Electrochemical Impedance Spectroscopy
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Lecture – 24
Two Step Reaction with an Intermediate - III

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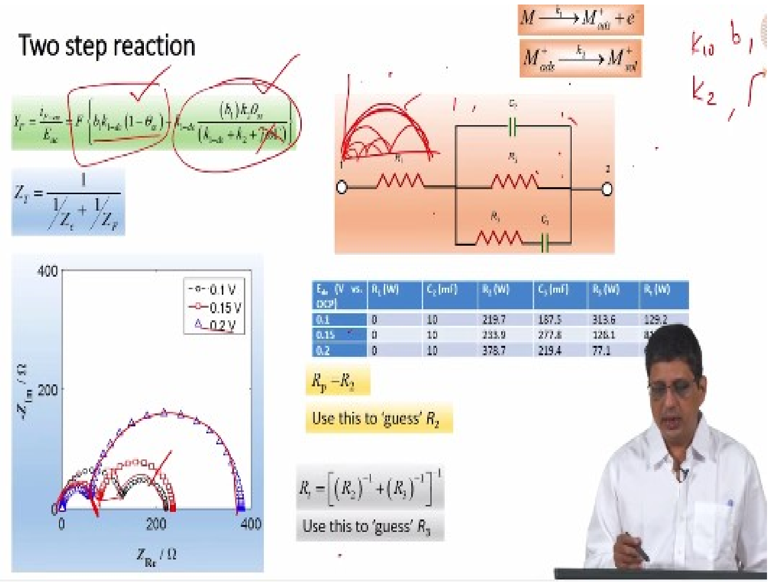

Two step reaction

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

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

k10, b1,
k2, Γ

$Y_F = \frac{\tilde{i}_{F-ac}}{\tilde{E}_{ac}} = F\left\{ b_1 k_{1-dc}(1-\theta_{ss}) - k_{1-dc}\frac{(b_1)k_2\theta_{ss}}{(k_{1-dc}+k_2+j\omega\Gamma)}\right\}$

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

E_{dc} (V vs. OCP)	R_1 (W)	C_2 (mF)	R_2 (W)	C_3 (mF)	R_3 (W)	R_t (W)
0.1	0	10	219.7	187.5	313.6	129.2
0.15	0	10	233.9	277.8	126.1	[illegible]
0.2	0	10	378.7	219.4	77.1	[illegible]

$R_p - R_1$

Use this to 'guess' R_2

$R_t = \left[(R_2)^{-1} + (R_3)^{-1}\right]^{-1}$

Use this to 'guess' R_3

In the last class we saw an example of a reaction two step reaction which is Metal going to Metal^{+} adsorbed and then Metal^{+} adsorbed going into the solution and then derived the expression for the impedance for this reaction.

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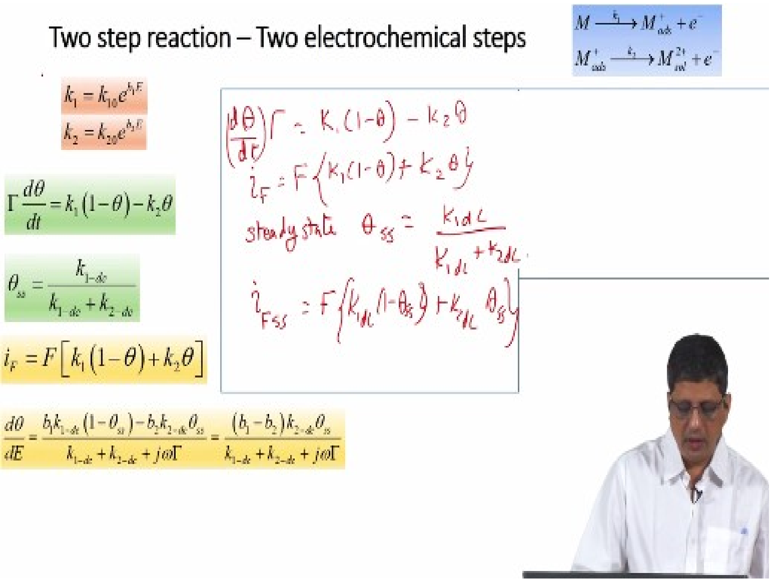

