Electrochemical Impedance Spectroscopy
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Lecture - 22
Two Step Reaction with an Intermediate-I

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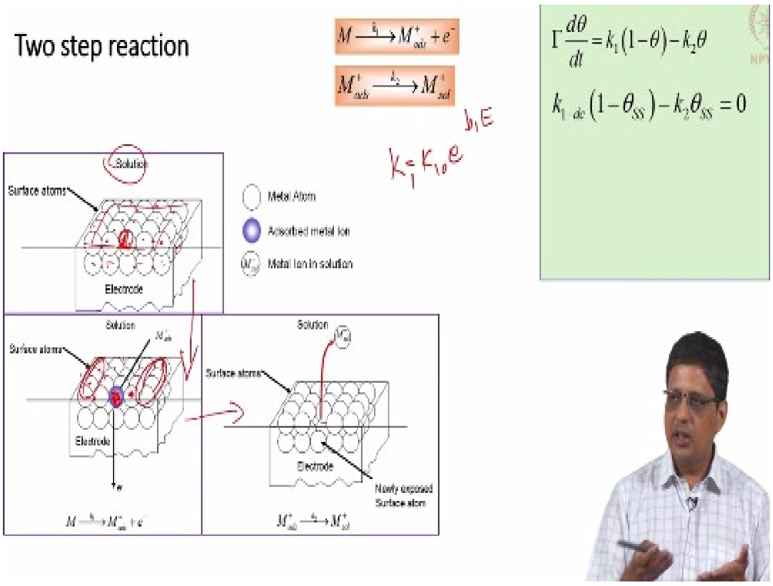

Two step reaction

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

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

$k_1 = k_{1,0} e^{b_1 E}$

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$k_{1\ dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$$

[So I want you to look at this carefully because this forms the basis of all the other examples that we see later]. We are looking at a reaction with two steps; metal losing an electron and forming a species which is normally called as Metal$^+$ adsorbed (M^+_{ads}) [in this literature] and in the second step, M^+_{ads} goes into solution. So here I have drawn a picture with spheres representing metal atoms (refer video). The top level represents the surface. The next level is below it. The electrode is exposed to the solution and solution is exposed to the top layer and the metal atoms at lower layer are not exposed to solutions. If the first step happens at particular rate k1, first step involves the transfer of electron. We can guess that k_1 is going to depend on the potential. If I give more positive potential, I will pull up or I will remove all the electrons that I will drive the reaction in the forward direction. k_2 on the other hand, on the left side it is M^+_{ads} and on the right side it is M^+_{sol} . Therefore if I change the potential, k_2 will not change. [I do not have any reason to expect that the k_2 will change]. If the electron is not involved and if there is no charge transfer, then the rate constant is not going to depend on the potential.

Now let us consider one atom (refer to video). It loses an electron. We are giving positive potential and the electron is pulled into the metal [we are of course connecting with the potentiostat]. Therefore when we apply a positive potential, it means that we are removing the electrons. It goes in, and this atom is called as M^+ adsorbed species. It is not an atom anymore; it is an ion. Normally in chemical engineering literature or even in other science literature if material comes from outside and sits on top you will call it as adsorbed material.

In this literature, the adsorbed here means you can lose an electron and this is a different species now. They would be called as adsorbed species. Here the metal atom, adsorbed metal ion and the metal ion in solution; if that goes into the solution, which is a second step. The transfer of an electron resulting in a blue colored ion here is the first step and this picture represents the second step (refer video). This metal adsorbed species has gone into solution and that is called M_{sol}^+. This metal atom is now exposed to the solution and this forms a surface. Now this can lose an electron and become M_{ads}^+ and this can go into solution, this can lose an electron and become M_{ads}^+ (refer video 3:12). We do not think this is going to lose an electron, surface can lose an electron only after this goes, the atom below becomes exposed and that can go into the solution. So the first step is represented here and the second step is represented here (highlighted in orange colour).

Let us say total number of sites available on the surface is given by the letter capital Γ. I am going to call θ as fractional surface coverage of M_{ads}^+. So what I do is, I calculate how many such sites are occupied by M_{ads}^+ and see what the total number of sites are. That ratio tell us that say 30% of the sites are occupied by M_{ads}^+, which means 70% of the sites are metal atoms. Now the first reaction can proceed only from vacant sites. We call the remaining metal atom as vacant sites. So a metal atom can become M_{ads}^+. If it is already M_{ads}^+, it may stay there or leave. If I say this reaction is reversible, then I can say it can take an electron and become metal atom again [but we are not considering that case now]. We are considering only a simple forward step for the first step and a simple forward step for the second step which means once it goes into solution, it is not going to come back again. That is an assumption here. These are only 2 forward step. Once we learn how to handle this case, we can derive the expression for reversible reaction, more complicated reactions etc. [and I will show you with examples].

I want to know what happens to the fractional surface coverage of M_{ads}^{+} with respect to time. k_1 tells the rate at which the forward reaction can proceed. Forward reaction can proceed when k_1 is a finite number and when M species here is available. If all the surface is covered with M_{ads}^{+}, I will not have any more of the forward reaction because no vacant metal is available. In the forward reaction, first reaction rate is given by $k_1(1-\theta)$, θ tells how much fraction of the surface is covered by M adsorbed, $1-\theta$ tells how much of the surface is remaining as M. Therefore I want to write the reaction here are considered as elementary reactions. If I know the species and I know the rate constant, I can write the rate of the first reaction as $k_1(1-\theta)$. Rate of the second reaction is going to be $k_2\theta$. If θ is 0, it means there is nothing on the surface in the adsorbed metal state, and then I cannot have any second reaction. If θ is full, I will expect lot of reaction and lot of this second reaction will happen. Also rate of the reaction will be high. Here, θ is between 0 to 1. It does not have units because it is a fractional surface coverage. That means how many sites are available with M adsorbed species and that will be in moles/cm^2 divide by total number of sites that are available in moles/cm^2. It means the way we have written, θ does not have any units, but units of Γ is going to be moles/cm^2. The units of k is going to be moles/cm^2sec and units of k_1 and k_2 will be the same here. Some literature may give k_1 as second inverse and then it will use Γ minus another notation maybe β, where beta is going to be moles/cm^2. When you read the literature, you have to see how they are defining those terms. Here instead of $d\theta$, it is going to be $d\beta/dt$. So instead of having $\Gamma d\theta/dt$, I might write it as $d\beta/dt$ and it is going to be $k_1(\Gamma-\beta)-k_2\beta$. It is just a different notation. The equation we have written is called as mass balance equation. Here we are assuming certain things: we assume mass transfer is fast, we are going to make an assumption that k_1 is going to be written as k_1e^{b1E}. It is is exponentially dependent on potential. We are assuming that Langmuir isotherm model works here. That means if I have M adsorbed here, what is the probability that this atom will lose an electron and will become M adsorbed. We have a number. What is the probability that another atom which is far away, will lose an electron and become an M adsorbed? We assume that they are all the same, they are not dependent on whether the neighboring site is already M adsorbed or not. So another assumption is that there is no interaction between the species. We assume that all sites are equal which means we do not think one present on this row is more likely to lose an electron compared to one present on this row (refer video 8:56). These are in pictorial and that's why I am representing in terms of one row and another row. We are saying all of them have equal energy levels.

If they have different energy levels you will have to use another isotherm called Temkin isotherm. If you think that there are interactions, which means presence of one species can help or hinder formation of same species or different species, we will use what is called Frumkin isotherm with interaction parameter. If it is positive or negative, it is going to say that is more likely to happen or less likely to happen etc. However for simplification, we are going to say this is Langmuir isotherm.

