Electrochemical Impedance Spectroscopy
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Lecture - 23
Two Step Reaction with an Intermediate-II

What we saw in the last class is development of impedance equations for two step reaction with a single adsorbed intermediate. We will continue with the development of the equation [we did not complete that].

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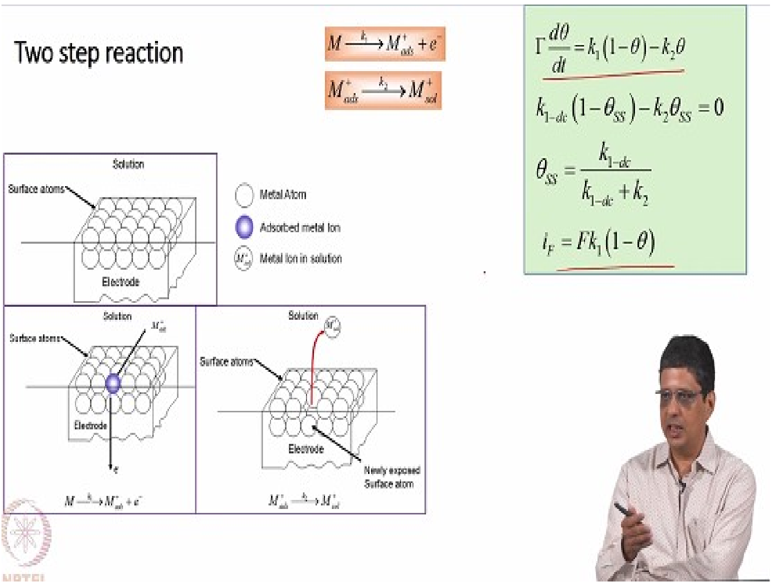

Two step reaction

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

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

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

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

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

$$i_F = Fk_1(1-\theta)$$

[This is just to refresh your memory]. We have a two-step equation, the first step is electron transfer reaction, second step is dissolution movement of the atom from the surface to the solution, and we have written the mass balance equation for the adsorbed intermediate what form this intermediate that is the positive sign $k_1(1-\theta)$ the second step removes this intermediate. Whenever you a propose mechanism, we say this maybe the reaction actually happening we propose a reaction mechanism then for each intermediate in this case there is only one intermediate each intermediate we have to write the mass balance equation. For the overall reaction you should write the charge balance equation. Faradaic current is given by the first step it is nothing from the second step for each step if you have n number of step for each step you have to look and see whether electron is involved in it.

If it involves an electron transfer, then whenever electron is generated you can use a convention say it is positive, and when its consumed it is negative. If it is deposition of a metal, then you can say whenever the electron is consumed it is positive and whenever it is generated it is negative it does not matter you will get the same expression. We write the mass balance equation, (and) the charge balance equation.

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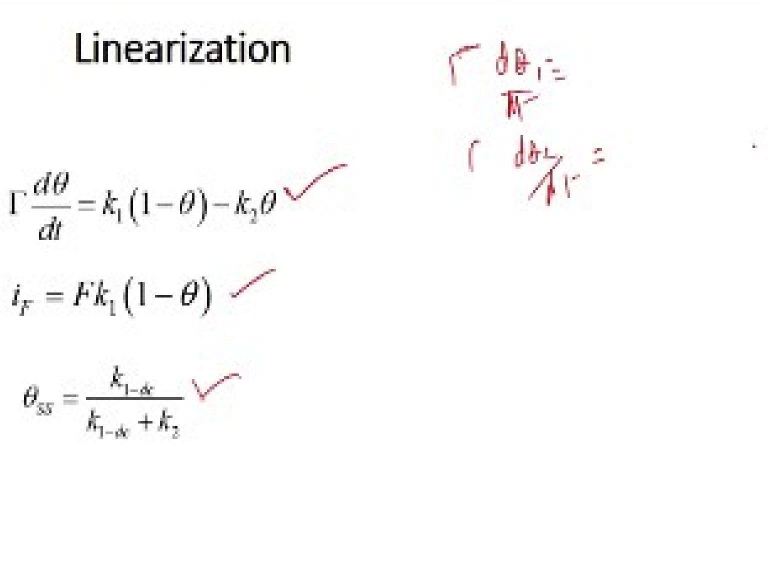

Linearization

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

$$i_F = Fk_1(1-\theta)$$

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

$\Gamma\, d\theta_1 / dt =$

$\Gamma\, d\theta_2 / dt =$

For each species we write the mass balance equation for the total reaction we write the charge balance equation. If we have multiple species you will get multiple equations for the mass balance term. Instead of writing θ you might write it as θ_1, θ_2 for each intermediate\s. Here, we have only one adsorbed intermediate the remaining is vacant side. We call it as θ for the intermediates and (1-θ) for the vacant side.

If we have two or three intermediates I would write θ_1, θ_2 may be θ_3, 1 minus all these θ gives the remaining sites. Now if I have multiple equations for each one of them under steady state condition, I can get the steady state surface coverage. In this case, I have only one equation I set it till zero. If I have more number of equations I will write it as $\Gamma\, d\theta_1/dt$ = some expression, $\Gamma\, d\theta_2/dt$ some expression and so on.

I can set all of them to be equal to zero and solve them simultaneously. If there are simple equations with first order reaction you would get a linear [sort of] equation you can use matrix inversion or similar method and solve. If you get second order or higher order equation you may get non-linear term you will still end up getting only one set of solution for this. If you have non linear equation you can get multiple solution, but only one set will come where all θ's are between 0 to 1.

A fraction of surface coverage cannot exceed 1 or go below 0. I will get physically meaningful solution for one case only even if we get multiple solutions [we can verify]. The point is that you will get one set of solution here it is a very simple equation so I will just rearrange and write this you will get an answer here (refer video, 03:29). After this, we said we want to know what happens when you supply an ac potential, ac potential can be supplied at zero dc or at any other dc. We take an arbitrary value E_{dc}.