Two step reaction – Two electrochemical steps

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

$k_2 = k_{20}e^{b_2E}$

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

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$

$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

$\frac{d\theta}{dE} = \frac{b_1k_{1-dc}(1-\theta_{ss}) - b_2k_{2-dc}\theta_{ss}}{k_{1-dc}+k_{2-dc}+j\omega\Gamma} = \frac{(b_1-b_2)k_{2-dc}\theta_{ss}}{k_{1-dc}+k_{2-dc}+j\omega\Gamma}$

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

$i_F = F\{k_1(1-\theta) + k_2\theta\}$

steady state $\theta_{ss} = \frac{k_{1dc}}{k_{1dc}+k_{2dc}}$

$i_{Fss} = F\{k_{1dc}(1-\theta_{ss}) + k_{2dc}\theta_{ss}\}$

What I want to do today is to take a similar reaction and I would like you to try getting the impedance expression for this [I will guide you through the steps]. The first step is same as what you saw in the last example, [which is] M going to M^+ adsorbed [i.e., metal losing an electron and it becomes an ion]. Second, [that] ion losses one more electron and goes out. The first step is [also] a faradaic reaction, second step is also a faradaic reaction. Now, if you write the mass balance equation for this, it is going to look similar to the equation you wrote yesterday. You have to recognize that k_1 depends on potential, k_2 also depends on potential [because both of them involve electron transfer right]. In the previous example we would write k_1 as k_10 exp(b_1E). [Previous example] k_2 was a constant, [but] in this case it is going to be similar dependence, exponential dependence (and) b_2 may or may not be equal to b_1. [Now] if I say that 'θ' is the fractional surface coverage for M^+ adsorbed. I can say $\Gamma(d\theta/dt)$. First step it is going to be $k1(1-\theta)$, second step is going to be $k_2\theta$. The expression will look similar to what you got before except that k_2 is a function of potential [now previously k_2 was a constant].

If I want to write the expression for the faradaic current what should I do? How many moles of electrons do I get from the first term? So many moles per square centimeter per unit times multiply by Faraday constant I will get the current [current density actually] (refer video, 02:25). Now the second step that also gives us an electron. I should write the faradaic current as coming from the first step as well as the second step.

[Now] can you find the steady state θ value? If we apply only a dc potential we can set the mass balance equation to zero and rearrange. We are looking at a slightly different equation where the second step also involves transfer of electron. In the first step metal loses an electron, but it still sits on the top of the surface. So, it is M adsorbed [M+ adsorbed]. The second step it loses one more electron and goes into the solution. [it maybe] like Cu becoming Cu^+ it is still on surface, Cu^+ becoming Cu^{2+} and going into the solution. In this case k_2 depends on potential, it contributes to the current [the second step contributes to the current], therefore the mass balance equation will look similar. [Because previously also we would have written $k1(1-\theta)$- $k_2\theta$ as Γ $d\theta/dt$, but there k_2 was a constant, now k_2 is a function of potential].

Faradaic current of course has one more term now and both are additives. The first step produces an electron; second step produces an electron. I can get the expression for 'θ_{SS}', it looks similar, but k_2 value will keep changing with potential [previously k_1 value was changing, but k_2 was not changing in this example k_2 will keep changing]. You can write the expression for faradaic current under steady state condition [it is pretty straight forward].

[All that we need to say is that] recognize that potential is E_{dc}, k_1 is k_{1dc}, k_2 is k_{2dc} (and) θ is θ_{SS} here. [Now what I would like you to do is to] derive the expression for the faradaic current when you apply an ac along with the dc. [I had done this before for a slightly simpler case] let us do it now for case where second step also contributing to the faradaic current.

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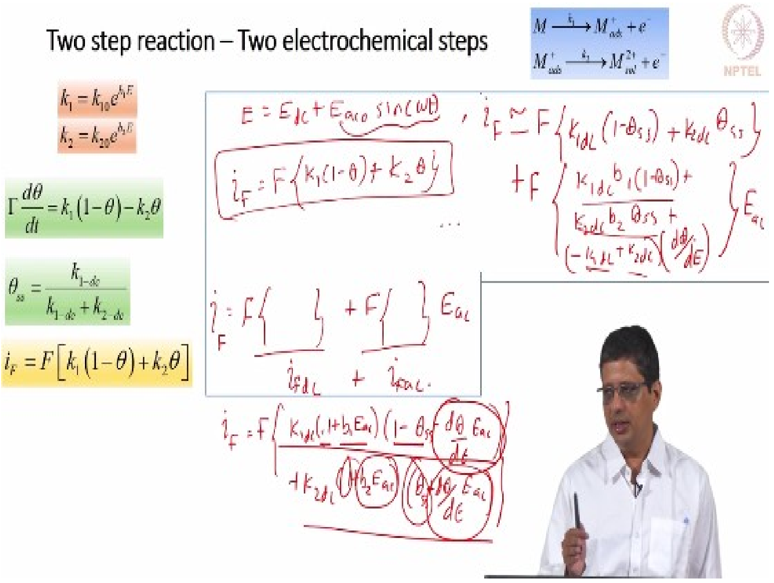