If we say it is under steady state, it means the fractional surface coverage of θ is independent of time. You would expect steady state if you do not apply any potential and if the solution concentration and other things remains the same, or you apply constant potential, wait for sufficient time and system reaches a steady state. Then I can say dθ/dt is 0 and it is not varying with time.

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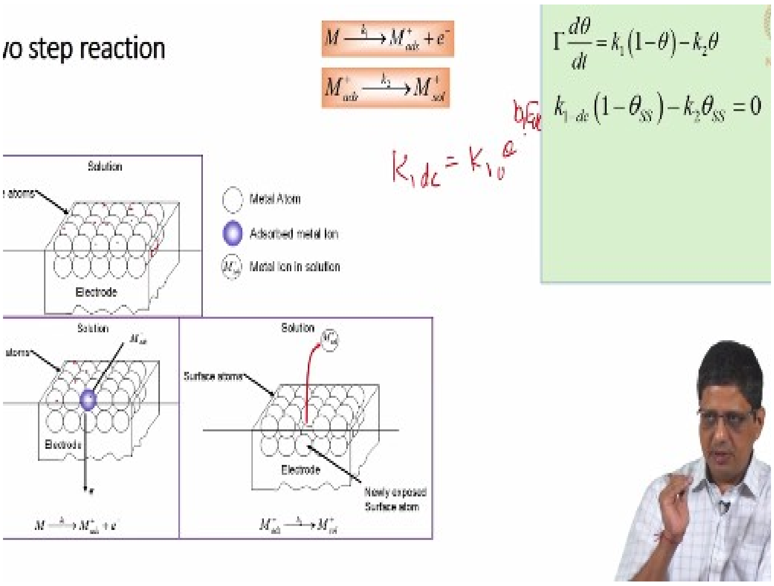

/o step reaction

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

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

$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

$k_{1\,dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$

$K_{1dc} = K_{10}e^{b_1E_{dc}}$

Then I am going to call that k_1 at that DC potential as k_{1dc} which means $k_{10}e^{b1Edc}$. We have applied a DC potential, it maybe 0 (in which case we are not applying any potential), it may be a fixed number, non-zero number and we wait for enough time, we will get a stable current and we will get a stable surface coverage. If we change the DC potential, go to another value, wait for enough time, I will get another surface coverage and another current value.

So at this condition I can set this to 0 and I will call the k_1 as k_{1dc} which corresponds to that specific DC potential and I will call the θ, fractional surface coverage as θ_{ss} to indicate it is steady state. We have done this before in Langmuir isotherm model [not in this course, perhaps you would have done it in chemistry]. You can rearrange this and get the steady state value of θ_{ss} [I would like you to actually do that. You can see it in the PPT, but why not try this it is not that difficult. So I would like you to start with this and get a value of θ_{ss} in terms of k_1 and k_2, k_{1dc} and k_2. The reason is next I am going to tell you how to calculate the impedance. It is a lot easier if you actually try this, learn the steps then we will go through one or two more types of reaction. Once you try it and then get this it will be lot easier for you to look at a new mechanism and do this. If you see it in the PPT here, you will feel that you have learnt it, but you may or may not have learnt it well].

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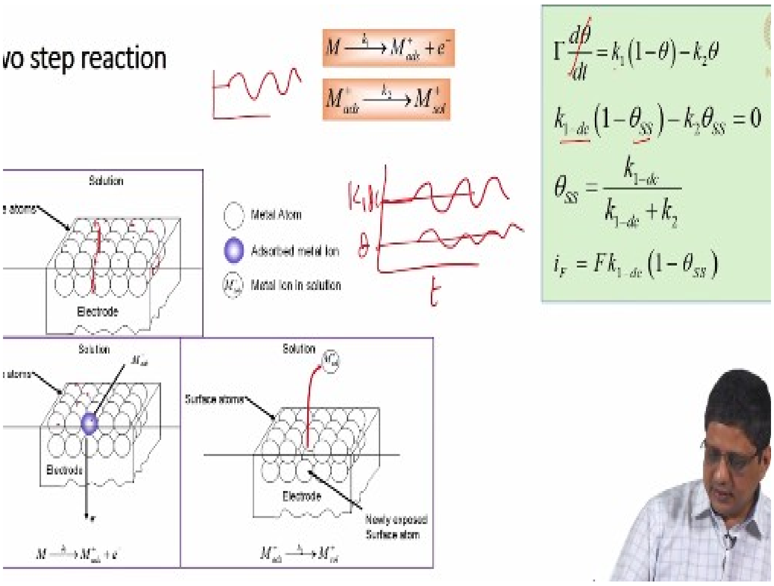

vo step reaction

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

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

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$k_{1-dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$$

$$\theta_{SS} = \frac{k_{1-dc}}{k_{1-dc}+k_2}$$

$$i_F = Fk_{1-dc}(1-\theta_{SS})$$

Calculate the value of θ_{ss}, it is very simple rearrangement and you would get $k_{1dc}/(k_{1dc}+k_2)$. Now I want you to guess, k_2 is a constant, k_1 is going to increase when I increase the DC potential. When k_1 is a very small value, θ will tend towards 0 and if k_1 is a very large value, θ will tend towards 1, it would not tend towards infinity. [so it makes sense]. Fractional surface coverage has to be in between 0 to 1 and it will go to 0 when you go to very negative potentials. We are assuming that the reverse reaction is not possible. When you go to negative potential, you cannot assume that. Even when you go to 0 potential, you have to assume that reverse is possible. If you are on the very positive potential, then you can neglect the reverse reaction, because you are just going to take out all the electrons. It is not going to come back to the M species.

The current under steady state condition, current for the faradaic reaction comes only from the first step. Current for the capacitor will be there if you are applying an AC potential. If you apply DC potential, that metal solution interface which you can visualize as a capacitor will not pass any current under steady state condition.

If you apply an AC potential, capacitor will pass current, in addition, applying AC potential will make this reaction go faster or slower. When the potential increases, it is going to go faster when it decreases it is going to go slower. If it is periodic, we expect the reaction to become faster and slower accordingly. So if I say this is the rate constant value at a DC potential, this is the k_{1dc} (refer video 13:55). So potential is DC up to sometime and then if you apply an AC, rate constant will also move up and down. Along with the movement of rate constant the fractional surface coverage will also move up and down that is θ will also move. Combination of θ and k_1 together will tell us how the fractional surface coverage will move as per this equation. So when we apply AC we cannot neglect this and we cannot say dθ/dt is 0. When we have a DC when it is under steady state only we can set this to 0; under AC we have to use the full equation.

"Professor - student conversation starts"

Sir can you repeat what $k_1(1-\theta)$ represents. Is it the number of electron transfer?.

$k_1(1-\theta)$ tells the rate of first reaction. It is moles/cm^{2}sec. $k_1(1-\theta)$, θ does not have units; moles/cm^{2}sec.