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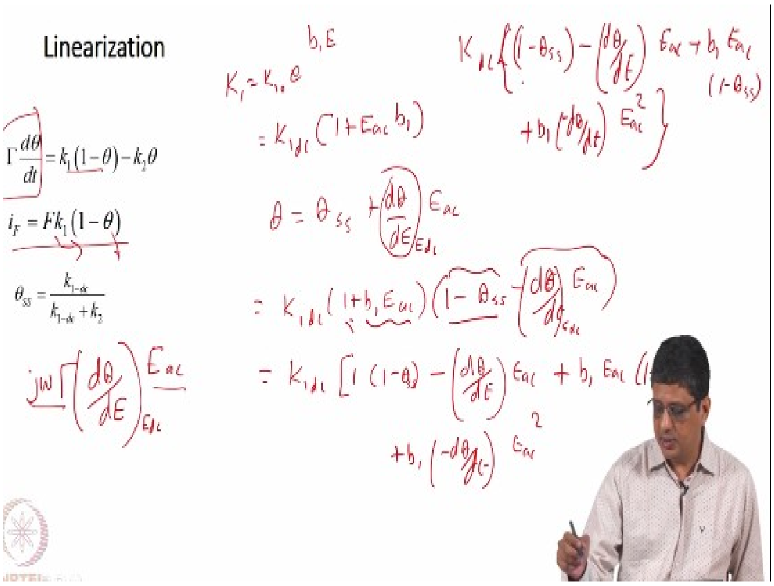

Linearization

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

$$i_F=Fk_1(1-\theta)$$

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

$$j\omega\Gamma\left(\frac{d\theta}{dE}\right)_{E_{dc}}E_{ac}$$

$$k_1=k_{10}e^{b_1E}$$

$$=k_{1dc}(1+E_{ac}b_1)$$

$$\theta=\theta_{SS}+\left(\frac{d\theta}{dE}\right)_{E_{dc}}E_{ac}$$

$$=k_{1dc}(1+b_1E_{ac})\left(1-\theta_{SS}-\left(\frac{d\theta}{dE}\right)_{E_{dc}}E_{ac}\right)$$

$$=k_{1dc}\left[1(1-\theta_{s})-\left(\frac{d\theta}{dE}\right)E_{ac}+b_1E_{ac}(1\right.$$

$$+b_1\left(-d\theta/dE\right)E_{ac}^2$$

$$k_{dc}\left\{(1-\theta_{SS})-\left(\frac{d\theta}{dE}\right)E_{ac}+b_1E_{ac}(1-\theta_{SS})+b_1\left(-d\theta/dE\right)E_{ac}^2\right\}$$

Then we wrote this equation after expanding this k_1 we wrote it as k_{10} and then saying that ac potential is a small amplitude. We wrote this as k_{1dc} as an approximation. Any other rate constant which depends on potential you can write accordingly. If it is independent of potential it just going to remain as a constant anyway, this part we took care of.

Second part when we expand this in Taylor series we realize this 'θ' can be written as first derivative, and then we neglect the remaining term. In order to find this, we need to use mass balance equation. [Remember] whenever you propose a new equation or somebody gives you the equation, you write the mass balance equation [it may be one or many depending on how many adsorbed intermediates are there]. You write the charge balance equation it gives you one equation. We want to expand this in Taylor series and then truncate it after the first term, (this is called) linearization. '*k*' values (rate constant values) can be linearized without much difficulty. θ values have to be expanded in this and in order to solve this θ values [in this case one θ value] we have to solve in terms of the dθ/d*E*. We want to get this we have to expand and linearize (refer video, 05:10). If you have multiple equations, you will have to do that for all of them and solve them simultaneously. Just like steady state value we set it to zero and solve you get steady state value. Here we saw this left hand side [this is at that particular E_{dc}] can be written as dθ/dE, dE/dt, but then dE/dt we can write it as E_{ac} j ω. Γ remains here, dθ/dE remains here dE/dt becomes j ω Eac, that expression or that form is going to be remain even if you have multiple θ_1, θ_2, θ_3 (refer video, 06:00). For all of them, we will end up writing j ω Γ Eac dθ_1/dE, dθ_2/dE or dθ_3/dE etc on the left hand side. Right hand side we recognize k_1 should be written as k_{1dc} (1+b_1 E_{ac}) (1- θ_{SS}- dθ/dE) E_{ac}. [It is an approximation. I should actually write each time as evaluated at E_{dc}. [I am just going to write like this now, but] you have to remember it has to be evaluated as E_{dc}.

First k_1 (1-θ) I can write like this I can write this as k_{1dc} [1(1-θ)] here θ_{SS}, 1*(1-θ_{SS}) 1* 1 multiplied by this term, this term multiplied by this term and then fourth is going to be b1(-dθ/dE) E_{ac}^2. It is a negative sign E_{ac}^2 this now we have truncated this series and always set E_{ac} is small number E_{ac}^2 , E_{ac}^3 etcetera are all going to be very small (refer video, 07:25). Therefore, we are going to neglect this fourth term here and all that we have done now is to write the first part of the right hand side. We have to do the same thing for the second part. we have to expand this in Taylor series, truncate after the first term, multiply the terms and then and then make sure that only the first order terms are retained and everything else is taken out or neglected. That means we have to write for the k_2θ. k_2 is a constant [we do not have to worry], it is not depended on potential.

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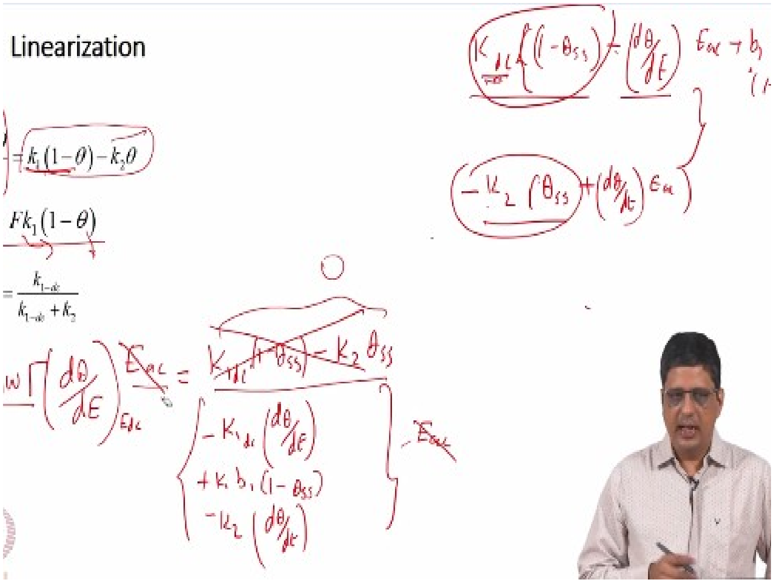