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$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{2-dc}}$

$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$

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

$\boxed{i_F = F\{k_1(1-\theta)+k_2\theta\}}$

$$i_F \simeq F\{k_{1dc}(1-\theta_{ss}) + k_{2dc}\theta_{ss}\} + F\left\{k_{1dc}b_1(1-\theta_{ss}) + k_{2dc}b_2\theta_{ss} + (-k_{1dc}+k_{2dc})\left(\frac{d\theta}{dE}\right)\right\}E_{ac}$$

$$i_F = \underbrace{F\{\quad\}}_{i_{Fdc}} + \underbrace{F\{\quad\}E_{ac}}_{i_{Fac}}$$

$$i_F = F\left\{k_{1dc}(1+b_1E_{ac})\left(1-\theta_{ss}-\frac{d\theta}{dE}E_{ac}\right) + k_{2dc}(1+b_2E_{ac})\left(\theta_{ss}+\frac{d\theta}{dE}E_{ac}\right)\right\}$$

[I am going to say] the potential is dc + ac_0 sin (ωt) and I will use certain approximation. k_{1dc} multiplied by (refer video, 06:00), likewise k_{2dc} multiplied by E_{ac}, where E_{ac} is the time dependent function here. What this means is, [we look at] k_1 is a function of potential. We write it as E_{dc}+ E_{ac} (and) we expand the $\exp(b_1E_{ac})$ in Taylor series, we truncate it [we go through few steps and then come to this approximation].

[Since we are going to do this frequently you should be able to write under small E_{ac} value] under small amplitude perturbation we can make this approximations (neglect the higher order terms). Whenever case are dependent on potential [exponential depended on potential] you should be able to write this. We expand θ in Taylor series around the dc, and approximate this again after truncating the second and higher order terms.

We just keep the first order term and leave the remaining. if I can approximate k_1, k_2 and θ, I can substitute here (refer video, 07:15) and I would get an expression for the faradaic current. I would write all the constant terms (separately) [constant meaning is not depend on E_{ac}], constant term would come here and all the term with first order E_{ac} would come here and then second order and higher order I will neglect them.

I would write this as i_{dc} + i_{ac} for the faradaic current (refer video, 07:51). what I would like you to do is first group this. We still have to find what ($d\theta/dE$) is here. I have not given that yet and that is not going to be the same as what you got in the previous class. All that I need to do is substitute for k_1, θ, k_2. I am going to get 4 terms from the first expression, 4 terms from the second expression, and we neglect E_{ac}^2. I would get effectively 3 terms from there (refer video, 09:06), first expression here, and 3 terms from the second expression here, second expression is this first expression is underlined here. Out of that the first term is going to be constant. Likewise here the first term is going to be constant. please write that and group it so you can guess or you can verify that the constant term will become the steady state condition. If you put k_{1dc}, θ_{SS}, and when you get all this product sorted out and rearranged the first term corresponding to this will become F (k_{1dc} ($1-\theta_{SS}$)+ k_{2dc} θ_{SS}), and that is going to be the i_{dc} for the faradaic current. The second and third term of the first part and the second and third term for the second part will give you something like this which is E_{ac} and then the fourth term we are going to throw it anyway (10:04).

The second term is (refer video, 10:06) so I get 4 in the first, 4 in the second out of which the fourth term is we are going to throw it away. First term is going to go towards that constant, mid 2 terms are going to come as the first order term. And you got mid 2 terms for the first expression mid 2 terms for the second expression. So, we get four terms within the E_{ac}, 1, 2, 3 and 4 for E_{ac}. [When you may not get it exactly in this form maybe in a slightly different form, but it should be equal to this]. In order to do this, you should be able to expand in Taylor series truncate, rearrange and do the algebra correctly. [If you have done with this then] I would like you to get the expression for $d\theta/dE$ by taking the mass balance equation expanding each term in Taylor series, truncate after the first term [first order] and rearrange. Now, the faradaic current is written in term of i_{dc} and i_{ac}.