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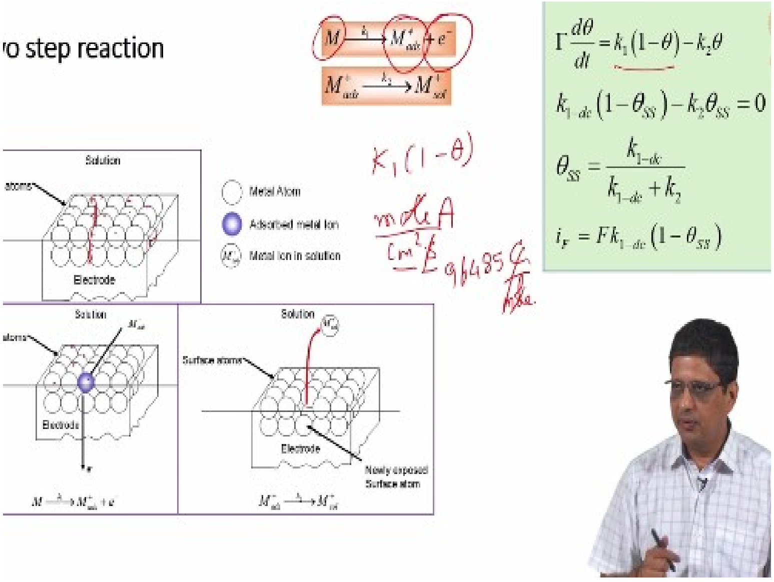

o step reaction

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

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

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$k_{1\text{-}dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$$

$$\theta_{SS} = \frac{k_{1\text{-}dc}}{k_{1\text{-}dc} + k_2}$$

$$i_F = Fk_{1\text{-}dc}(1-\theta_{SS})$$

So $k_1(1-\theta)$ represents the rate of the first reaction. Now the first reaction gives one electron. I can have another reaction where M becomes M^{2+}_{ads} + 2 electrons and M^{2+}_{ads} goes into solution. Copper can become Cu^{2+}, Cu^{2+} can go into solution. In that case, I will say, rate of the first reaction consumes M surface at this rate of $k_1(1-\theta)$, number of electrons produced is 2. This is still moles/cm^2sec.

Now faraday constant converts the electrons to Coulomb or moles into Coulomb. So I had to multiply by F which is Faraday constant, Coulomb per mole of electron. So in this case because it is single electron transfer, I am not showing the number one multiply by this to tell how much current will come. It is going to be Coulomb/cm^2sec; Coulomb per second will become amperes, amperes per centimeter square. So although I say it's current, it is actually current density. It is not current.

[……….]

$k_1(1-\theta_s)$ is a number of surface atoms that are consumed, so it is number of surface atoms that are consumed by the first step. It is also equivalent to the number of M^+_{ads} produced by the first step, it is also equal to number of electrons produced by the first.

[………….]

So number of electrons will become 2×rate of that reaction.

[………….]

No here the $k_1(1-\theta)$ represents the number of M surface atoms that are consumed by the first reaction, because you can look at this equation and say this equation gives one electron. Therefore, it is equal to the number of electrons produced by this step. [I do not know where the confusion is].

[…………]

Surface atoms and we calculate how many electrons are produced by that.

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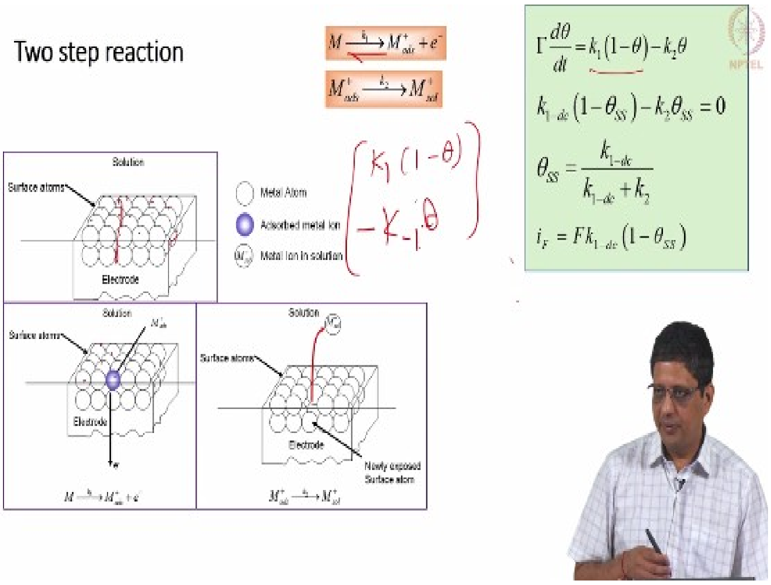

Two step reaction

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

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

$\left(k_1(1-\theta) - k_{-1}\theta \right)$

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$k_{1-dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$$

$$\theta_{SS} = \frac{k_{1-dc}}{k_{1-dc} + k_2}$$

$$i_F = Fk_{1-dc}(1-\theta_{SS})$$

I would write $k_1(1-\theta)$ as a number of electrons produced by the first step or forward step I might write reverse reaction as $k_{-1}\theta$. That tells number of electrons consumed. So the net number of electrons produced are given by $k_1(1-\theta)-k_{-1}\theta$.

[…………..]

Yes, for example here, the second step does not produce or consume any electron, therefore it is not all showing up in this equation. Whereas when you look at θ, θ equation first produces θ and therefore it is positive number here. Second reaction consumes θ and therefore it is a negative number there. So we write the equation based on the reactants usually. We will say k_1 (1-θ) represents the number of moles of M consumed (moles per unit area that is consumed). For electrons we had to calculate as per the equation. First equation produces M^+_{ads}. So when I look at M^+_{ads} balance, I will consider first equation and the second equation because it is involved in both. When I look at electrons produced, I do not have to look at the second equation because it is not at all there. I have to look at only the first equation.

“Professor - student conversation ends”

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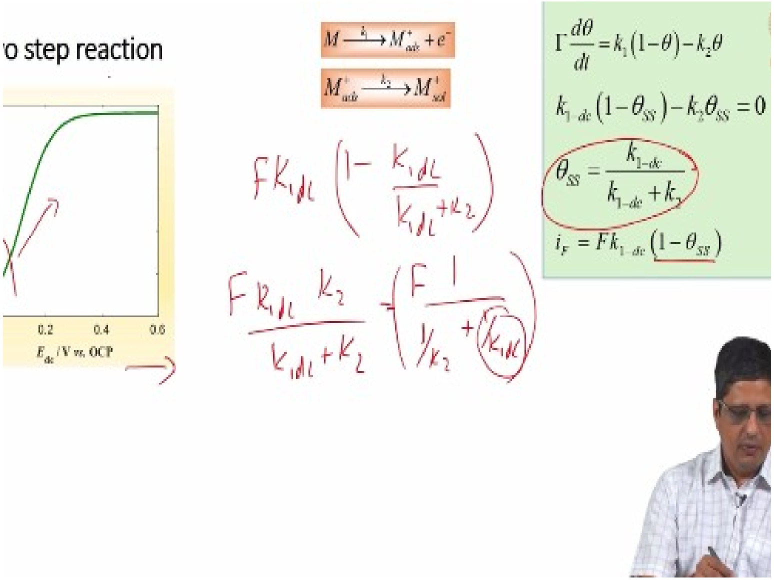
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$k_{1-dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$

$\theta_{SS} = \frac{k_{1-dc}}{k_{1-dc}+k_2}$

$i_F = Fk_{1-dc}(1-\theta_{SS})$

$Fk_{1dc}\left(1 - \frac{k_{1dc}}{k_{1dc}+k_2}\right)$

$\frac{Fk_{1dc}\,k_2}{k_{1dc}+k_2} = \left(F\frac{1}{1/k_2 + \boxed{1/k_{1dc}}}\right)$

So if we look at the steady state current, it is going to look like this (refer video/slide). It is not really going to be valid at DC potential of 0, because at DC potential of 0, that is equilibrium. I will have reversible equation, but we will not worry about that now we will say when it is little farther away from 0, it is in the positive direction. k_1 will keep increasing with potential, θ is going to increase with potential. When E_{dc} is large, θ is going to be close to 1. 1-θ is going to be close to 0 and this expression $Fk_{1dc}(1-\theta)$ can be calculated from this. This is going to give you $F_{k1dc}\, k_2/(k_{1dc}+k_2)$. When I take this into numerator and to the algebra and this I can divide it by k_1k_2 on the numerator and denominator. The numerator divided by k_1k_2, the denominator/k_1k_2 and when k_{1dc} is going to be very large number because I am going to very large DC potential. This term I can neglect it; it is going to remain a constant. So the Faraday current is going to increase up to some level and then it is going to remain a constant although we have assumed that mass transfer is not a problem. The signature if you look at this will look somewhat similar to a mass transfer limited case, even though mass transfer is rapid. [Does it make sense?]