Linearization

$=k_1(1-\theta)-k_2\theta$

$Fk_1(1-\theta)$

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

$j\omega\Gamma\left(\frac{d\theta}{dE}\right)_{E_{dc}}E_{ac} = \cancel{K_{1dc}(1-\theta_{ss})-k_2\theta_{ss}}$

$\left\{\begin{array}{l}-K_{1dc}\left(\frac{d\theta}{dE}\right)\\+K_1b_1(1-\theta_{ss})\\-k_2\left(\frac{d\theta}{dE}\right)\end{array}\right\}E_{ac}$

$K_{dc}\{(1-\theta_{ss})-\left(\frac{d\theta}{dE}\right)E_{ac}+b_1$

$\left(-k_2(\theta_{ss})+\left(\frac{d\theta}{dE}\right)E_{ac}\right)$

We will write the second part as $-k_2\theta_{SS}$ + dθ/dE * E_{ac} and then we neglect the remaining components. This equation we have written the left hand side we have written the first part in the right hand side, second part in the right hand side we can equate them and then see if we can simplify it further. Left hand side I have written like this right hand side I am going to say k_{1dc} (1-θ_{SS}) (I want to look at this. I am going to take this) -$k_2\,\theta_{SS}$. It is a constant term it is not multiplied by E_{ac}. Here also it is a constant term not multiplied by E_{ac}, this and this I am keeping them together everything multiplied by E_{ac} right I am going to write them together. This is going to be k_1 dθ/dE. it is going to k_{1dc} (dθ/dE) with a negative sign because this is positive this is negative here.

(refer video, 09:38) I am going to pull out E_{ac} here. k_1 b_1 (1-θ_{SS}). k_1 here multiplying the b_1 (1-θ_{SS}) E_{ac}, E_{ac} is taken out here (does it make sense?). Third, $-k_2$ (dθ/dE)*E_{ac}. Now left hand side you see it depends on E_{ac} right hand side has a (constant +E_{ac}). This is not going to work unless this is set to zero and of course you do not have to set to zero it automatically goes to zero. If I double E_{ac}, the right hand side should also double and that means a constant term has to be zero. In this case we know θ_{SS} is defined as $k_{1dc}/k_{1dc}+k_2$ which actually comes from this equation under steady state condition. When I say $k_{1dc}\theta_{SS}$, I know k_{1dc}(1-θ_{SS}) is going to be= $k_2\,\theta$. when you expand this in Taylor series truncate after the first term [do all the algebra] multiply them throw away all the E_{ac}^2 in higher order term, you will get a constant term [constant meaning not depended on E_{ac} and group of terms which depends on E_{ac}], those constant will go to zero that essentially if I expand this in Taylor series and chop off everything including E_{ac}, then it should go to zero. Because on the left hand side if E_{ac} is zero left hand side will go to zero. This will go towards zero which means I can divide it by E_{ac} on both sides. As long as E_{ac} is small, our assumption that this can be linearize is valid and as long as E_{ac} is small I will get an equation which says j$\omega\Gamma$ dθ/dE on the right hand side it has to be these terms here 1, 2, 3 terms here (refer video, 11:45).

On the right hand side, you have 3 terms, one of it does not contain dθ/dE other term contain dθ/dE. We can bring them to the left side rearrange.

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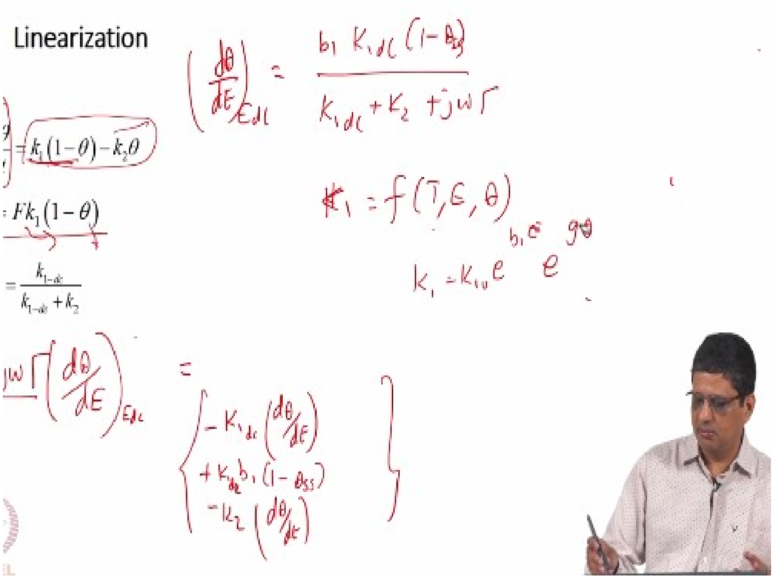

Linearization

$$= k_1(1-\theta) - k_2\theta$$

$$= Fk_1(1-\theta)$$

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

$$\left(\frac{d\theta}{dE}\right)_{E_{dc}} = \frac{b_1 k_{1dc}(1-\theta_{ss})}{k_{1dc}+k_2+j\omega\Gamma}$$

$$k_1 = f(T, E, \theta)$$

$$k_1 = k_{10} e^{b_1 E} e^{g\theta}$$

$$j\omega\Gamma\left(\frac{d\theta}{dE}\right)_{E_{dc}} = \left\{ -k_{1dc}\left(\frac{d\theta}{dE}\right) + k_{1dc} b_1 (1-\theta_{ss}) - k_2\left(\frac{d\theta}{dE}\right) \right\}$$

We can write an expression for dθ/d*E* evaluated at E_{dc}. [I would like you to try that so again] If you see this needs little patience, but it is not very, very complicated, but in terms of depth of mathematical knowledge you need it is not that difficult. You need to expand each term for one equation you get this when you get many equations you can still solve them and get solution especially if they are linear you will definitely get a solution. [You can write the expression] Here it is going to be dθ/d*E* is a some number when it is many more intermediates you will get much longer or larger expression you will still get the expression in terms of known values here. Here, I have written it as k_1, (it is actually k_{1dc}) b_1 k_{1dc} $(1-\theta_{SS})$ comes in the numerator you are going to get $k_{1dc}+k_2+j\ \omega\ \Gamma$ (in the denominator) [is that correct?]. If I give you θ_1 and θ_2 another set of equation you would still be able to solve it.