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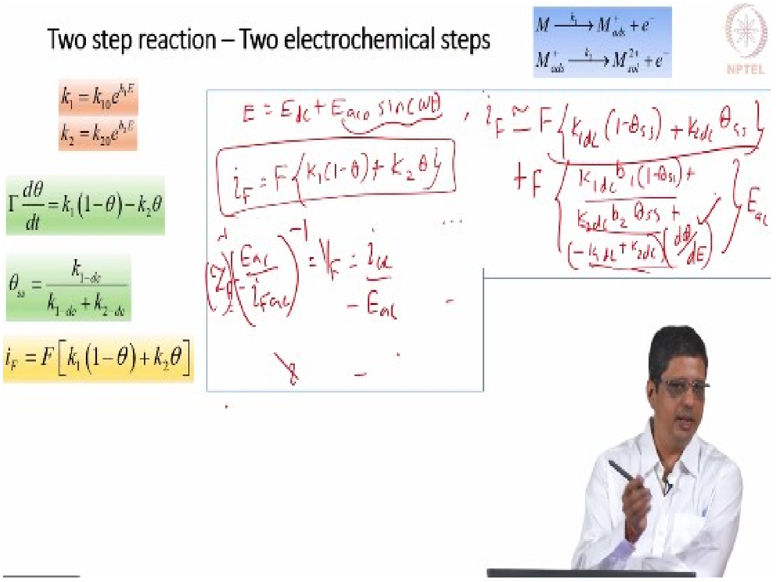
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$\boxed{i_F = F\{k_1(1-\theta) + k_2\theta\}}$

$i_F \simeq F\{k_{1dc}(1-\theta_{ss}) + k_{2dc}\theta_{ss}\} + F\{k_{1dc}b_1(1-\theta_{ss}) + k_{2dc}b_2\theta_{ss} + (-k_{1dc} + k_{2dc})(\frac{d\theta}{dE})\}E_{ac}$

$Z_F = \left(\frac{E_{ac}}{i_{Fac}}\right)^{-1} = Y_F = \frac{i_{ac}}{E_{ac}}$

If I want the impedance I should write it as E

If I want the impedance I should write it as E_{ac}/i_{Fac} for the faradaic impedance, or I can write the admittance as i_{ac}/E_{ac}. This as i_{dc} and i_{ac} (refer video, 12:35). It is easy to write i_{ac}/E_{ac}. This term here is the faradaic admittance. As long as I can get this dθ/dE correctly, I have an expression for the faradaic admittance, which means I can get the faradaic impedance, therefore, the total impedance.

For this reaction if you give me the parameter values of k_10, k_20, b_1, b_2, and Γ at any frequency, I should be able to tell you the total impedance of this system. [of course] you should also give me the double layer capacitance value. Mechanistic analysis basically requires that you will be able to write the impedance for a given reaction. That is the first step. Next is try various values of k_10, k_20 etcetera, and see if that result can match with the observed impedance. Not just that you are not going to only match the impedance, you can also measure the dc current as a function of dc potential. You can go to dc potential, measure the current, and go to another potential measure the current. Usually it is done at a slow rate. It is almost like we are measuring it waiting for some time and going to the next level, measuring waiting for some time and then going to the next level. Although most of the time people go at the rate of 1 mV/s or 0.1 mV/s, depending on how fast or how slow the reaction is. You would get an expression for i_{Fdc} which should match with the observed dc polarization current. In addition, the impedance taken at multiple dc potential should match with whatever you are predicting here.

In the electrical circuit analogy [what we did just] take the impedance and see if we can model that with another circuit, but we never worried about what is the dc current. There is a difference between taking the dc current and taking the impedance at zero frequency.