If you look at the current versus potential, when I go to intermediate level of potential, current increases with potential, and when I go to large potential, current saturates and if we have a simple reaction which you have seen earlier, when it is kinetic limited and mass transfer is very rapid, we know that it is going to give an exponential curve (refer video). Whereas when it is mass transfer limited, although we have not derived it, I have showed you the example it is going to go like this and saturates. So when you look at the signature you cannot always immediately come to the conclusion that it is going to be reaction number one with mass transfer limitation or it is going to be reaction number two which we are seeing now with large potential even though there is no mass transfer limitation.

Here what happens is, when you go to large potential entire surface is covered by M adsorbed. k_2 is not going to increase with potential because it is independent of potential. There is no electron transfer. So the rate of production of this species M^+_{sol} is limited by this, it is saturating and you cannot have anymore of the first step because it is already pretty much covered by M^+_{ads}. It is not 100% covered and it will never go to zero current. It will go to a maximum current and remain there and therefore this is steady state behavior.

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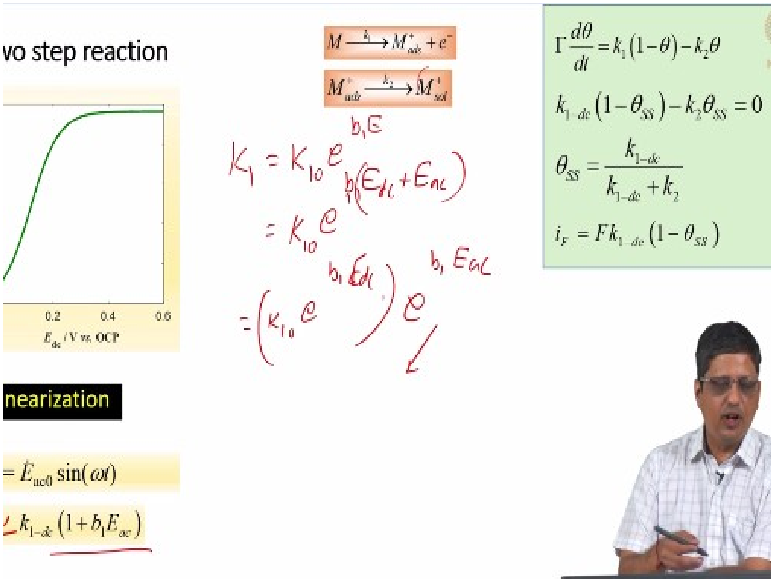

vo step reaction

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$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$k_{1-dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$$

$$\theta_{SS} = \frac{k_{1-dc}}{k_{1-dc}+k_2}$$

$$i_F = Fk_{1-dc}(1-\theta_{SS})$$

$$K_1 = K_{10}e^{b_1E}$$

$$e^{b_1(E_{dc}+E_{ac})}$$

$$= K_{10}e$$

$$= \left(K_{10}e^{b_1E_{dc}}\right)e^{b_1E_{ac}}$$

nearization

$= E_{ac0}\sin(\omega t)$

$k_{1-dc}(1+b_1E_{ac})$

[Now the fun starts]. When you to AC, we used the notation that E_{ac} is going to be E_{ac0}sin ωt, we will vary the ω, we are going to assume E_{ac0} is small and we know that we can write k_1 as $k_{10}e^{b1E}$ and in general, we will write it as $K_{10}e^{b1(Edc+ Eac)}$ where E_{ac0}sin ωt. And in general, we know we can write it as b_1E_{dc} and this can be approximated by $1+b_1E_{ac}$ when E_{ac} is small. E_{ac} is small when E_{ac0} is small, because sign can be between + or -1.

We have done this in the previous case when we have simple electron transfer reaction, we said $k_{forward}$ if I apply DC+ AC, I will write it as $k_{fdc}(1+b_fE_{ac})$. In this case, it is b_1E_{ac}. k_2 remains a constant. It is independent of the potential.

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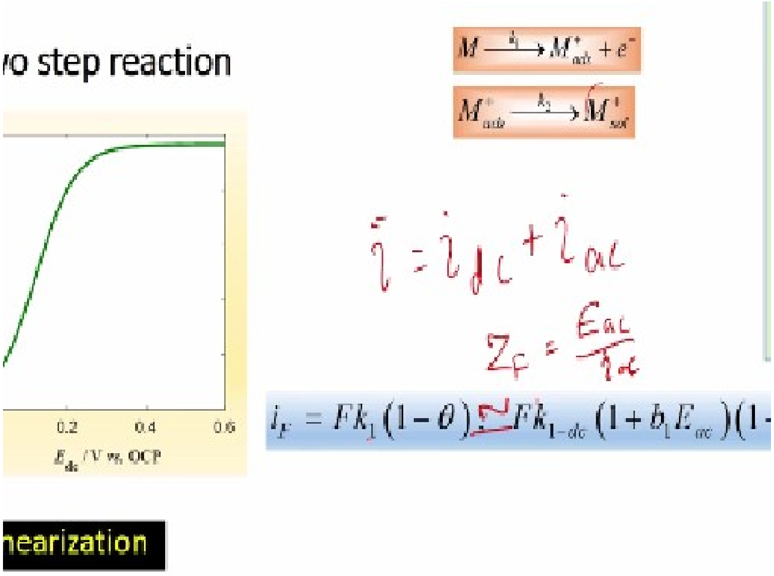

/o step reaction

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

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

$i = i_{dc} + i_{ac}$

$Z_F = \frac{E_{ac}}{i_{ac}}$

$i_F = Fk_1(1-\theta) \simeq Fk_{1-dc}(1+b_1E_{ac})(1-$

nearization

Now I want to write the faradaic current. When I apply a DC potential and super impose an AC on top, I expect a current to also have an oscillation. I want to know what the oscillation is, so I can write the current as DC current + AC current. Then I can write the faradaic impedance as E_{ac}/i_{ac}. So I am really measuring the differential impedance. So what I want to do is take the current, this is given for DC and I want to write it for AC and derive the expression for impedance. In general, the current is going to be $Fk_1(1-\theta)$ where k_1 can be time varying and θ can be time varying.