We will see an example later. Here I want you to see [this] that you would get an expression for dθ/d*E* under small amplitude perturbation (and) you can get an analytical expression. It basically needs you have to look at mass balance equation and rearrange the terms. This theme is going to be there for any of this mechanistic analysis. We are assuming mass transfer is fast, [we are assuming] solution resistance is negligible, [we are assuming] Langmuir model is valid. Which mean k_1, k_2 all these things they can depend on potential; they can depend on temperature we are always looking at isothermal condition so we would not go into that. They depend on potential or they maybe constant. They are not going to depend on θ. If we use Frumkin or Temkin isotherm model, k_1, k_2 all these things will depend on possibly θ also in which case when you linearize it becomes lot more complex. You will have to write as k_1 as k_{10} $\exp(b_1E)$ x $\exp(g\theta)$. when I say expand this I cannot just put *E* as E_{ac} and E_{dc} I also have to write here θ as θ_{SS} as dθ/d*E* and then expand this exponential again. It is again possible, but it becomes even more complex and you may or may not get a simple analytical solution. You may have to use numerical method.

And if you are going to go through that much pain there are better methods to handle it, better meaning it is more complex than this, but simpler in terms of visualization. [we get an expression here]. Now I want to look into the faradaic current and then say I got an expression for dθ/d*E* now can I get the impedance expression.

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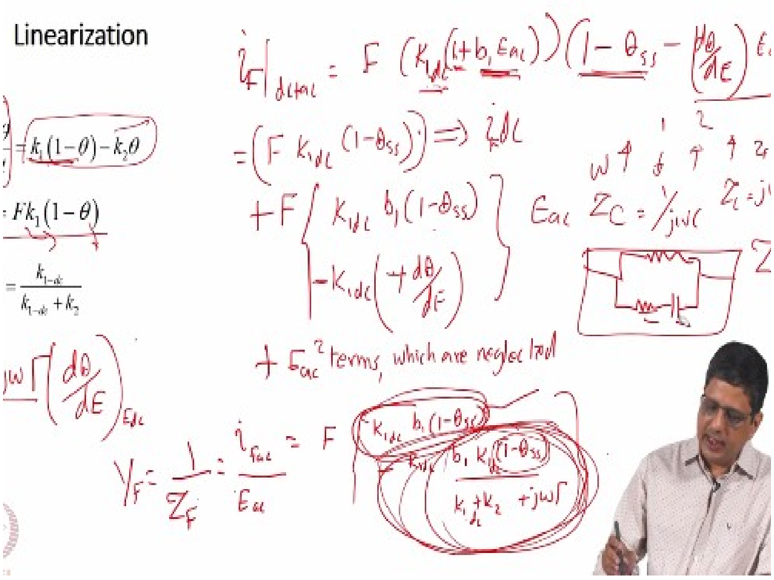

Linearization

$= k_1(1-\theta) - k_2\theta$

$= Fk_1(1-\theta)$

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

$j\omega\Gamma\left(\frac{d\theta}{dE}\right)_{E_{dc}}$

$i_F|_{dc+ac} = F\left(k_{1dc}(1+b_1E_{ac})\right)\left(1-\theta_{ss}-\frac{d\theta}{dE}\right)$

$= \left(F k_{1dc}(1-\theta_{ss})\right) \Rightarrow i_{dc}$

$+F\left\{k_{1dc}\, b_1(1-\theta_{ss}) - k_{1dc}\left(+\frac{d\theta}{dE}\right)\right\} E_{ac}$

$+ E_{ac}^2$ terms, which are neglected

$Z_C = 1/j\omega C$

$Y_F = \frac{1}{Z_F} = \frac{i_{Fac}}{E_{ac}} = F\left(k_{1dc}\, b_1(1-\theta_{ss}) - k_{1dc}\frac{b_1 k_1(1-\theta_{ss})}{k_{1dc}+k_2+j\omega\Gamma}\right)$

i$_{\text{faradaic}}$ in presence of dc+ ac we wrote it as….(refer video, 15:28). This is how we wrote it and at that time we got stuck saying that we do not know how to write the dθ/d*E*, of course the remaining terms are neglected. This I can rewrite it I will take the first term here first term and first term here first term here meaning (1-θ_{SS}). I will write this as k_{1dc} *(1-θ_{SS}) that is going to be dc current. I have k_{1dc} 1, 2, 3, 4 terms here and I recognize E_{ac} *E_{ac}^2, I can throw it away, so I am going to get 1* this term b_1 E_{ac}*this term they will be retained. I am going to write it as F {k_{1dc} b_1 (1-θ_{SS})} [It is going to be F k_{1dc} second term here and the first term there] E_{ac} is taken out here. Now F I will keep it here, k_{1dc} I can still write it here. [I can write it as – here it does not matter] (refer video, 17:02) Now I want to write i_F as i_{Fdc}+ i_{Fac}. I will write i_{Fac} is going to be F {k_{1dc} b_1 (1-θ_{SS})-k_{1dc}}. [is that correct what is dθ/d*E*?] Now if I bring it here when I apply an ac potential I get this ac current the ratio of current to potential is going to be admittance that is inverse of impedance. [Faradaic impedance] if I apply an ac potential the reaction will respond with an ac current and that impedance can be written as iF_{ac}/E_{ac} and this is the expression for the faradaic impedance.

Given a reaction we should be able to get the expression for faradaic impedance. Given a reaction we have to know the parameter value k_{10}, b_1, k_2. We need to know Γ. You need to be given at this dc potential and applying at this frequency and applying the ac tell me what the response is going to be and you can write that response. [You can write the response] you can write the expression for the faradaic impedance.

