surface which is free. So, if you take the surface and let us say this is the front face of this electrode this is facing the solution, these areas we have A_{ads}^- and releases an electron so it is becomes A_{ads}, A_{ads} here means it is a bond between metal and A this is how it looks like in these locations. We will not have this reaction happening in other locations where bare metal is present, this reaction can happen.

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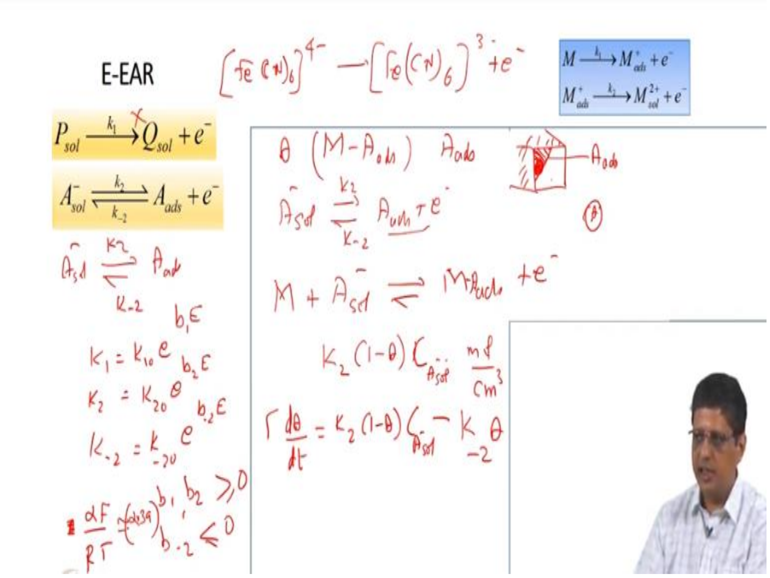

With that I would like you to write the mass balance equation and the charge balance equation. We are going to call θ as the fractional surface coverage of this species which is written in the shorthand as this. It is actually metal A adsorbed. What happens when the first reaction proceeds? Does it alter the formation or does it create a deplete A_{ads}, A_{ads} is not even there.

So, first reaction does not contribute to the formation of θ, In the second reaction forward reaction that creates A_{ads}, reverse reaction removes A_{ads} ?So if I want to say what is the rate of the forward reaction in the second reaction. The corresponding rate constants are k_2 this is k_{-2} so I would like you to look at this condition and then visualize, let us say these are all insulators only this areas square area is visible to the electrolyte.

In this electrolyte we are going to say a particular fraction is already covered with A_{ads} species the remaining material is available. So, if I want to write this in detail whatever reaction I have written here in the shorthand as $A_{sol}k_2$ and k_{-2} forms A_{ads} and releases an electron. I should actually write a vacant site and equal to A^- in the solution will go and sit on a vacant site and release an electron.

Only then it is it is going to convert in a site so it is going to increase θ and when this A_{ads}species collects an electron it goes out into solution as A_{sol}^- and it releases this site it becomes a bare metal site then. So, when the reverse reaction happens bare metal site number of bare metal sites will increase when the forward reaction happens it consumes the bare metal site, it consumes A_{sol}^-.

So, if it is an elementary reaction we would write k_2 concentration of the species A-N solution if that increases you are going to have more of the forward rate correct forward rate is going to be given with k_2 (1- θ) (multiplied by the) concentration of A^- in solution. So, we are going to assume the following; we are going to say master transfer is not rate limiting we are going to say that the reaction when it happens, it is not going to alter the concentration of A^- in solution to a significant level. That is, we have a large tank with significant amount of A^-_{sol}, P_{sol}, Q_{sol}it is completely well mixed. So, in the electrode the reaction happens but in the bulk the concentration change is not significant. We can measure the current we can control the voltage measure the current, we can control the current measure the voltage but by and large we are not altering the concentration of the species in the solution.

That means concentration of P, concentration of concentration of Q concentration of A^- all these solutions are fixed numbers that makes it a little easier to handle this. What are the unit is of k_2? this rate is going to be moles per area per time, unit of concentration is going to be moles per volume it can be typically mol/L but we can convert this to mol/cm^3, θ does not have any unit k_2 unit is going to be cm/s~~,~~

So now I would like you to write the rate of the reverse reaction, I want to say the rate of increase in θ with respect to time it is going to be it is a $C_{A\text{-}sol}$ is a constant for now. So, $C_{A\text{-}sol}$ is the notation that I use here, you can put it in different ways some of the publication we will put this in a square bracket indicates it is an activity which is also taken as a concentration because activity coefficient is taken as one in these cases. So forward reaction will produce A adsorbed species reverse reaction will consume it what is going to be the rate of reverse reaction k_{-2} θ. The rate constants k_1 k_2 k_{-2}, will they depend on potential. All of them will depend on potential so we are going to write that as $k_2=k_{20}\exp(b_2E)$ and in our notation the b_{-2} is going to be negative or at least it can be 0. But it cannot be positive number, because if I increase the potential the forward reaction will happen more. If I make it more positive, I am pulling out all electron from this electrode, there for the forward reaction will become more the first reaction will also become more reverse reaction in the second reaction that will become less. So, k_{-2} will decrease in potential k_1 and k_2 will increase with potential which means b_1 b_2 will be positive and b_{-2} it is going to be the negative side these are not arbitrarily large numbers they involved one electron transfer.

So, these numbers are going to be given by αF/RT, α is a charge transfer coefficient. Because number of electrons involved is one, I am not showing it here and α can vary between 0 to 1. So, at room temperature this is of course universal gas constant R at room temperature this is going to be around 38 or 39 V^{-1} with α being if it is 0.5, it is going to be 19 something in that range ~~19 20 18~~18-20 if it is 0.5 and b -2 is going to –(1 – α)F/RT, where F is the faraday constant which is 96485 C/mol. R is the universal gas constant, T is the temperature in kelvin. You can get these values from literature you can get this from standard textbooks, ~~just~~ so that you know you cannot put b_1 as 1000 for example it is not some any positive number it has a physical meaning for simplicity we are writing at this notation in literature some time you will find or maybe many time you will find instead of writing it as b_1 they would write in terms of α and the transfer correction, first one they will call it as α1 and second one as α2 extra.
“Professor - student conversation starts” Sir Yeah the backward reaction would happen when there are no electrons right yeah so why are we not adding the electron in the number of electron equation.