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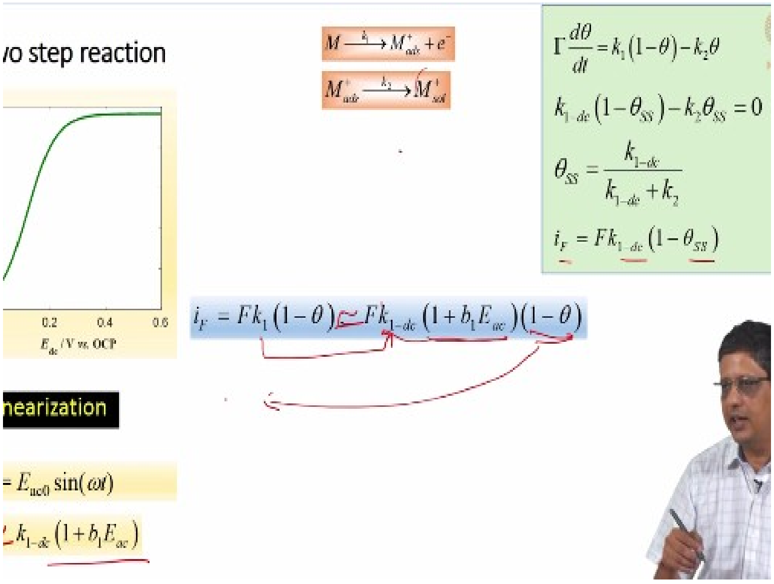

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$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

$k_{1-dc}(1-\theta_{SS}) - k_2\theta_{SS} = 0$

$\theta_{SS} = \frac{k_{1-dc}}{k_{1-dc}+k_2}$

$i_F = Fk_{1-dc}(1-\theta_{SS})$

$i_F = Fk_1(1-\theta) \simeq Fk_{1-dc}(1+b_1E_{ac})(1-\theta)$

nearization

$= E_{ac0}\sin(\omega t)$

$\simeq k_{1-dc}(1+b_1E_{ac})$

So I know how to approximate k_1, $k_{1dc}(1+b_1E_{ac})$ when E_{ac} is small. This θ also, I know it is going to vary with time because the rate constant k_1 is varying with time, surface coverage also will vary with time. I have to find how these are going to vary. [So our goal is to find, this is not a constant, this is going to vary, how is that varying]. It is going to help me figure out how to write I_F as i_{Fdc} and i_{Fac}.

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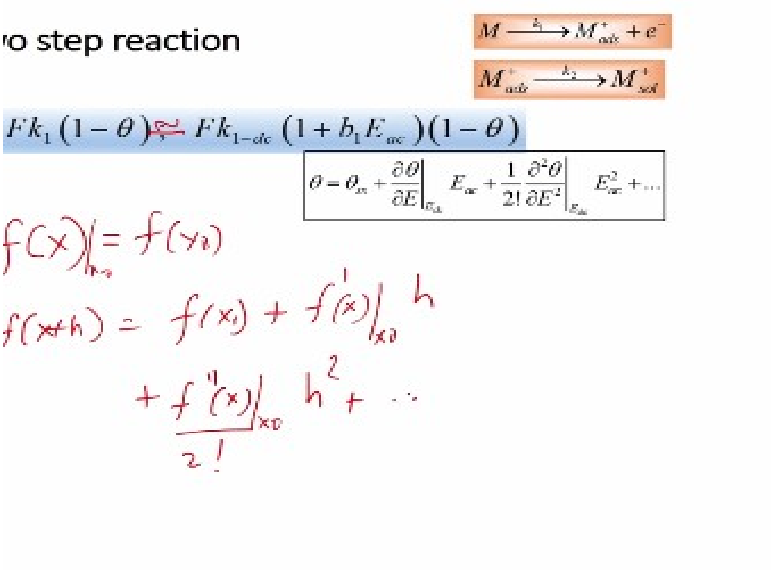

o step reaction

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

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

$$Fk_1(1-\theta) \approx Fk_{1-dc}(1+b_1E_{ac})(1-\theta)$$

$$\boxed{\theta = \theta_{ss} + \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac} + \frac{1}{2!}\left.\frac{\partial^2\theta}{\partial E^2}\right|_{E_{dc}} E_{ac}^2 + \ldots}$$

$$f(x)|_{x_0} = f(x_0)$$

$$f(x+h) = f(x_0) + f'(x)|_{x_0} h + \frac{f''(x)|_{x_0}}{2!} h^2 + \ldots$$

So we have this expression, this is an approximation symbol. In general, surface coverage is going to vary with time, it is going to vary with potential. We are going to write it as Taylor series. Initially surface coverage was at steady state value. DC potential was applied then we start applying an AC potential we will say it deviates slightly from the DC value. Therefore we will write θ as θ_{ss}. It is like if we have a function of x and you know the value at x_0, we can write x+ h. If you know the value at some location very close to that location, it is going to vary a little and we are going to write like this. So here θ is the function. We will write θ at steady state+ first derivate evaluated at 0. Here it is E_{dc}. Small change we are going to write it as E_{ac}. It is still a variable, but we are going to just use the same formula here. E_{ac} is not a constan. E_{ac} is E_{ac0} sin ωt. Then 2 factorial, second derivative, E_{ac}^2 and so on. It is going to have more derivatives. Since we say E_{ac} is a small number, we can say E_{ac}^2 and higher order numbers can be neglected.

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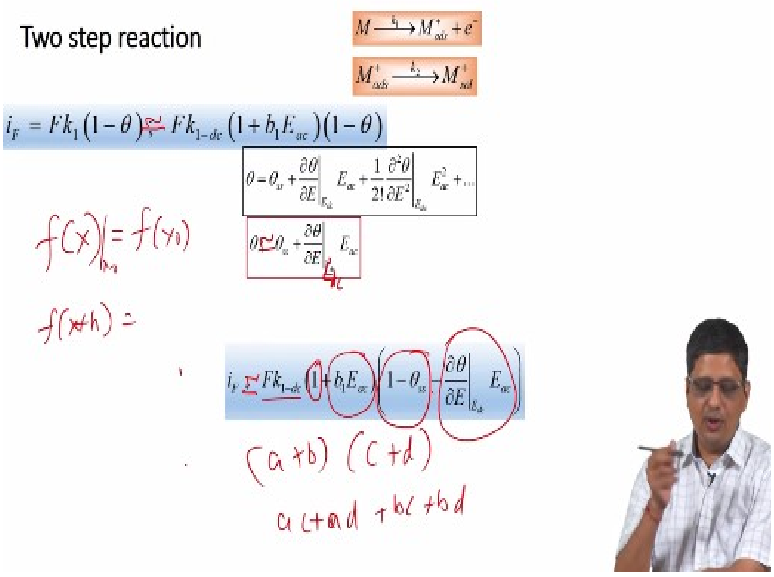

Two step reaction

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

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

$i_F = Fk_1(1-\theta) \cong Fk_{1-dc}(1+b_1E_{ac})(1-\theta)$

$\theta = \theta_{ss} + \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac} + \frac{1}{2!}\left.\frac{\partial^2\theta}{\partial E^2}\right|_{E_{dc}} E_{ac}^2 + \dots$

$f(x)|_{x_0} = f(x_0)$

$\theta \cong \theta_{ss} + \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac}$

$f(x+h) =$

$i_F \cong Fk_{1-dc}(1+b_1E_{ac})\left(1-\theta_{ss} - \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac}\right)$

$(a+b)(c+d)$

$ac+ad+bc+bd$

That means we can write θ as approximately equal to θ_{ss}+ dθ/dE at E_{dc}. I need to evaluate θ as a function of E. We need to see how the surface coverage is going to change with respect to potential, which means I can go to the original current equation [please substitute and write this]. So originally this equation was $Fk_1(1-\theta)$. Instead of k_1, we are writing it in Taylor series and then truncating. Instead of θ, we are writing it in Taylor series and truncating. [Now I want you to do this]. Fk_{1dc} remains outside, this is one term here and another term here. Here I would like you to consider this as third term and this as fourth term. You have something like (a+ b) multiplied by (c+ d). We are going to get ac + ad + bc+ bd, four terms are going to come out of this. One is a constant, 1-θ is a constant. This depends on Eac this depends on Eac (refer video). So you will get four terms out of which, one is going to be a constant, another is going to have E_{ac}, third term is going to have E_{ac}, fourth term will have E_{ac}^2, and since we have neglected E_{ac}^2 and higher order terms earlier, saying they are not significant, here also, after getting the 4 terms, we are going to throw away the 4th term and keep only 3 terms. θ is going to vary with potential. How would you write a Taylor series for F(x) (Refer slide or video for expansion)? [We have to find that I have not yet come to that, so that is a next step]. What we do here is to say, I want to write the current in terms of AC and DC components. In order to do that, I have to write any variable as Taylor series, truncate after the first term, first term here meaning E_{ac} is significant, but E_{ac}^2 and E_{ac}^3 and so on are negligible.