You should also be able to guess by looking at this what kind of result you would get. How do you know what we are going to get. When ω increases what will happen? When ω increases this term b_1 is going to be positive k_1 is a positive number, θ is going to vary between 0 to 1 that means this is also a positive number. (1-θ) is going to be positive number. k_1 and k_2 [k_2 is not k_2 dc right it is just k_2] are going to be positive numbers. ω is a positive number, Γ is a positive number. When I increase ω this term is going to decrease (refer video, 20:10). When this term decreases this is a negative sign so the actual value is going to increase. -2, -10 among this -2 is a larger number so when ω increases this term decreases, first level. Second level with this it increases third, that means $1/Z_F$ is increasing, Z_F is decreasing. [remember] For a capacitor impedance is written as 1/jωC and for an inductor it is written as jωL. For a capacitor when you increase ω, impedance will decrease. For an inductor when you increase ω, impedance will increase. If you have to guess you can say this is going to look like a capacitor, but this is not a pure capacitor. It is not just 1/jωΓ. it has k_1, k_2 in addition to that. It also has another constant term here. All these things put together will look like this (refer video, 21:30). Remember this can be written as Y_F, inverse of impedance can be written as admittance. If I have two electrical circuits in parallel I will add the admittance. This is admittance of one circuit, this is the admittance of another circuit. Admittance of one circuit this looks like a resistance. Admittance of second circuit has a constant value and a capacitor behavior. [And] this is going to be represented by resistors and capacitor. This entire thing is going to represent faradaic impedance. Now here you can look at this and say it is going to increase, decrease etcetera if I have more complex expression here you will come with a condition saying if this term is more than this term then it will increase. If this term is less than this term it is going to decrease.

Same circuit will work except that some of them will have negative values, and if we have negative values here this will become an inductive loop. This particular example it can never become an inductive loop, because all this terms we can check and verify that they are only positive values.

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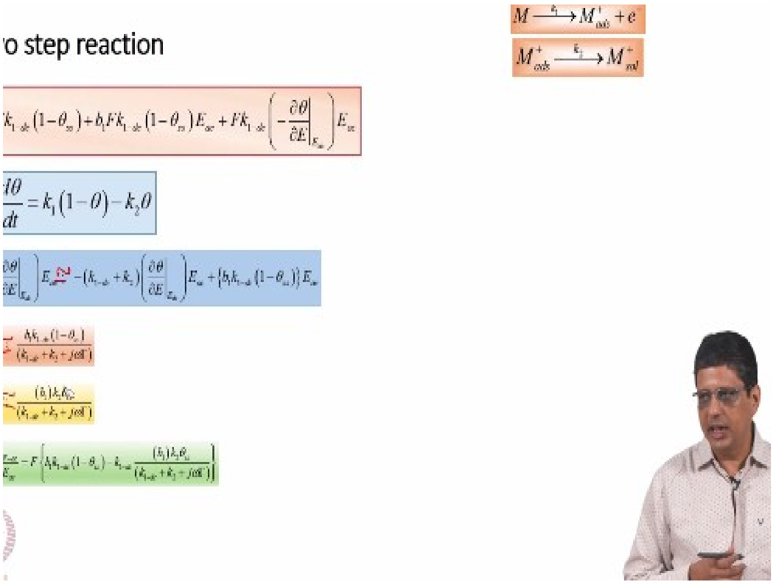

o step reaction

$M \xrightarrow{k_1} M'_{ads} + e$

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

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

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

[These are just given in the power point as] look at the left term, and [look at] the right term, and expand that, simplify it further set the first term till zero. Among the 4 terms the fourth term goes because ac square is too small. First term goes because it is steady state equation and then you can rearrange and get the value for dθ/d*E*. All these approximate terms become semicolons here. And you can write the expression for faradaic impedance [which is exactly what you have done now]. Now because k_1 (1-θ) under steady state condition is= k_2 θ, you can write the same expression in different ways it is all equivalent anyway.

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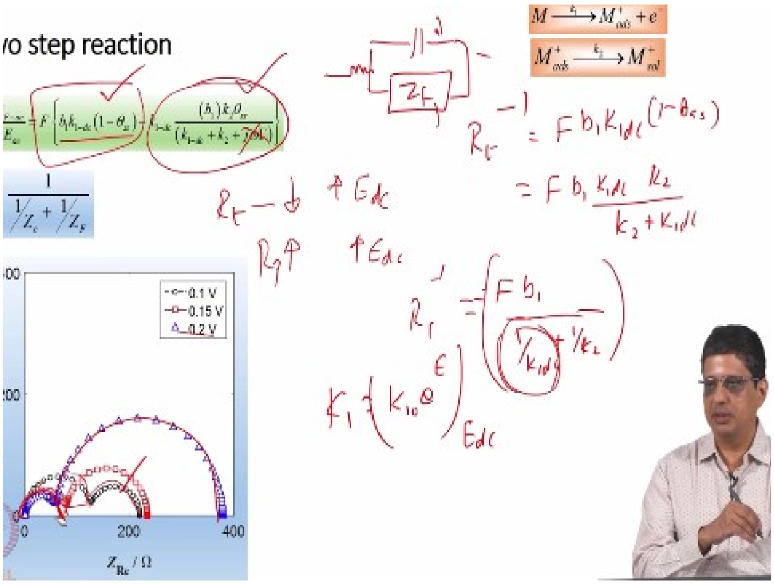

o step reaction

$M \xrightarrow{k_1} M'_{ads} + e$

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

$\frac{1}{1/Z_c + 1/Z_F}$

And once you know the expression for faradaic impedance you can recognize that you may have a solution resistance. In this case I assume this is zero. You have a double layer capacitor, and you have a faradaic impedance which looks like this (refer video, 23:33). I can add admittance of the capacitor, admittance of the faradaic impedance and I would get at different dc values for a given set of parameters (realistic values of parameter) (At) 0.1 V of dc with respect to equilibrium [that] is giving me the black color line. I increase the potential dc potential, [ac is still a small number what is small number is 5 mV, 1 mV I have not mentioned that, but we will say it is small enough so that E_{ac} square and other terms can be neglected]. Then when I increase the dc potential it retains the semicircle shape, but the first loop hits at an earlier stage, the second loop hits at a later stage. I increase it further the first loop hits at even earlier stage that means charge transfer resistance in this example decreases when I increase dc potential.