The electrons influence the reaction by changing the rate constant.

The rate constant is proportional to the exponential of the potential so the electrons. So, are accounted for in the rate constant, through k and the relationship is not, you can increase the electronic decrease electron we do not count the electrons it is easier to measure the potential and when you change the potential the rate constant actually changes. That is why whenever electron is involved in the reaction we make the rate constant as a function of potential.

When there is no electron transfer we say it is independent of potential. So you would like to write this as k2θ×number of electrons? no it does not work that way it rather works by changing the k-2 or k2 here. We do account for it it is just not that linearly increasing with potential“**Professor - student conversation ends”**.

Now can you write the expression for the current? Faraday current; when we change the potential how will the current change so when they changed the potential we know how the rate constant changes that depends exponentially on the potential, but just because the rate constant changes exponentially with potential does not mean the current that we measure will change exponentially with potential.

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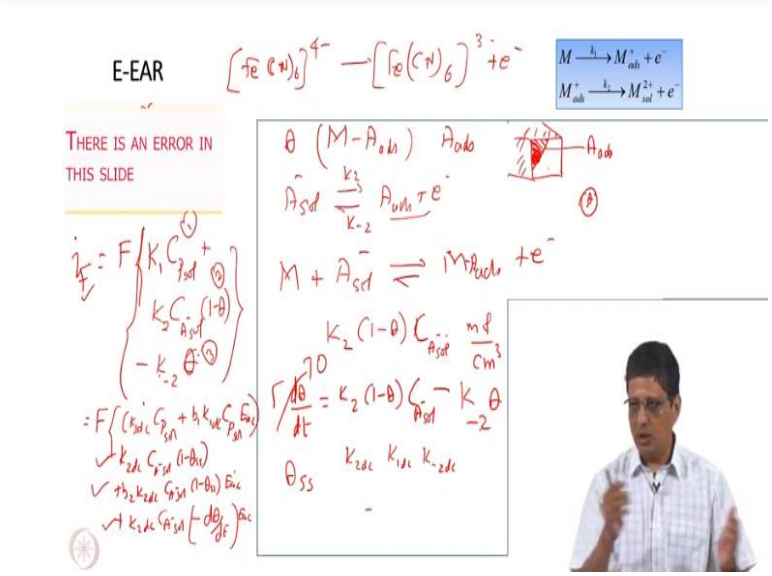

E-EAR

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

THERE IS AN ERROR IN THIS SLIDE

$\theta \quad (M-A_{ads}) \quad A_{ads}$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$M + A^-_{sol} \rightleftharpoons M\text{-}A_{ads} + e^-$

$k_2 (1-\theta) C_{A^-_{sol}} \quad \frac{mol}{cm^3}$

$\Gamma \frac{d\theta}{dt} = k_2 (1-\theta) C_{A^-_{sol}} - k_{-2}\theta$

$\theta_{ss} \quad k_{2dc} \quad k_{1dc} \quad k_{-2dc}$

$i_F = F\{k_1 C_{P_{sol}} + k_2 C_{A^-_{sol}} (1-\theta) - k_{-2}\theta\}$

How much current can you expect from the first reaction? What is the number of moles of electron produced by the first reaction? (It is given by the expression It is F×k_1×C_{psol}). It depends on the rate constant k_1 which depends on potential, of course it depends on the concentration of P in solution so that is going to give us one electron therefore we are multiplying by 1 which means we are just leaving it as it is now.

Second reaction has a forward and reverse reaction therefore the current is going to be dependent on three terms here k_1, k_2, and k_{-2}. It depends on the concentrations of P and A which we assume to be fixed, it depends on θ. θ will vary with potential therefore the current in general will not be exponentially changing with potential the rate constants still we assume that they changed exponentially with potential.

So, when you are given the reaction you should be able to write the faraday current for this you should be able to write the mass balance equation for this And you should be able to write the steady state surface coverage that means can you write the expression for θ_{ss} when I want to set this to zero? that means dc potential is applied there is no change of θ, there is no change of potential with respect to time.

I am going to get k_2 as k_{2dc}, k_1 as k_{1dc}, but it does not participate in this it does not come into play here k_{-2dc} , can I write θss is that correct? θ steady state expression is given as $k_{2dc}\ C_{Asol}/(\ k_{2dc}\ C_{Asol} + k_{-2dc})$, both k_2 and k_{-2} is dependent on potential if I increase potential k_2 will increase k_{-2} will decrease when you practice when you are given a new mechanism first thing you do is to write the mass balance then charge balance, right?.

You can write the steady state expression for the surface coverage you can write the steady state value for the faraday current that will give you polarization curve. That is if we go to a potential and wait there, and if you scan it at a very slow scan rate what is the slow rate, that depends on the system. But if you go that 1 mV/s, 0.5 mV/s, 2 mV/s, many times you would not see any difference between those data then you would say these are okay.

The contribution from double layer charging is negligible and pretty much everything happens because of the reaction. Then you would get the polarization curve if you propose a mechanism first the polarization curve given by the model and polarization curve that you obtain from the experiment they should match within the experimental level, that is within the noise level.

Next we have to linearize this to get the impedance, I have to linearize this that means first I have to expand this as potential as $E_{dc} + E_{ac}$. Where E_{ac} is $E_{ac0}\sin(\omega t)$ that means k_1 will be approximately $k_{1dc}(1+b_1E_{ac})$ and likewise k_{-2} is going to be approximately = $k_{-2\ dc}(1+b_{-2}\ E_{ac})$. The right way is you have to write the entire thing in Taylor series truncate it after the second term and then get here, when we do it frequently we can directly write this approximate expression.