“Professor - student conversation starts”

Depends on the system. I will tell you practically how it is. If you measure a 10 millivolt for normal system, (I am not talking about batteries and fuel cells where you usually use galvanostatic method). For corrosion, for electro deposition, if you are using 10 millivolts, nobody will complain. 10 millivolts peak or 20 millivolts peak, you can probably get it accepted in most cases. 20 millivolts rms maybe, 50 millivolts people will start complaining. 5 millivolts nobody will complain, but the signal to noise ratio may not be good. Noise level is going to remain at whatever level it is in. everybody will be happy for 1 millivolt, but the people will start doubting the authenticity of the data if it looks really good. So the correct answer is, it depends. [that probably is not going to make you happy]. 5 millivolt to 20 millivolt you can probably manage. I do not know if it is going to be linear at 20 millivolt, it may not be linear, but people will not question the assumption that you can approximate that as a linear response. If you want to know whether it is linear or not you have to measure what are called as harmonics and at 20 millivolt you will get some harmonics.

[…………]

You also have to measure, if I do it at 10 millivolt and if I do it 20 millivolts, if the impedance values are same in the entire frequency range, I can take that as a linear system.

You have to do that and we also have to measure the harmonic and show that they are below the noise level. Then you can say this is linear, but it is going to take lot of work. So 5 millivolt is considered good. If you go to fuel cells, or batteries, it is usually done in galvanostatic mode, which is a completely different story. It means, with whatever little evidence we have, if you apply a perturbation sign wave of 10 milliamps, 100 milliamps, 200 milliamp you may get higher harmonics. But for whatever reason it appear that, if I measure just the impedance, look at the potential perturbation and calculate the impedance, it does not seem to vary that much with increase in i_{ac0}. [We do not know why, but that seems to be the one we have seen so far]. So there I do not have a real number to tell below this value it is really linear, above this value it is not linear. It looks like it is going to be linear in a large range linear which means if I apply 100 milliamps or 200 milliamps per square centimeter of perturbation, I may get more or less same impedance although the second or third harmonic are there to significant level. [Why it behaves that way I do not know it].

“Professor - student conversation ends”

Coming back to where we stopped, we are basically expanding k_1 in Taylor series, we are expanding θ in Taylor series because we recognize that they are going to depend on potential. When potential varies with time this is going to vary.

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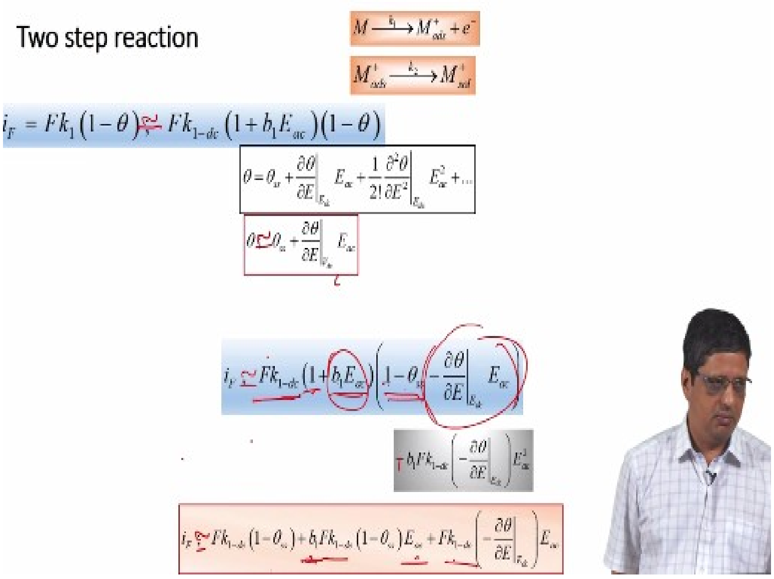

Two step reaction

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

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

$i_F = Fk_1(1-\theta) \simeq Fk_{1-dc}(1+b_1E_{ac})(1-\theta)$

$\theta = \theta_{ss} + \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac} + \frac{1}{2!}\left.\frac{\partial^2\theta}{\partial E^2}\right|_{E_{dc}} E_{ac}^2 + \ldots$

$\theta \simeq \theta_{ss} + \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac}$

$i_F \simeq Fk_{1-dc}(1+b_1E_{ac})\left(1-\theta_{ss} - \left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}} E_{ac}\right)$

$+ b_1Fk_{1-dc}\left(-\left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}}\right)E_{ac}^2$

$i_F \simeq Fk_{1-dc}(1-\theta_{ss}) + b_1Fk_{1-dc}(1-\theta_{ss})E_{ac} + Fk_{1-dc}\left(-\left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}}\right)E_{ac}$

If I substitute it back here, I would get four terms here, F_1k_{dc} is there. I will get 1 multiplied by 1-θ. I will get b_1E_{ac}, so I will have $F_1k_{1dc}\,b_1E_{ac}$ (1-θ). I will get F_1k_{dc}; constant here 1; this is going to be –dθ/dE multiplied by E_{ac} and the fourth term is going to be this term multiplied by this term which is going to give me [actually I think I miss the sign here], –dθ/dE b_1E_{ac}, b_1 is here F_1k_{dc} is there. Therefore, it is going to give me 4 terms out of which the greyed out term I am removing because it has E_{ac}^2.

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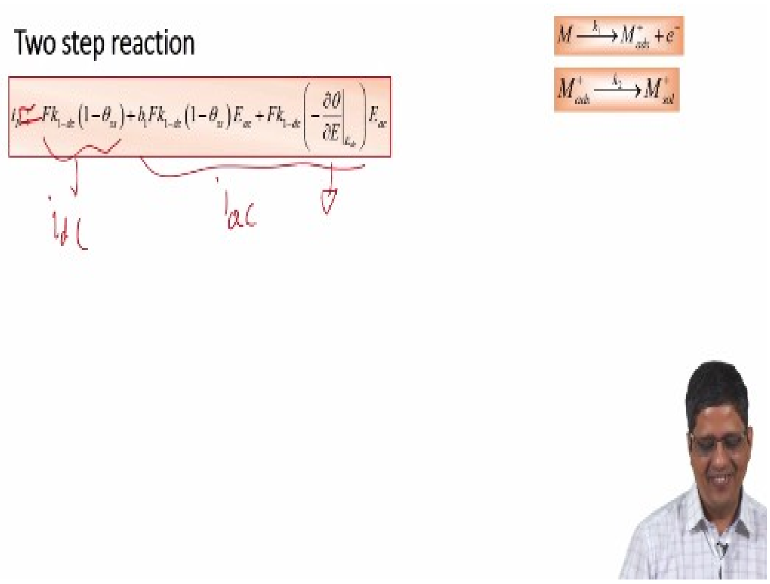

Two step reaction

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

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

$i_F \simeq \underbrace{Fk_{1-dc}(1-\theta_{ss})}_{i_{dc}} + \underbrace{b_1Fk_{1-dc}(1-\theta_{ss})E_{ac} + Fk_{1-dc}\left(-\left.\frac{\partial\theta}{\partial E}\right|_{E_{dc}}\right)E_{ac}}_{i_{ac}}$

So for this reaction with linearization, I can write the faradaic current as this. I am going to call this as the DC, which means, it depends only on DC potential and it does not depend on AC. This is the AC components which depends on the DC potential as well as on the AC. Now the only problem here is we do not know what dθ/dE is. In order to get the dθ/dE, we need to look at the mass balance equation.