Polarization resistance increases when I increase dc potential. It is for a particular set of values. If I give you different kinetic parameter you may get a different type of result. This case, I think in general charge transfer resistance will decrease in increase in potential for this particular type of reaction. [Polarization resistance I do not remember now how it is going to be you can still guess it].

If ω is going to go towards infinity this will go away correct (refer video, 25:04). When ω goes to infinity only this term will be retained and that is the charge transfer resistance. When ω goes to zero you can calculate the value this term will be retained, this term will also be retained, except this is gone, but then it becomes difficult to guess unless you go through lot of arguments to figure out under what condition will this keep increasing with potential and under what condition it will keep decreasing with potential. This example, R_t it is little easy to guess. k_{1dc} $(1-\theta_{SS})$ you can write the value [R_t it is not R_t it is going to be R_t inverse because it is admittance]. R_t is the impedance at infinite frequency, it is going to $Fb_1\, k_{1dc}\, (1-\theta_{SS})$ and that is going to be same as $F\, b_1\, k_{1dc} / k_2 + k_{1dc}$ [and we have seen this before]. k_2 is a constant as I keep increasing voltage k_1 will keep increasing this term will keep decreasing, this term will keep increasing may be little by little that means R_t inverse is going to keep increasing R_t is going to keep decreasing.

As I increase the potential, initially it will decrease a lot after that it may decrease very little because when this (26:35) term becomes very k_{1dc} becomes very large further increase is not going to show up as a much more different value as k_1 is going from small value to medium value you see significant difference. If you go to a large value, you will see slight asymptotic behavior, but it is always going to decrease a little.

k_{1dc} is k_1 value at dc value. If I keep changing the dc potential what will happen to the Rt? (that is what I am looking at now). k_{1dc} is basically k_1 evaluated at E_{dc}. [So there is no Taylor series business here]. When I apply a small amplitude perturbation on top of a dc, [we have derived all this equations at that time] I will get an impedance spectrum which goes like this. This value where this first loop appears to hit the real axis is the charge transfer resistance. And from measured data [I am assuming that we will measure data] we will propose a model, come up with an equation. With this spectrum unless you are lucky it would not fit the spectrum very well at many potentials. If you are getting it at only potential, there is a problem we will come to that later. You should not measure the impedance spectrum at one potential and then propose a model and fit it. That is like taking one data point x and y and fitting it to linear equation A+ Bx, you will get infinite number of solutions. But here because of the way we fit it you might get one solution and you might be happy that I can fit it well this is a solution. [I will give you another solution] we may get one solution because we are not familiar with the process of getting multiple solutions in these cases.

If it is a pair of points x, y and you have to fit to Y=A+B x we know how to get it and we can recognize that it has infinite number of solutions. This case also, later stage I will show you how to find the minimum number of dc points at which you have to acquire impedance spectrum. This case you need to acquire impedance spectrum at least 2 dc potential, but there is a way to get this systematically. This expression is to estimate R_t quickly. You do not have to really go to lot of calculations of course you have to get lot of equations to come up to this level, but once you come to this level to give it to an Excel or MATLAB and guess what the value of R_t is going to be, [not guess calculate the value of R_t is going to be], R_p is going to be. It does not need complex number because the ω will go away. ω goes to infinity once expression goes away ω goes to 0, $j \omega \Gamma$ goes away.

I can use normal equations, meaning no complex numbers, and get the values that helps you get an idea is this parameter value I am guessing here is it going to be reasonable enough to model this spectrum. So, once you derive the expression for impedance you can also get the value for R_t and R_p by simplifying this expression.

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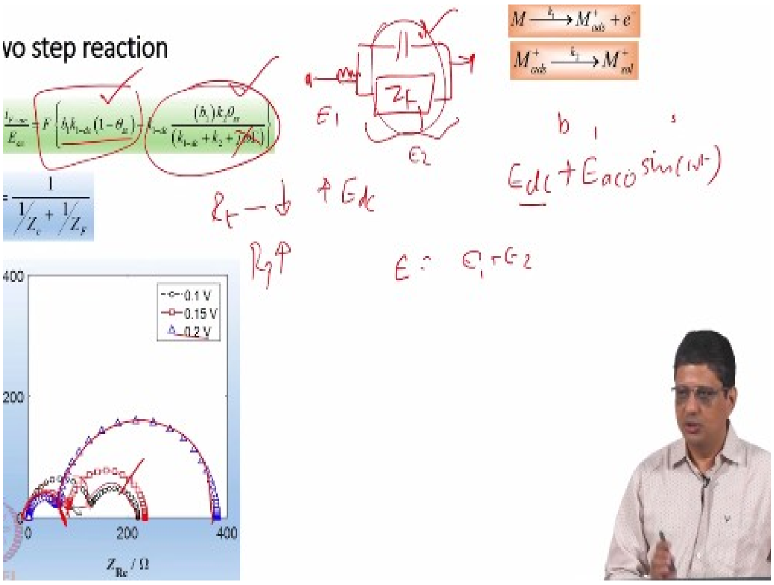

[It does not work that way. what happens is this] say this is solution resistance we measure impedance between these 2 points, correct. We apply a dc potential and on top of it we apply an ac potential which can be written like this (refer video, 30:21). Now if you apply dc potential, how much potential drop occurs here and how much potential drop occurs here? This I call it as E_1 this I call it as $E2$, $E1+E2$ is going to be E. Now what is the impedance on the right side? that depends on ω because capacitance impedance depends on ω, faradaic impedance depends on ω. This offers a variable impedance. a fraction of this potential is dropped here and the remaining fraction is dropped here and that fraction varies with ω just like E_{dc} is divided into 2, E_{ac} is also divided into 2, E_{1ac} and E_{2ac}. E_{ac} that falls here is variable. E_{dc} that falls there is variable. Therefore, I am not evaluating all these across the interface. The faradaic reaction is not seeing same E_{dc} at all times. Each point it sees different E_{dc}. So, the spectrum will get distorted. It is difficult to actually solve it. We know how to solve it, but you cannot derive an expression like this. Here once you derive the expression we may take if you are not familiar you will take 2 hours to solve this, if you are familiar you will solve with this 10 minutes. Write the MATLAB code [once you written the MATLAB code] you click and say at these frequencies I want the impedance spectrum. Within a minute you will get all the impedance values so you can get the plot without any problem. If you want to take the solution resistance into account and do it properly, it will take probably 30 minutes to get one spectrum and if I want optimization, that means I have real data, I want to try various parameters and see which one will fit it. Normally the program will take one parameter fit it, it will not match it will change it see whether the error is becoming worse or better and then it will decide which direction to go how much to go etc. It takes 30 minutes, sometimes few hours to get for one set of parameters. You cannot realistically or practically do optimization there. Although we know that it is not correct to do that many times we end up taking the solution resistance out of this take the real data, [take the solution resistance out], model the remaining system with this method. And at the end say if I add this solution resistance the spectrum [I get the spectrum] I generated assuming solution resistance is negligible plus this solution resistance we will match with actual spectrum to some level. So, there are many approximations to use. One of them is that E_{ac} is very small and sometimes E_{ac} that we apply may or may not be very small. If the noise level is high we will end up applying a little larger E_{ac}.