If I expand k_1, k_2, k_{-2} I also have to expand the θ I am going to say concentration of A and P solution are constant, so therefore I am not going to worry about that I will get an expression which says k_1 can be expanded as $k_{1dc}+b_1k_{1dc}E_{ac}$ so this would contribute to the faraday current basic condition this would contribute to the $I_{F\text{-}ac}$. Similarly k_2, I am going to write it as $k_{2dc}\ C_A^-$ sol$(1-\theta ss)$ + $b_2\ k_{2dc}\ C_A^-$sol $(1-\theta ss)\ E_{ac}$.

See if you remember k_2 is expanded and then truncated so you would get two terms that θ would be expanded and truncated you would get two terms there, and when we multiply we are going to get 1 constant two E_{ac} term, one E_{ac}^2 which you are going to neglect. So, out of the four terms we are going to keep one dc term we are going to get two ac terms. So, this is the dc term here the next is the ac term and then one more is going to be an ac term there.

So ,this faraday current expression the way it is written it has 3 terms the first term it is expanded there is no θ there it just gives you two terms there second term has k_2 and θ. So, you would get four terms out of which we throw away one we have three terms so 1 2 3 comes here third term has k_{-2} θ again we would expect 2 multiplied by 2 to give us four terms out of which we are going to keep three terms. But please do write it down now you can always copy from the board but if you write it even if you make mistakes it is fine no you can check with the expressions here and then correct it, this way you would actually learn how to handle it.

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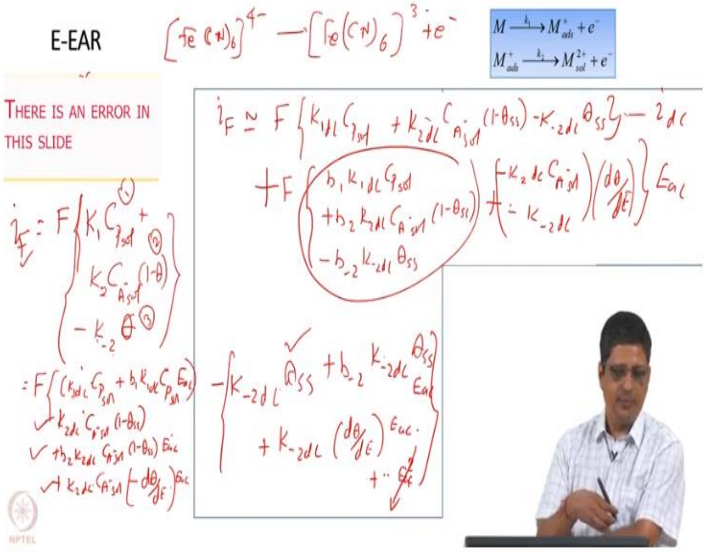

E-EAR

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

THERE IS AN ERROR IN THIS SLIDE

$i_F = F\{k_1 C_{P_{sol}} + k_2 C_{A^-_{sol}}(1-\theta) - k_{-2}\theta\}$

$= F\{(k_{1dc} C_{P_{sol}} + b_1 k_{1dc} C_{P_{sol}} E_{ac})$

$k_{2dc} C_{A^-_{sol}}(1-\theta_{ss})$

$+ b_2 k_{2dc} C_{A^-_{sol}}(1-\theta_{ss}) E_{ac}$

$+ k_{2dc} C_{A^-_{sol}}\left(-\frac{d\theta}{dE}\right) E_{ac}$

$-\{k_{-2dc}\theta_{ss} + b_{-2} k_{-2dc}\theta_{ss} E_{ac} + k_{-2dc}\left(\frac{d\theta}{dE}\right) E_{ac} + \cdots\}$

$i_F \simeq F\{k_{1dc} C_{P_{sol}} + k_{2dc} C_{A^-_{sol}}(1-\theta_{ss}) - k_{-2dc}\theta_{ss}\} - i_{dc}$

$+ F\{b_1 k_{1dc} C_{P_{sol}} + b_2 k_{2dc} C_{A^-_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2dc}\theta_{ss} + (-k_{2dc} C_{A^-_{sol}} - k_{-2dc})\left(\frac{d\theta}{dE}\right)\} E_{ac}$

So, I got the third term should be minus and then expand the entire product of k_{-2} θ as $k_{-2\,dc}$ θss is the dc term b_{-2} $k_{-2\,dc}$ θ_{ss} E_{ac} then $k_{-2\,dc}$ × $d\theta/dE$ × E_{ac} and then E_{ac}^{2} square term which goes away. I can rearrange all this, I got ~~1 2 3 4 5 6 7~~ 8 terms here, three of the terms contribute to dc then remaining five terms go to the ac.

Out of the five terms two of them depend on $d\theta/dE$ remaining three terms are independent of $d\theta/dE$. That means when you do the impedance spectra, When you measure the impedant spectrum when you apply different frequencies, the three terms here do not depend on frequency. The term here $d\theta/dE$ will depend on frequency that we are going to derive later but right now just take it for granted, that $d\theta/dE$ depend on frequency and when we apply infinite frequency very high frequency, $d\theta/dE$ will go to zero, that means if I apply very high frequency ac potential then potential changes very quickly, the rate constant will change very quickly surface coverage cannot keep up with that it cannot change that much so it is going to be negligible change in surface coverage with respect to potential change in surface coverage with respect to time will be close to zero.

When theoretically if we say infinite frequency we will say zero here that means this is the part that remains if frequency is very high these parts will go to zero when frequency is very high. This entire box here is $I_{F\text{-}ac}$, top box here is dc current is everyone okay with this? Can you kind of check and make sure it is what I have written here is fine? Now I would like you to think and tell me what would happen to the dc current what would happen to the steady state surface coverage θ when potential is increased.