“Professor - student conversation starts”

Yes, we are at DC and then we apply AC. Therefore θ is going to vary away from the DC value.

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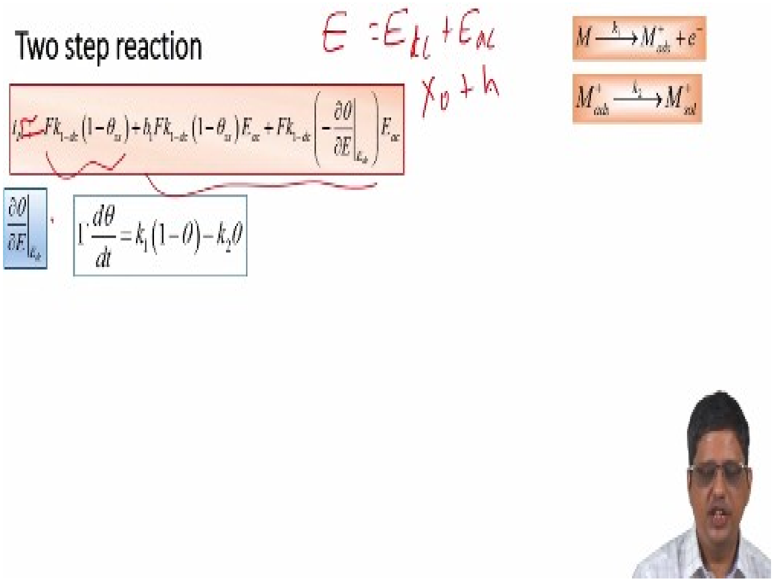

Two step reaction

$E = E_{dc} + E_{ac}$

$x_0 + h$

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

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

$i_f = Fk_{1-dc}(1-\theta_{ss}) + b_1 Fk_{1-dc}(1-\theta_{ss})E_{ac} + Fk_{1-dc}\left(-\frac{\partial\theta}{\partial E}\bigg|_{E_{dc}}\right)E_{ac}$

$\frac{\partial\theta}{\partial E}\bigg|_{E_{dc}}$

$\Gamma\frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

[…………….]

E is the potential and that is E_{dc}+ E_{ac}. So this is like x_0+h. so h is representing the small deviation and x_0 is representing the DC level.

[…………]

Yes, the way in fact we have written is θ_{ss} corresponds to θ at the DC potential of E_{dc}. That is what we have told earlier that θ_{ss} can be derived at a steady state potential.

“Professor - student conversation ends”

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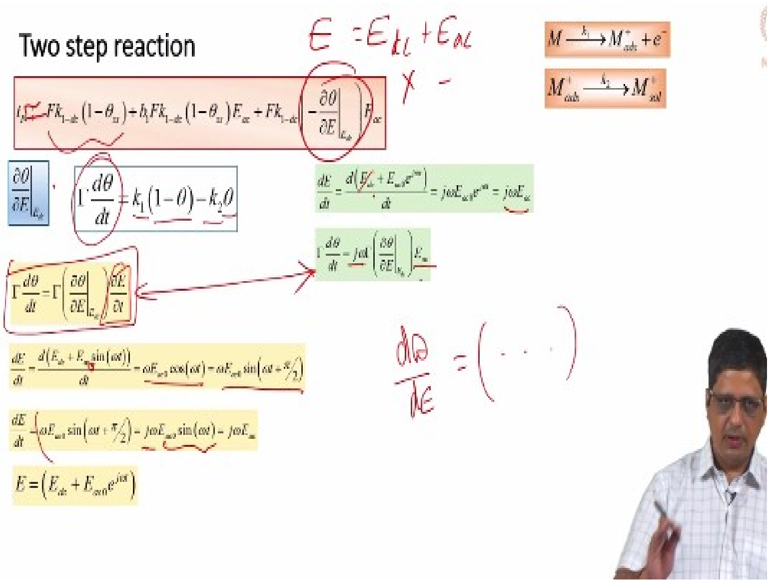

Two step reaction

$E = E_{dc} + E_{ac}$

X -

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

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

$i_F = Fk_{1-dc}(1-\theta_{ss}) + b_1 Fk_{1-dc}(1-\theta_{ss})E_{ac} + Fk_{1-dc}\left(-\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$

$\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}$

$\Gamma\frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

$\frac{dE}{dt} = \frac{d(\cancel{E_{dc}} + E_{ac0}e^{j\omega t})}{dt} = j\omega E_{ac0}e^{j\omega t} = j\omega E_{ac}$

$\Gamma\frac{d\theta}{dt} = j\omega\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$

$\Gamma\frac{d\theta}{dt} = \Gamma\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)\frac{\partial E}{\partial t}$

$\frac{d\theta}{dE} = (\cdots)$

$\frac{dE}{dt} = \frac{d(E_{dc} + E_{ac0}\sin(\omega t))}{dt} = \omega E_{ac0}\cos(\omega t) = \omega E_{ac0}\sin(\omega t + \pi/2)$

$\frac{dE}{dt} = \omega E_{ac0}\sin(\omega t + \pi/2) = j\omega E_{ac0}\sin(\omega t) = j\omega E_{ac}$

$E = (E_{dc} + E_{ac0}e^{j\omega t})$

This equation we have seen before and it is for unsteady state (Refer slide or video). For steady state, we said dθ/dt to 0 and then get the values. Now I want to write first the expression on the left hand side dθ/dt, the θ varies because we are applying in AC potential. We know how the potential changes with time. So I want to write it as dθ/dE dE/dt. There are couple of ways to write dE/dt. One, we can call dE/dt as this where E is the sum of DC+AC. When you take the derivative of DC, it goes to 0. When you take AC, this is E_{ac0}sin ωt. [There is a small mistake here]. It is DC+ E_{ac}, which is written as E_{ac0}sin ωt. The ω comes, sine becomes cosine. I would write it as ωE_{ac0}cos ωt and this I can write it as omega ωE_{ac0}sin ωt with a phase off set of π/2.

In a complex plane, if this is a vector, a phase off set of π/2 pushes it up. This is real this is imaginary (refer video). So one way to write that is, if you multiply a number by j it is causing rotation by 90 degree in the complex plane. If you give any complex number, multiply by j, that j is the square root of -1. It is going to be equivalent to rotating that with this origin as the center. So I can write this expression as, take this value of sin ωtE_{ac0} multiply by ω and then say that it is equivalent to multiplying by j and I would get this expression as jωE_{ac}. It is another way to derive this. You can say E is E_{dc}+ $E_{ac0}e^{j\omega t}$ where it is actually cosωt+ j sin ωt. So it is a complex representation of the potential. When you take the derivative of this, it is going to be jω. This E_{dc} is going to go away. It is going to jω multiply by $E_{ac0}e^{j\omega t}$ which means jωE_{ac}. So the point to note is dE/dt in the complex notation that we write is going to be jωE_{ac}. Substitute it back here, you can write Γdθ/dt as jωE_{ac}Γdθ/dE. [I would like you to be able to derive this properly because everything else that follows depend on you doing this correctly in the next few steps. I will start with the next one and continue tomorrow].