And yet we still do this because the actual procedure is lot harder, but even this approximation helps us get a very good feel about what happens in the system. See if I give you data and you can get a set of kinetic parameters which can generate the same spectrum you can say this is likely to be the reaction that happens there. If you change the catalyst you want to know which a slower reaction is. This kinetic parameters gives you an idea you get the k_{10} k_2 with various dc potential this what happens k_1 value increases up to this level it is still smaller than k_2 or larger than k_2. If you want to increase the overall reaction, I should do this versus you get a circuit this fits well then what. It gives you better physical insight. If I get loops like this I can tell I need at least one adsorbed intermediate to model this reaction.

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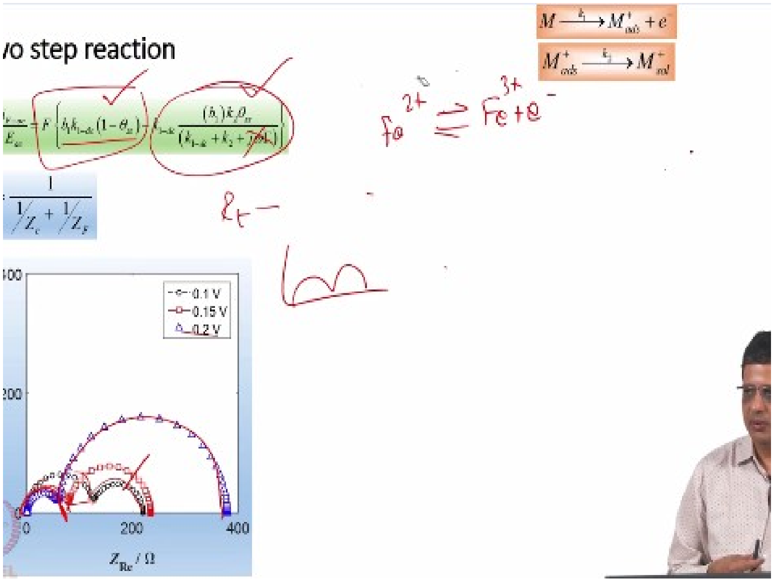

o step reaction

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

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

$\frac{1}{1/Z_c + 1/Z_F}$

$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$

I cannot get this loop like this from the reaction of ferro going to ferri in one step with no intermediate that will give me only this loop. If at all I get the second loop there it is because of mass transfer limitation and of course here we are not taking mass transfer into consideration. If I say I rotate the electrode fast, I rotate the electrode slow, both cases I get the same spectrum which means mass transfer is not playing a role which case if we get 2 loops like this for sure it cannot be modeled by a simple reaction. It has to have this it may need more points, more intermediates, but it will definitely need at least one.

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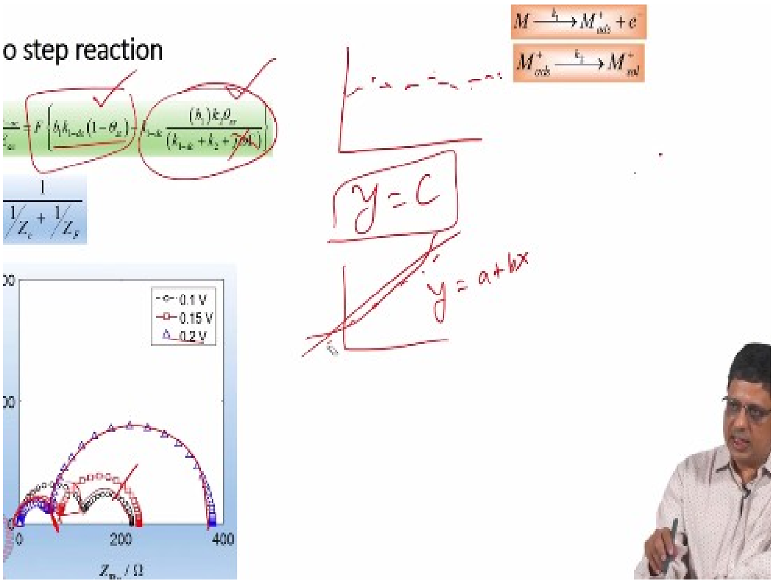