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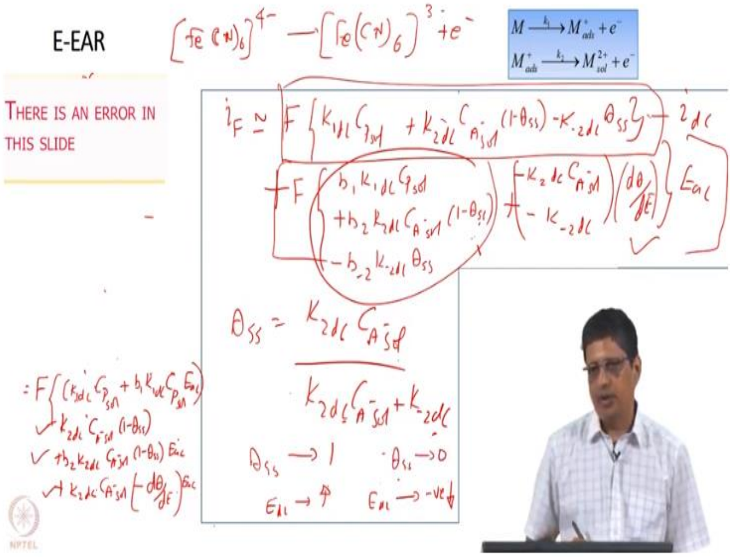

E-EAR

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

THERE IS AN ERROR IN THIS SLIDE

$$\theta_{ss} = \frac{k_{2dc} C_{A^-sol}}{k_{2dc} C_{A^-sol} + k_{-2dc}}$$

$\theta_{ss} \rightarrow 1$ $\theta_{ss} \rightarrow 0$

$E_{dc} \rightarrow \uparrow$ $E_{dc} \rightarrow -ve \downarrow$

You have the expression for θ under steady state condition you have the expressions for faraday current under steady state condition. For the given A_{sol} concentration, if I increase potential what happens to k_2, increases? What happens to k_{-2}, decreases. So, if I have large potential this becomes very small, this becomes large this also becomes a large we are fixing the A^-_{sol} anyway.

Therefore θ_{ss} will approach one when dc potential is increased, when dc potential is decreased what happens? k_{-2} will increase k_2 the numerator and denominator that term will decrease, so, when dc potential is moved to negative values θ_{ss} will approach zero, it would not become zero it will become close to zero. So I would expect to be like an s shaped curve, where the slope occurs depends on the parameter values and the concentration values. But the slope will occur at some location very large potential it is going to be close to one very small potential is going to be close to zero. Anything in between it is going to be a value between zero to one. Now what happens to the faraday current just the dc faraday current not the I am not looking at the ac yet, dc part is given by this top in the box. What I have written is actually not correct can you identify a problem here?

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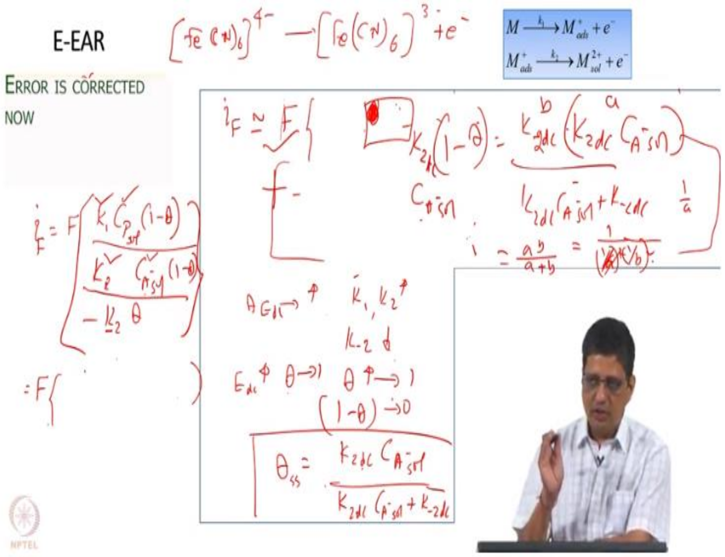

E-EAR

ERROR IS CORRECTED NOW

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^+_{ads} + e^-$

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$i_F = F\{k_1 C_{P_{sol}}(1-\theta) \; k_2 C_{A^-_{sol}}(1-\theta) \; - k_{-2}\theta\}$

$= F\{ \quad \}$

$A_{G_{dc}} \uparrow \quad k_1, k_2 \uparrow \quad k_{-2} \downarrow$

$E_{dc} \uparrow \; \theta \rightarrow 1 \quad \theta \uparrow \rightarrow 1 \quad (1-\theta) \rightarrow 0$

$$\theta_{ss} = \frac{k_{2dc} C_{A^-_{sol}}}{k_{2dc} C_{A^-_{sol}} + k_{-2dc}}$$

$i_F \simeq F\{$

$k_{2dc}(1-\theta) = \frac{\overset{b}{k_{-2dc}} (\overset{a}{k_{2dc} C_{A^-_{sol}}})}{k_{2dc} C_{A^-_{sol}} + k_{-2dc}}$

$\frac{1}{a}$

$= \frac{ab}{a+b} = \frac{1}{(1/a + 1/b)}$

First reaction can happen only on the bare metal surface, is that correct? therefore if the entire surface is covered by A_{ads} you will not get any reaction any significant amount of reaction in the first step so the current is actually going to be given by dc, correct. So, please do not blindly copy what I write here, θ_{ss} still okay, the theta equation, mass balance equation is still okay. First reaction does not contribute to the mass balance equation right?.

But the faraday current and the expansion, expansion Taylor series, truncation that we got all of them are not correct. So, please do rewrite it now

"Professor - student conversation starts" yeah can you explain why first reaction is not valid the reaction has happened with a solution right reaction happens on the electrode surface the reactants and products are in solution. So, the reactant comes sits on the bare metal.

Not for sufficient term to be considered as an adsorbed species as long as it touches the bare metal it becomes a product Q and then comes into solution. Yeah that mechanism should be mentioned right without mentioning we cannot know. We did mention it we did say if you have a surface like this the surface is covered the reaction first reaction can happen only on the bare metal.