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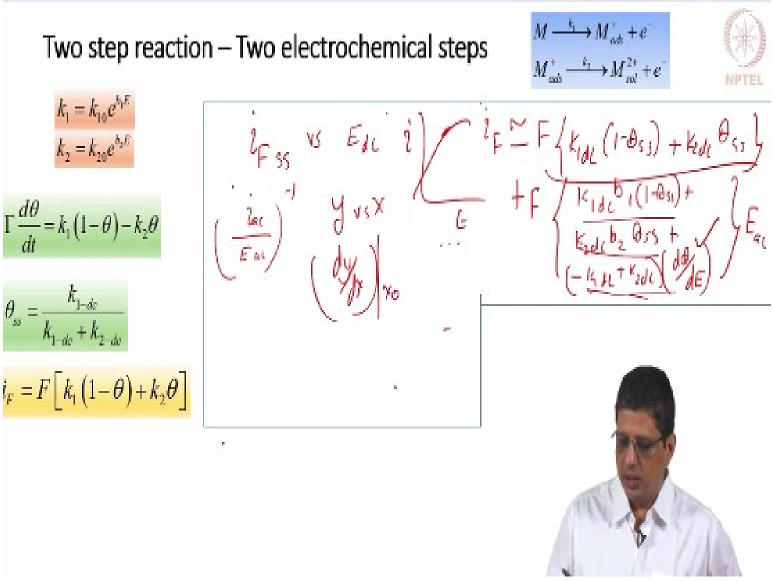

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$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$

$i_{F\,ss}$ vs E_{dc}

$\left(\frac{i_{ac}}{E_{ac}}\right)^{-1}$

y vs x

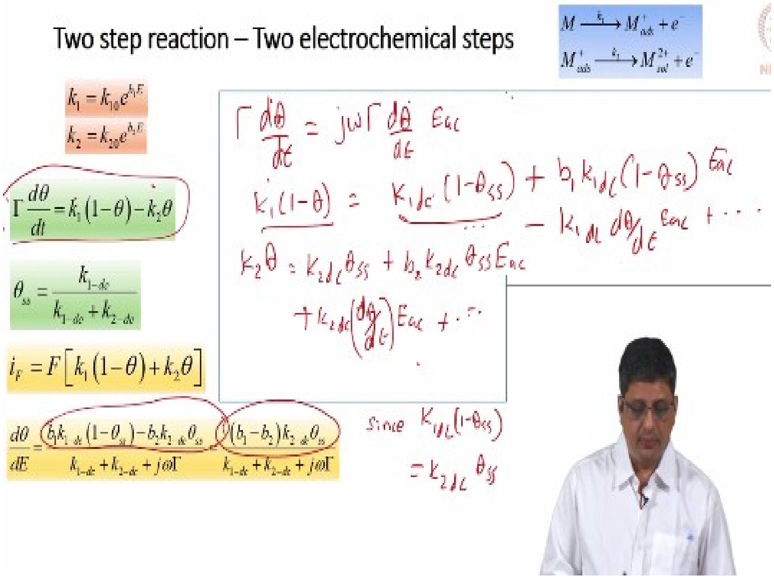
$\left(\frac{dy}{dx}\right)\Big|_{x_0}$

$$i_F \simeq F\left\{k_{1dc}(1-\theta_{ss}) + k_{2dc}\theta_{ss}\right\} + F\left\{k_{1dc}b_1(1-\theta_{ss}) + k_{2dc}b_2\theta_{ss} + (-k_{1dc}+k_{2dc})\left(\frac{d\theta}{dE}\right)\right\}E_{ac}$$

This is dc current (14:40). We will get dc current as a function of E_{dc} current [or current density to be precise]. Total current in the system when we say solution resistance is not significant, and dc capacitance is not going to allow any current to go through, total current is going to be same as the faradaic current. Now faradaic impedance on the other hand [faradaic admittance is i_{ac}/E_{ac} faradaic impedance is inverse of that] is going to be slope even at zero frequency it is going to be equal to slope of that (refer video, 15:28). It is like saying, dy/dx at some point x, x_0 or some point in a y versus x plot. I have an expression for faradaic impedance, I have an expression for faradaic current i_{ac}. i_{ac} at $\omega=0$ is not the same as i_{dc}. $\omega=0$ or ω tending towards 0 means you are still changing the potential very slowly and monitoring the changing current. You change the potential little faster and monitor the change in current or change the potential little slowly monitor the change in change. Then I can go asymptotically and say when I change it extremely slowly this is how much the current will change. It still telling you the value of change in current not the actual current. In the electrical circuit model we never use the dc data.

Here [I do not know whether everybody does], but we should fit both the polarization data and the impedance data using one kinetic expression. We will come to that point again later when we compare different methods. Right now I would like you to get the value for dθ/dE by taking the mass balance equation. When you take the mass balance equation and expand in Taylor series [in the last example we would have said k_2 is a constant, now I cannot do that here].