We have expanded the left side, we had to expand all terms in Taylor series, chop off the term after E_{ac}, E_{ac}^2 and so on can be removed. Rearrange to get an expression saying dθ/dE equal to something where everything on the right side is known to us. Then we can go and substitute it here. [This is lengthy, but it is not very difficult as long as you do the algebra correctly, and expand this term correctly, as long as you recognize this part, it can be written as $j\omega\Gamma d\theta/dE \times E_{ac}$. You will find that regardless of how many steps are there in a given mechanism, how many intermediate species are there, you will be able to write the impedance for all of these. [It may need 10 pages of derivation, but it is not going to take anything more than writing in Taylor series chopping off after some time, doing up some algebra and recognizing this mass transfer equation]. The left side of this mass transfer equation can be written like this (refer video). And all these are applicable when we say mass transfer is very fast and it is mass balance equation right not mass transfer equation.

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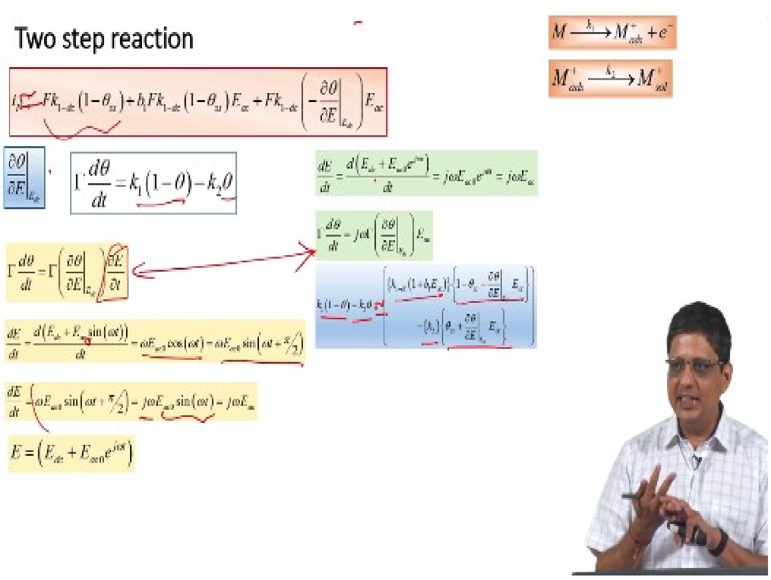

Two step reaction

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

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

$i_F = Fk_{1-dc}(1-\theta_{ss}) + b_1 Fk_{1-dc}(1-\theta_{ss})E_{ac} + Fk_{1-dc}\left(-\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$

$\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}$

$\Gamma\frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

$\frac{dE}{dt} = \frac{d(E_{dc} + E_{ac0}e^{j\omega t})}{dt} = j\omega E_{ac0}e^{j\omega t} = j\omega E_{ac}$

$\Gamma\frac{d\theta}{dt} = j\omega\Gamma\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$

$\Gamma\frac{d\theta}{dt} = \Gamma\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)\frac{\partial E}{\partial t}$

$k_1(1-\theta) - k_2\theta \approx \left\{k_{1-dc}(1+b_1E_{ac})\right\}\left\{1-\theta_{ss} - \frac{\partial\theta}{\partial E}\Big|_{E_{dc}}E_{ac}\right\} - (k_2)\left\{\theta_{ss} + \frac{\partial\theta}{\partial E}\Big|_{E_{dc}}E_{ac}\right\}$

$\frac{dE}{dt} = \frac{d(E_{dc} + E_{ac0}\sin(\omega t))}{dt} = \omega E_{ac0}\cos(\omega t) = \omega E_{ac0}\sin(\omega t + \pi/2)$

$\frac{dE}{dt} = \omega E_{ac0}\sin(\omega t + \pi/2) = j\omega E_{ac0}\sin(\omega t) = j\omega E_{ac}$

$E = (E_{dc} + E_{ac0}e^{j\omega t})$

So $k_1(1-\theta)-k_2\theta$, I am going to write approximately as k_1, I am going to write in Taylor series and chop off, I am going to write $1-\theta$ in Taylor series and chop off, k_2 is a constant and θ, I can write again in the same way, get all the terms, keep the constant, keep the term with E_{ac} and throw away the term with E_{ac}^2. In this case, you would not get anything beyond E_{ac}^2. In some cases, you might get even more than that, you may get E_{ac}^3, if I have 3 products k_2, θ_1, θ_2 in some expression, does not matter, keep only E_{ac} on the constant term.

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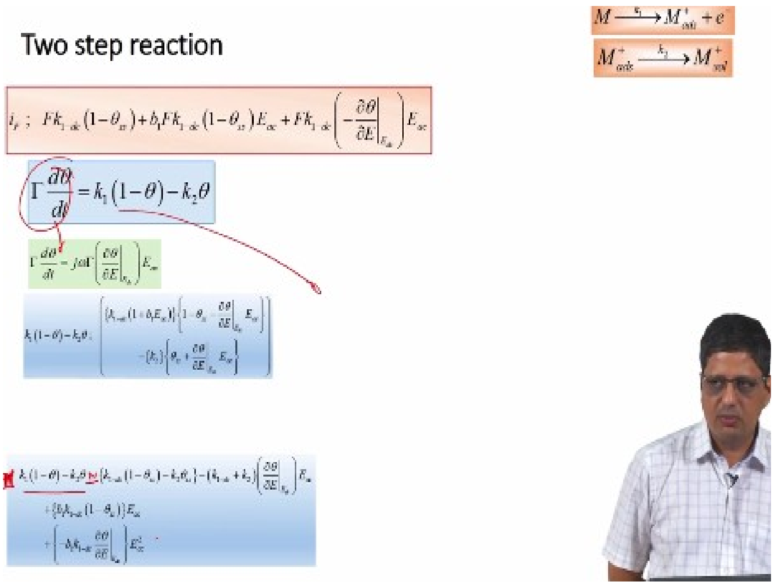

Two step reaction

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

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

$$i_F \; ; \; Fk_{1-dc}(1-\theta_{ss}) + b_1 F k_{1-dc}(1-\theta_{ss}) E_{ac} + F k_{1-dc}\left(-\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right) E_{ac}$$

$$\Gamma \frac{\partial\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$\Gamma\frac{d\theta}{dt} = j\omega\Gamma\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$$

$$k_1(1-\theta)-k_2\theta \; ; \left(\begin{array}{c}\{k_{1-dc}(1+b_1E_{ac})\}\left\{1-\theta_{ss}-\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}E_{ac}\right\} \\ -\{k_2\}\left\{\theta_{ss}+\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}E_{ac}\right\}\end{array}\right)$$

$$k_1(1-\theta)-k_2\theta \approx \{k_{1-dc}(1-\theta_{ss}) - k_2\theta_{ss}\} - (k_{1-dc}+k_2)\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)E_{ac}$$
$$+\{b_1k_{1-dc}(1-\theta_{ss})\}E_{ac}$$
$$+\left\{-b_1k_{1-dc}\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right\}E_{ac}^2$$

We are going to keep the equation here, substitute it. For this, we are going to substitute from here. $k_1(1-\theta)-k_2\theta$. [I have shown it here, but I would like to actually do that and get it because first time you may or may not get it correctly. I would like you to actually try that and get it. I will stop here now, but I will continue with this tomorrow and then finally we will see the expression for faradaic current write it as DC+ AC and we will get the expression for impedance and then if you plot it, how will it look like in the nyquist plot or complex plane plot. I will show now how it looks like. After doing all this, it is going to look like 2 semicircles possibly 2 semi circle depending on the DC potential. The radius or diameter of this semicircle will vary, but you can represent all of them by this Maxwell circuit or equivalent wide circuit or ladder circuit].