Second reaction forward reaction can happen only on the bare metal reverse reaction, of course happens only from the adsorbed species. But first reaction does not contribute to increasing or decreasing A adsorbed it can happen on the bare metal I think I mentioned that **Professor - student conversation ends”**.

Now it is a little more complex expression we will have to derive that for ac. But before that I would like you to check what will happen to the faraday current when potential is large. When potential is large θ becomes close to one. k_1 becomes a large number k_2 becomes a large number, ? k_{-2} becomes a small number. So, as E_{dc} increases k_1 and k_2 increases, k_{-2} decreases, θ increases, 1-θ will tend towards 0. So, k_1 will increase C_p of course remains constant, (1-θ) will tend to ,zero the product of that will tend towards zero.

You should not believe me, you should actually try that and see, k_2 (1- θ) will tend towards zero. θ is given by ($k_2 \times C_{A^{-}\text{-sol}}$ at any given dc) / (k_{2dc} $C_{A\text{-sol}}$ + k_{-2dc}) so (1-θ) is going to be given by $k_{-2\,dc}$ divided by ($k_2 \times C_{A^{-}\text{-sol}}$ at any given dc) / (k_{2dc} $C_{A\text{-sol}}$ + k_{-2dc}) this number correct.

“Professor - student conversation starts” Sir but the rate constant states that if we are increasing the value of k_2 so we are saying that we are increasing the second reaction rate of reaction wherein we are making it faster. So, if that reaction is getting faster than previous one automatically will not get faster because you said electrons will part if are participating in any reaction then rate constant depends on potential, and if the potential that thing is increasing so that simultaneously with rate constant is increasing. We are not denying that yeah but I am saying that increasing the second potential reaction, potential second reaction simultaneously. So, it means you are increasing the potential of the whole system yeah increasing the potential of the electrode yeah therefore k_1 will increase, k_2 will increase, k_{-2} will decrease, k_{-2} will decrease because of the negative electrons participating the reaction as a reactant for k_{-2}, for k_2 it is a product for k_1 it is a product. So, when an increased potential I am pulling out the electron when I am pulling out the electron I will facilitate the forward reaction.

If I say theoretically if we go with this one that you said if we increase the value of k_2 and decrease the value of k_{-2} and so on we are increasing the potential therefore k_2 increases and k_{-2} decreases, that is the state yeah. so how this θ will increase and theta must because θ states that how much space is available. For the steady state θ correct we took the mass balance equation which was correct anyway and then derived this.

Now what happens when potential is increasing? Forget the k_1, k_1 is not here. Concentration of A^- solution is fixed number, k_2 is going to increase, k_2 in the numerator and denominator is going to increase, k_{-2} is going to decrease. So it is going to become almost close to 1. Because numerator and denominator are large numbers equal more or less equal therefore as E_{dc} increase θ will tend towards 1.

Here I say it increases I should say it tend towards 1 if θ tends to 1, 1-θ will tend to 0. So, what happens is when I increase potential more and more of A^-_{sol} species adsorbs on the surface, but as it adsorbs vacant metal site become number of vacant metal site becomes fewer. That means the rate of that reaction will not increase. Rate k_2 will increase but the rate will not increase.

Because the rate is given $k_2 \times C_A$-sol×(1-θ) rate of the first reaction is $k_1 \times C_{p\ sol} \times (1-\theta)$ we will take this factor out it is a constant how does $k_1 \times (1-\theta)$ change? (1-θ) is k-2 dc given by this number correct [Please refer video 32.42]? θ is here you can do the algebra and prove that (1-θ) is this expression here, $k_2 \times (1-\theta)$ is going to be k_{2dc} in fact we will keep this the rate of the second reaction is k_2 $C_{A\text{-}sol}$, correct?

I am going to call this as a this as b so it is basically ab /a+b [Please refer video 33.04] ? now when I increase the potential, put realistic values for this and check the values. θ will tend towards zero of course it may be possible that for certain values of k_{-2} in the value of k_2, k_{20}, k_{-20}, b_1, b_2 it may not happen that easily but I will have to check the values for the values we have tried we find that it fully covers the surface. Once it fully covers the surface the reaction rate is basically reduced (33:50)we have the space available for the 1- θ is space available for reaction theta is the space of the A_{ads} “**Professor - student conversation ends”** so what would happen is when you have a large potential k_2 is increasing, so $1/k_2$ will decrease becomes a small number, $1/k_{-2}$ will become a large number, one of them is going to be large one of them is going to be small.

I can ignore the small number keep the large number. So if this is a large number 1/large number is going to go towards zero. So, 1-theta will go towards zero in fact for I think any realistic parameter value k_{20} has to be a positive number any realistic parameter value and b_{-2} is negative number we would get θ as going towards 1, 1-θ is going towards 0 and the rate of the second reaction will go towards 0.

“Professor - student conversation starts” Sir can we say that the increase in value of k_2 and k results more in the resistance in the system. Because according to the formula no wait increase in value of k_2 and k_1 we cannot increase the value of k_2 and k_{-2} simultaneously. sir we are decreasing it, yeah because we are proving that θ is increasing as we increased the k_2 and k_{-2} right?

Wait, not we are not saying that any small change in potential from any value will give this when potential is very large when potential is very large k_{1dc} is going to be very large k_{2dc} is going to be very large and k_{-2dc} is going to be very small under those conditions we are showing that the surface is fully covered by adsorb rate of the reaction has you can have the current here written in three terms when theta is going towards 1.

But k_{-2} is very small this product will become tend towards 0 the second step forward reaction k_2 C_{Asol}×(1-θ) we can show that they tend towards 0. First step is going to be $k_1C_{p\ sol}$×(1-θ) and (1-θ) is this term [Please refer video 36.18] $k_{1dc}C_{Psol}$is here also we can divide by a similar expression. “**Professor - student conversation ends”**.