(Refer Slide Time: 17:20)



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$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$

$$\frac{d\theta}{dE} = \frac{b_1k_{1-dc}(1-\theta_{ss}) - b_2k_{2-dc}\theta_{ss}}{k_{1-dc}+k_{2-dc}+j\omega\Gamma} = \frac{(b_1-b_2)k_{2-dc}\theta_{ss}}{k_{1-dc}+k_{2-dc}+j\omega\Gamma}$$

$$\Gamma \frac{d\theta}{dt} = j\omega\Gamma \frac{d\theta}{dE} E_{ac}$$

$$k_1(1-\theta) = k_{1dc}(1-\theta_{ss}) + b_1k_{1dc}(1-\theta_{ss})E_{ac} - k_{1dc}\,d\theta/dE\,E_{ac} + \cdots$$

$$k_2\theta = k_{2dc}\theta_{ss} + b_2k_{2dc}\theta_{ss}E_{ac} + k_{2dc}\left(\frac{d\theta}{dE}\right)E_{ac} + \cdots$$

Since $k_{1dc}(1-\theta_{ss}) = k_{2dc}\theta_{ss}$

I will have to take this expression and say Γ (dθ/dt) = jωΓ*(dθ/dE)*E_{ac}. You should become familiar with the practice so that you would know dθ/dt can be written as (dθ/dE)*(dE/dt). (dE/dt) is going to give you jω E_{ac}. This is the first part. The second part k_1 (1-θ) is going to give me k_{1dc} (1-θ_{SS}). I am going to get k_1 as k_{1dc} multiplied by 1+b_1E_{ac}, θ I am going to write it as θ_{SS} + (dθ/dE)*E_{ac}. I am going to get 4 terms out of this, first term is a constant second and third term will be a function of E_{ac}, the fourth term is going to be E_{ac}^2 multiplied by some factors, I am going to neglect the higher order terms, therefore, I will get 3 terms out of this (refer video, 19:05).

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The moment you give me this equation and tell k_1 and k_2 are depended on potential, I can tell right away that numerator is going to be $b_1k_{1dc}(1-\theta_{SS})$- $b_2k_{2dc}\theta_{SS}$; k_1 is multiplying the θ, k_2 is multiplying the θ with a negative sign therefore, I am going to say that the denominator is k_{1dc}+ k_{2dc}+ jωΓ. I would take the factor here (20:00), and I know that is going to come in the numerator the constant terms will cancel out each other because of steady state conditions, E_{ac}^2 terms, I am going to neglect them.

(refer video, 20:48) [I can definitely tell this is going to give me b_1 k_1, this is going to give me b_2 k_2, all the first order terms with respect to θ will be rearranged and brought to the left side, and then brought down that is going to give me -k_1 would become +k_1 here, –k_2 will become +k_2 when it goes to the left side, but this comes after trying many of these types of reactions].

And if you have second order reaction you can still write the expressions but it becomes a little more complex. You should get familiar with that by practice. Now I can do this for one intermediate species. When it has multiple intermediate species, I will have to write the equation put it in matrix form and then invert them. [I think] writing the faradaic current you can do it without any difficulty. Given a mechanism you can write a faradaic current. Given a mechanism you can write the mass balance equation [it should not be too difficult], that is write this expression (refer video, 22:06), and write this expression expand the faradaic current in Taylor series and truncate it. The main trick is to find dθ/dE using the mass balance equation, whether it is one species or many species, you need to get the dθ/dE. That is, if I give a potential [sinusoidal potential] how will the surface coverage value change. In a very simple reaction when you do not have any intermediate species, whenever I give a potential, rate constant also goes up and comes down, current also goes up and comes down. It is in-sync with the potential for the faradaic reaction.

In these cases (with reactions with intermediates), you would find that it is not going to be in-sync. The surface coverage value when the potential changes like this [for me it is going from time t=0 to larger values], goes like this (refer video, 23:07). Surface coverage value will oscillate, but it will be not be in phase with potential. Current will also oscillate and by and large, it will not be in phase with this. That is why you get a capacitance, resistance, and another Maxwell element there. If it is going to be in phase you will get only a resistor. If dθ/dE is a constant, constant meaning, if it is independent of ω, you will get simple resistance. When ω is 0 or ∞, dθ/dE is going to be constant. When ω tends to ∞, dθ/dE is going to be 0. When ω is 0, it is not going to be necessarily 0 but it depends on the parameter values [but it is going to be a fix number]. When ω tends to 0, at very low frequency it will look like a resistor.