o step reaction

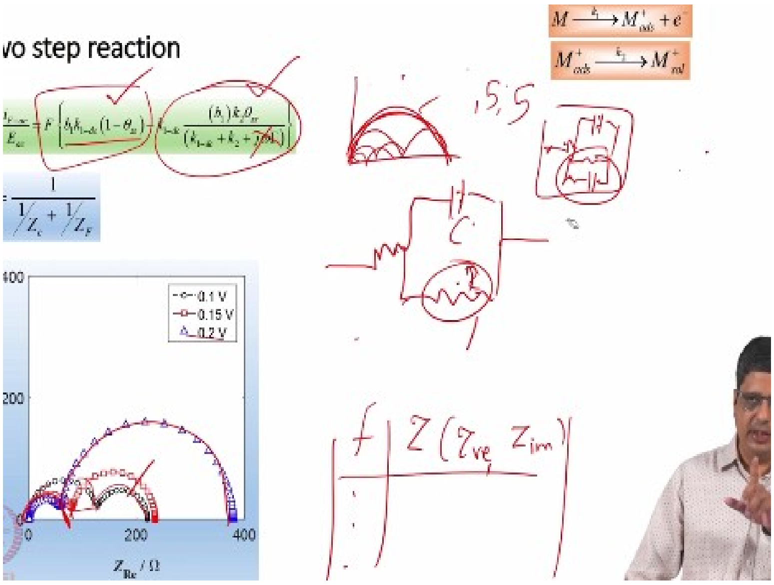
$M \xrightarrow{k_1} M^+_{ads} + e^-$

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

$$\frac{1}{\frac{1}{Z_c} + \frac{1}{Z_F}}$$

It is like this imagine you got data points x, y and you plot it this looks like this (refer video, 35:08). You are going to say y=constant is the model. You plot it, it varies you can tell for sure this model cannot this data of course if it looks little noisy I am assuming that we are having noisy data. You have to say I need at least 2 parameters to models this. You have some data you can try modeling with this if the residues [remaining values], look systematic you can say I need at least one more try [that out].

Likewise, here you can look at the numbers of loop that are visible it is possible that we take data up to some frequency [this is taken up to some frequency]. **(Refer Slide Time: 36:04)**



At one E_{dc} you get like this one semicircle. Another E_{dc} you get like, this another E_{dc} get like this. You have to say, as long as it is coming from the same reaction, same system it needs minimum one intermediates species (36:15). Although the first data looks like a semicircle I can model with a simple system like this. First data if I model with this I will get too much uncertainty here. One system 3 dc potentials I have taken 3 spectrum 3 spectra one of them is modeled by a Randell circuit another one need one more Maxwell element here another one need Maxwell element here. I basically have to use 2 types of electrical circuit to model 3 spectrum. Whereas I need one reaction to model 3 spectrum. Not only that, how many parameters do I need? [Very early in this] when I look at the impedance we looked at it and said if I want RCR I want 3 values from this for only one spectrum right. [We do not even worry about this] we do not even worry about the remaining, we just say one spectrum I need 3 data points minimum. Meaning one frequency I need one impedance, impedance contain real and imaginary or phase and magnitude. This way you need to give me data at minimum of 3 frequencies only then I can extract 3 values from this preferably more we will use reggression and get it. We will usually get [like] 30, 50 from the number of points in one spectrum.

[Of course] if the spectrum if I give 3 points here 1, 2, 3 it is very difficult to get this value with confidence. 3 point I would not get any confidence even if you give me 5 points 1, 2, 3, 4, 5 all of them are here I cannot really tell where this will end up. I cannot tell where this value of R_p is going to be. Generally, if we have wide enough frequency range many number of points your confidence in this will be better. So, I can extract 3 from this if I add this I need one more circuit (refer video, 38:27). [1, 2, 3, 4, 5] In the first spectrum I need 3 second spectrum I need 5 third spectrum I need 5. These element value these element values are going to be different maybe solution resistance is same (we will leave that part out) I need minimum of 2 here even remove the double layer capacitance. I need one point here, this represents faradaic reaction, here 3 points are needed for faradaic reaction one more dc 3 more points are needed.

When you take a multiple dc in the electrical circuit model I need more and more parameters that means I have equations which at one dc I get 3 parameters another dc I get 3 parameters another dc I get one parameter I am fitting one spectrum without fitting the other spectrum simultaneously. I fit one spectrum to this circuit I get this. I will take this model take the data fit it I get one circuit (39:15).

In reaction mechanism we take one reaction we generate all the spectrum at all E_{dc} using one set of parameters. Here the number of parameters may appear to be more.

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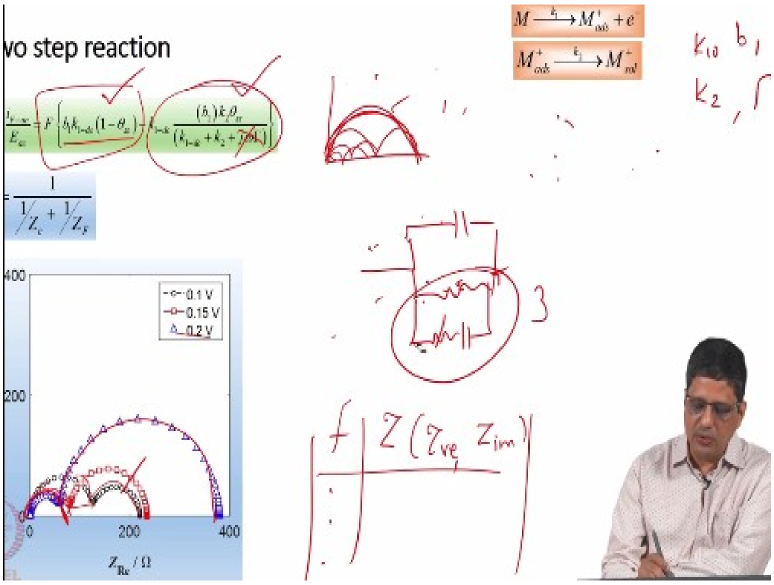

Meaning I have k_{10} b_1 k_2 and Γ right I have 4 parameters here. Somebody who looks at this Maxwell circuit, would say E_{ac} I have 3 parameters in reaction mechanism I have 4 parameters so I have more parameters you can fit it easily. Not true! One dc have 3 parameters another dc you are not going to relate the first resistance to the second resistance. It is just 3 more parameters. Whenever you keep adding more and more dc potential or dc current in case of galvanostaticstatic method, you are actually using more and more of parameters here in the electrical equivalent circuit. Kinetics, you make start with certain number of parameters you are not going to increase a number of parameters for that reaction.

Sometimes we will use 20 parameters in a kinetic model to model spectrum in 5 different dc potential, 6 different dc potential.

Maxwell circuit each one of them I might use 5 elements. If I use 5 elements and 6 potentials I am actually using 30 variables and yet I would not get physical inside. We will stop here today. Tomorrow I want to continue with another reaction which is a slightly different reaction still has one intermediate species, but something that can give rise to a capacitive loop at one potential inductive loop at another potential.

You go to circuit you have to say I want to model this with capacitor I have to model this inductor or a capacitor with negative value, but multiple types of patterns can arise one kinetic we will see that tomorrow.