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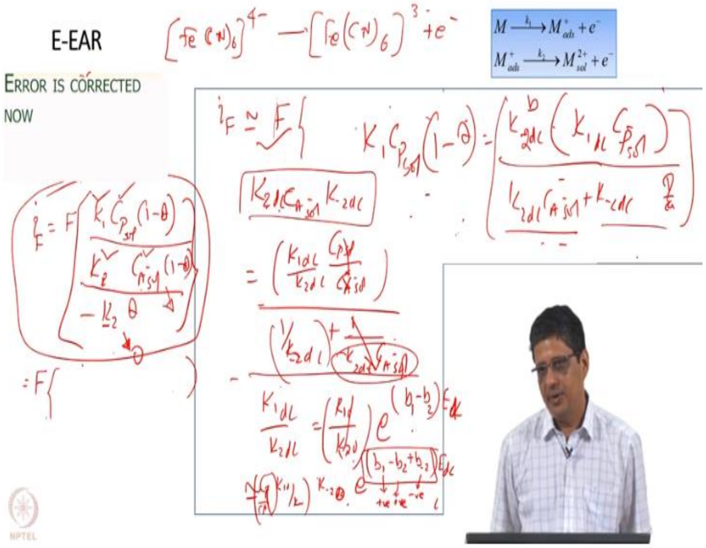

Let us divide the factor $k_{2dc} \times C_{A^-sol}$. k_{-2dc}.Numerator is going to be k_{1dc} k_{2dc} $C_{P\text{-}sol}$ solution/ $C\text{-}A^-_{sol}$ denominator you are going to get ($1/k_{-2dc}$ $1/k_{2dc}$ $C_{A\text{-}sol}$) **"Professor - student conversation starts"** sir by changing that we are maintaining the current system no we are not maintain the current system we are just increasing the potential to large value on observing the response, here we are predicting the response.

The response here it has 3 contributions. Contribution from the first reaction, contribution from the second reaction, forward and reverse, second reaction forward reaction will give rise to more or less zero current, reverse reaction will give this to more or less zero current. First reaction how much current is it going to give us? that is what we are finding here. So, the expression is going to be $k_1 \times C_{Psol} \times (1\text{-}\theta)$.

We have the expression for $(1\text{-}\theta)$ multiply by $k1 \times C_{Psol}$ under dc condition we have expression for $(1\text{-}\theta_{ss})$. So if you multiply with this this is expression you get of course you have a factor of faraday constant there divide by this expression $k_{2dc} \times C_{A\text{-}sol} \times k_{-dc}$ the entire product divide by this you are going to get k_{-2dc} here you are going to get k_{2dc} C_{A^-sol} here.

Numerator is going to be k_{1dc}/k_{2dc} whatever terms you get here, is that okay? you know how we got this? I got it I got this point that how you got this. But I am getting the point that we are maintaining the current we are not maintaining the current we are going to find whether we are getting more current less current how much current we are going to get you have already said that by increasing the value of k_2 and decreasing the value k_{-2} we are providing more potential.

“We are providing more potential but that does not mean will get more current” ‘that is what I am saying that if you are decreasing the current”, “so we are increasing we are not increasing the current, we are not decreasing the current we are changing the potential we are going to find what will happen to the current how do you know that current is going to decrease or increase”? “I do not know I am just saying that ’V=iR' no ’V=iR’ ”.

“When you have a resistance”, “that is what I am saying we do not have a resistance we have a electro chemical reaction. But something is absorbed, something maybe there is a possibility that the adsorbed layer may create a resistance”. “Why are you imagining that, when you have a reaction it will not act as a simple resistor in most of the cases it will act as a resistance in parallel with resistance and capacitance for example. And the resistance value you get maybe negative you cannot think it is an electron is passing through this adsorbed species it is just sitting there as a conducting medium. It does not happen that way when they give potential you have more reaction or less reaction and that causes the current to change. When you get an electron here you get a current so what we are measuring here is the current because of the reaction and it cannot be modelled in general by a resistor.

So, the example is taken here specifically to show that you can increase the potential and you will see a decrease in current. So, you cannot make a conclusion beforehand and then say I want the current to decrease show me how the current will decrease, or I want the current to increase show me how the current will increase. So, this reaction does not represent a resistor, when you change the potential, whatever happens to this expression here that tells you how much the current is going to be. We are looking at it one term by another term one by one we are looking at these terms. So, when you go to large potential third item goes to zero when you go to large potential second term goes to zero when you go to large potential what happens to the first term we are just analysing it now correct “**Professor - student conversation ends”**.

[please refer video 41.45] This is of course a constant number, this is also a constant number, this number when you look at the value here when I increase the potential what happens to k_{-2dc} it becomes a very small number this becomes a large number I can neglect that when the number here is large 1/that number is going to be negligible. So, this is approximately=k_{10}/k_{20} this came k_{-2dc} comes to the numerator $k_{-2dc} \times k_{-20} \times \exp(b_1-b_2+b_{-2})E_{dc}$.

Of course I am leaving out the other terms, C_{Psol}, C_{Asol} etc. I should write them down so this is approximately equal to $\exp(b_1-b_2+b_{-2})$ remember b_{-2} is negative b_2 is positive b_1 is positive. Now if this term is negative current will go to zero at $\log E_{dc}$ if this term is positive first term will not go to zero, does that make sense? basically I am evaluating what will happen to the first term when E_{dc} increases.

For the second term and third term definitely they will go towards zero, first term under certain conditions it will go towards 0 if $b_1>b_2$ it will definitely go to zero sorry if $b_1<b_2$ if $b_1-b_2+b_{-2}$ which is a negative number, if some of this becomes a negative number this will go towards 0 and at that condition you can tell the dc current faraday current will tend towards 0 when E_{dc} is increased to large value.