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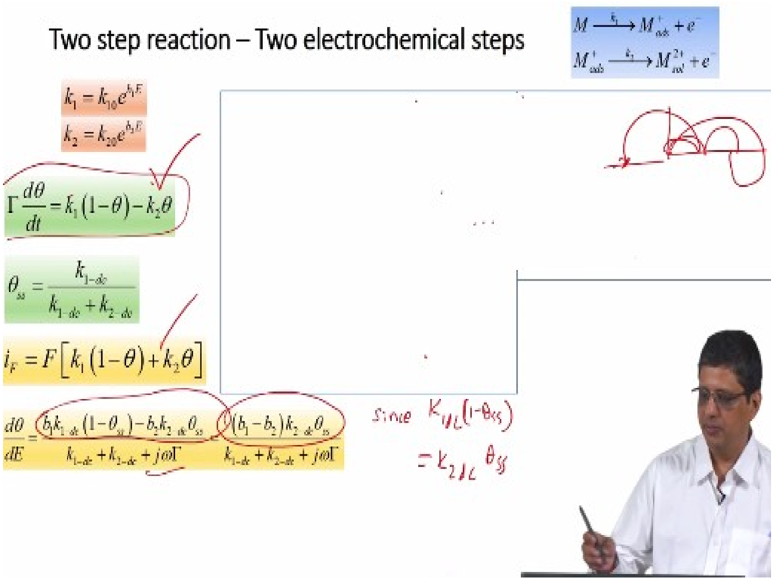

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$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

$\frac{d\theta}{dE} = \frac{b_1 k_{1-dc}(1-\theta_{ss}) - b_2 k_{2-dc}\theta_{ss}}{k_{1-dc} + k_{2-dc} + j\omega\Gamma} = \frac{(b_1 - b_2) k_{2-dc}\theta_{ss}}{k_{1-dc} + k_{2-dc} + j\omega\Gamma}$

since $K_{1dc}(1-\theta_{ss})$

$= k_{2dc}\,\theta_{ss}$

That is why whether it is this, whether it is this it always settles at the real axis (refer video, 24:07). It can even settle at this axis, but it has to settle at a real value it may or may not be a positive value, but anywhere else at intermediate frequencies it is not going to be a constant, it is going to vary with ω and this tell us how it is going to vary with ω. It gives us a proper expression for that.

[I can simplify it a little bit saying the dc expression for this mass balance equation it tells k_{1dc} (1-θ) that is going to be=k_{2dc} θ, therefore it becomes little simpler].

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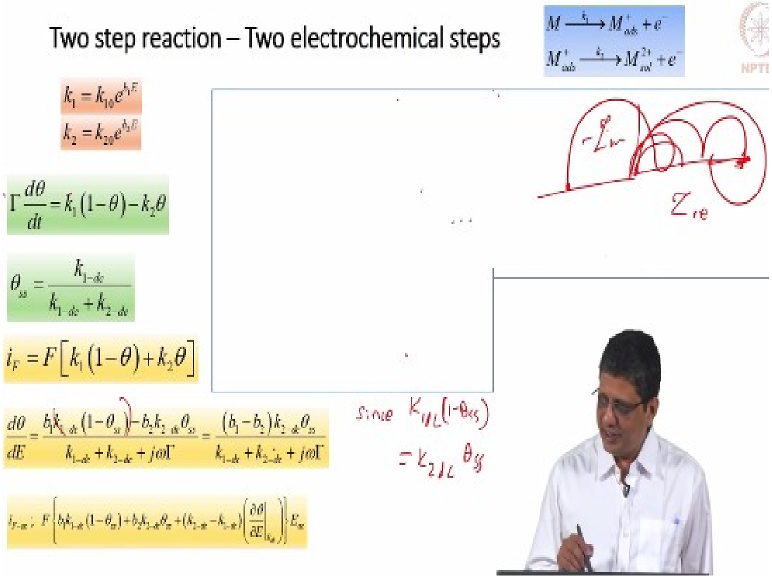

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$i_{F-ac} = F\left\{b_1 k_{1-dc}(1-\theta_{ss}) + b_2 k_{2-dc}\theta_{ss} + (k_{2-dc} - k_{1-dc})\left(\frac{\partial\theta}{\partial E}\bigg|_{E_{ss}}\right)\right\} E_{ac}$

since $K_{1dc}(1-\theta_{ss})$

$= k_{2dc}\,\theta_{ss}$

[(refer video, 25:42) Z_{real} *vs.* $Z_{imaginary}$ it is called Nyquist plot or complex plane plot, where you have impedance going like this, impedance going like this, impedance going like this, impedance going like this. And it starts at high frequency ends up at low frequency and my point was that it is going to end up on the real axis. As long as we keep our assumption that it is not mass transfer limited, solution resistance would not make any changes in this conclusion].