I am not saying from point towards 0.22 V point 0.23 V we have to really find how it is when it is very large it is going to be tending towards 0 when it is very small what will happen? Very small meaning, I do not mean it to zero it can be negative value E_{dc} can be negative with respect to the equilibrium potential. If we are at equilibrium then E_{dc} is 0, if we are well below equilibrium potential E_{dc} is a large negative number.

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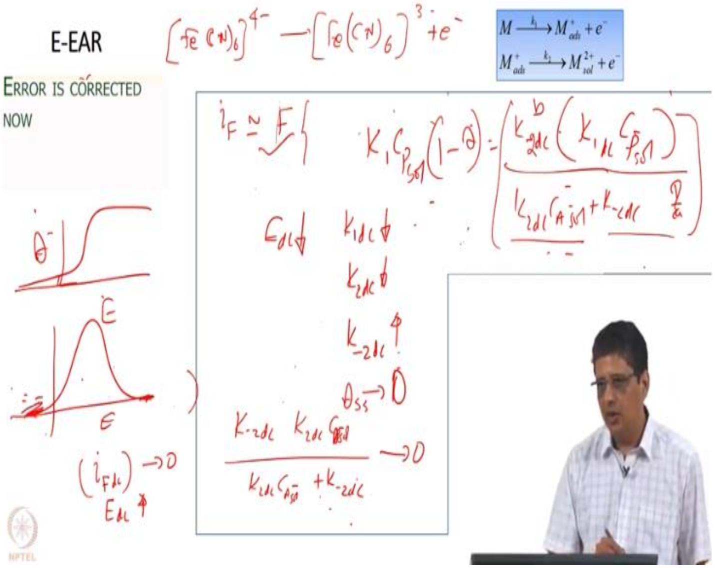

E-EAR

$[Fe(CN)_6]^{4-} \to [Fe(CN)_6]^{3-} + e^-$

$M \xrightarrow{k_1} M^{+}_{ads} + e^-$

$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

ERROR IS CORRECTED NOW

$E_{dc}\downarrow$ $k_{1dc}\downarrow$ $k_{2dc}\downarrow$ $k_{-2dc}\uparrow$ $\theta_{ss} \to 0$

$(i_{Fdc}) \to 0$ $E_{dc}\uparrow$

When it is large negative number, k_1 decreases k_2 decreases, θ_{ss} tends towards zero under those conditions k_1 decreases theta will tend toward zero this is a constant. So, the first term will go towards zero, because k_1 is very low this is a constant this at the maximum would be 1. First term goes zero second term also goes to zero. You have to look at the third term. ~~C_{Asol}~~ You can divide the numerator and denominator by the entire expression given in the numerator.

And you can show that this value will go towards zero when potential is very low this current will go to zero when potential is large under certain conditions current will go to zero in between it is going to have a value, it is a continuous function, large E_{dc} it is zero, low E_{dc} it is zero, in between it is going to increase and decrease only then you can make sure it is a continuous function, it has actually multiple derivatives so it is not a function with kinks is control at least maximum?

Now you can convince yourself by taking actual values given the expression for the θ given the expression for current of course to look at the impedance we need to get $d\theta$ values we will see tomorrow.

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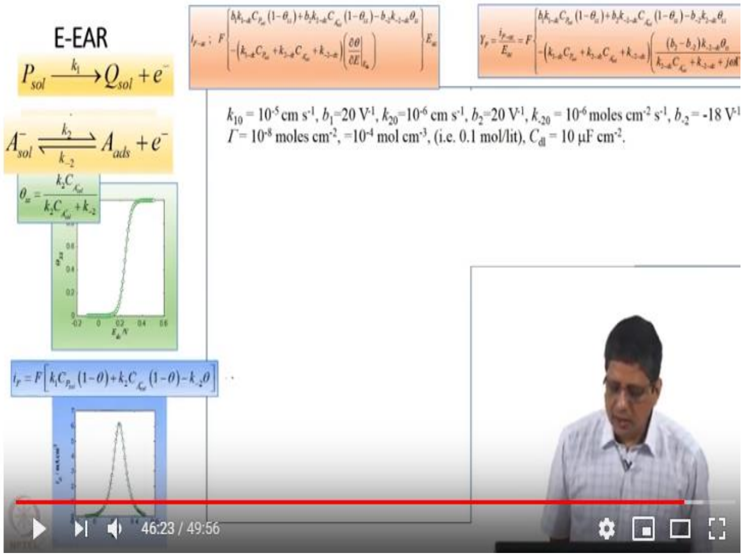

E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$\theta_{ss} = \frac{k_2 C_{A_{sol}}}{k_2 C_{A_{sol}} + k_{-2}}$

$i_F = F\left[k_1 C_{P_{sol}}(1-\theta) + k_2 C_{A_{sol}}(1-\theta) - k_{-2}\theta\right]$

$i_{F-ac} ; F\left\{\begin{matrix} b_1 k_{1-dc} C_{P_{sol}}(1-\theta_{ss}) + b_2 k_{2-dc} C_{A_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2-dc}\theta_{ss} \\ -\left(k_{1-dc} C_{P_{sol}} + k_{2-dc} C_{A_{sol}} + k_{-2-dc}\right)\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right) \end{matrix}\right\} E_{ac}$

$Y_F = \frac{i_{F-ac}}{E_{ac}} = F\left\{\begin{matrix} b_1 k_{1-dc} C_{P_{sol}}(1-\theta_{ss}) + b_2 k_{2-dc} C_{A_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2-dc}\theta_{ss} \\ -\left(k_{1-dc} C_{P_{sol}} + k_{2-dc} C_{A_{sol}} + k_{-2-dc}\right)\left(\frac{(b_2 - b_{-2}) k_{-2-dc}\theta_{ss}}{k_{2-dc} C_{A_{sol}} + k_{-2-dc} + j\omega}\right. \end{matrix}\right.$

$k_{10} = 10^{-5}$ cm s^{-1}, $b_1 = 20$ V^{-1}, $k_{20} = 10^{-6}$ cm s^{-1}, $b_2 = 20$ V^{-1}, $k_{-20} = 10^{-6}$ moles cm^{-2} s^{-1}, $b_{-2} = -18$ V^{-1}
$\Gamma = 10^{-8}$ moles cm^{-2}, $= 10^{-4}$ mol cm^{-3}, (i.e. 0.1 mol/lit), $C_{dl} = 10$ μF cm^{-2}.

But θ was dc and current versus dc for some specific values or constants. If you take them this is the plot that we get at low value it is zero at large value large here in this example is 0.5 V low here is close to zero. Of course when it goes to negative values P going to Q is going to be a reversible reaction unless there is no queue in the solution or tolerant we are taking it out as soon as it is formed.

If you have both P and Q in the solution you will have to consider the reverse reaction also, right now we are not considering it we are going to say we will go from zero to positive values and look at it current goes from zero to a peak value and then comes back to value of close to zero value close to zero value.

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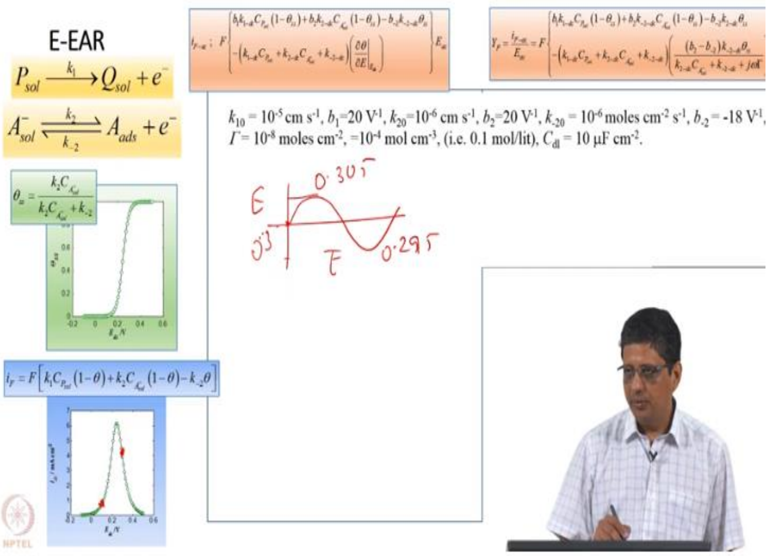

E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$\theta_{ss} = \frac{k_2 C_{A_{sol}}}{k_2 C_{A_{sol}} + k_{-2}}$

$i_F = F\left[k_1 C_{P_{sol}}(1-\theta) + k_2 C_{A_{sol}}(1-\theta) - k_{-2}\theta\right]$

$i_{F-ac} : F\left\{\begin{matrix} b_1 k_{1-dc} C_{P_{sol}}(1-\theta_{ss}) + b_2 k_{2-dc} C_{A_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2-dc}\theta_{ss} \\ -\left(k_{1-dc} C_{P_{sol}} + k_{2-dc} C_{A_{sol}} + k_{-2-dc}\right)\left(\frac{\partial\theta}{\partial E}\Big|_{E_{ac}}\right)\end{matrix}\right\} E_{ac}$

$Y_F = \frac{i_{F-ac}}{E_{ac}} = F\left\{\begin{matrix} b_1 k_{1-dc} C_{P_{sol}}(1-\theta_{ss}) + b_2 k_{2-dc} C_{A_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2-dc}\theta_{ss} \\ -\left(k_{1-dc} C_{P_{sol}} + k_{2-dc} C_{A_{sol}} + k_{-2-dc}\right)\left(\frac{(b_2-b_{-2})k_{-2-dc}\theta_{ss}}{k_{2-dc} C_{A_{sol}} + k_{-2-dc} + j\omega\Gamma}\right.\end{matrix}\right.$

$k_{10} = 10^{-5}$ cm s^{-1}, $b_1 = 20$ V^{-1}, $k_{20} = 10^{-6}$ cm s^{-1}, $b_2 = 20$ V^{-1}, $k_{-20} = 10^{-6}$ moles cm^{-2} s^{-1}, $b_{-2} = -18$ V^{-1},
$\Gamma = 10^{-8}$ moles cm^{-2}, $= 10^{-4}$ mol cm^{-3}, (i.e. 0.1 mol/lit), $C_{dl} = 10$ µF cm^{-2}.

Of course we are going to derive the expression for impedance what I want to show you is for this set of parameters at 0.1 V, and that little larger potential, if I take impedance at this location another location here, one time I am going to get through capacitance slopes with the second loop on the right side. Another time I am going to get capacitance loop coming on the negative side.

It is quite possible for this to arise and we can explain why it happens this way? You have a negative impedance you can show that this model will give you negative impedance you can say why does it become negative? Physically what can I say about the reaction? Why does it become negative? Why does it appear to show a negative impedance? It is not showing negative impedance, in the sense when I give potential increase the potential, If I go here look at this location when I increase the potential what happens to the current? it increases or decreases? Decreases, that means if I apply a sinusoidal potential this is the time this is the potential I am not a 0 this value is close to point 0.3 V this may be 0.305 this may be point 0.295 I am applying 5 mV amplitude. Current will decrease and then increase when potential increases and decreases, current here is going to be some values it is 3 mA.

Let us just make up that number and say it is 3 mA it is going to decrease and then increase whenever this increases current is going to decrease and whenever this decreases potential decreases current is going to show an increase. It has a 180 ° phase offset, it does not mean when

I apply positive potential here and negative potential here electrons are still going to travel from this direction to this direction only.

But only thing is when I increase the potential less or fewer number of electrons are traveling when I decrease a potential more number of electrons are traveling. So, it is the negative differential impedance, not negative resistance where I give voltage like this and current actually flows in the opposite direction, that is not the meaning of this negative impedance that we observe.

So, when you measure in experiment when you apply a sinusoidal potential and measure the impedance we are only measuring the differential impedance that is we are measuring the amplitude ratio and the phase difference between the potential and the current. We will stop here today.