As long as it is limited by kinetics, if you go to low in a frequency it will settle at a point on the real axis [that is not for the θ]. If you go to low in a frequency, dθ/dE will be a constant, it does not mean θ is going to be a constant. When it goes to infinite frequency, θ will be a constant because dθ/dE is going to be 0. Now that we have an expression for dθ/dE. iF$_{ac}$, we can write it in terms of dθ/dE and we can substitute for that.

Look at the first term and the second term, they are independent of ω. Third term has dθ/dE and when ω tends to infinity, dθ/dE is going to 0.

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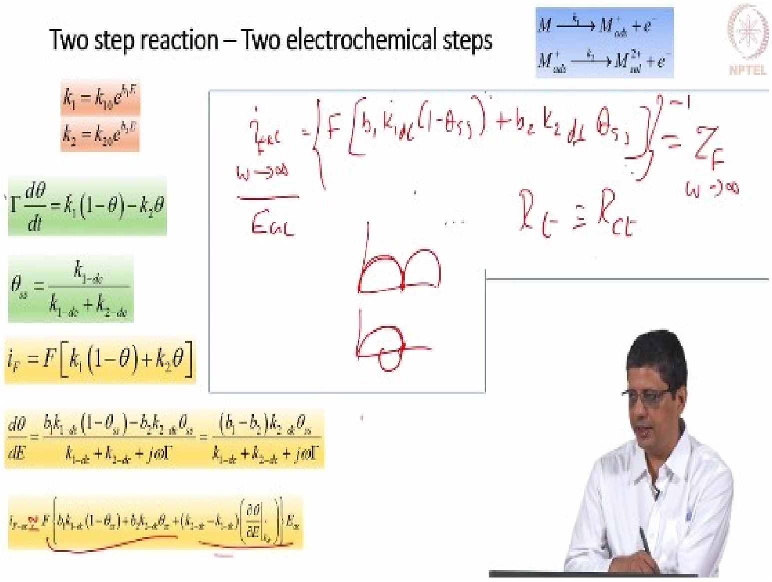

Two step reaction – Two electrochemical steps

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

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

$k_1 = k_{10} e^{b_1 E}$

$k_2 = k_{20} e^{b_2 E}$

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

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc} + k_{2-dc}}$

$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

$\frac{d\theta}{dE} = \frac{b_1 k_{1-dc}(1-\theta_{ss}) - b_2 k_{2-dc}\theta_{ss}}{k_{1-dc} + k_{2-dc} + j\omega\Gamma} = \frac{(b_1 - b_2) k_{2-dc}\theta_{ss}}{k_{1-dc} + k_{2-dc} + j\omega\Gamma}$

$i_{F-ac} \overset{\sim}{=} F\left\{\underbrace{b_1 k_{1-dc}(1-\theta_{ss}) + b_2 k_{2-dc}\theta_{ss}} + \underbrace{(k_{2-dc} - k_{1-dc})\left(\frac{\partial\theta}{\partial E}\Big|_{ss}\right)}\right\} E_{ac}$

$\frac{i_{Fac}\big|_{\omega\to\infty}}{E_{ac}} = \left\{F\left[b_1 k_{1dc}(1-\theta_{ss}) + b_2 k_{2dc}\theta_{ss}\right]\right\}^{-1} = Z_{F\,\omega\to\infty}$

$R_t \equiv R_{ct}$

That means when ω tends to infinity, this expression will remain this will go towards 0. That means, i_{Fac} under the condition ω tends to infinity, is going to be F b_1 k_{1dc} $(1-\theta_{SS})$ + b_2 k_{2dc} θ_{SS} multiplied by E_{ac}. Therefore, I can write this is going to be the admittance when ω tends to infinity [divided by E_{ac} I will get the admittance]. That means inverse of this value is going to be the impedance, when ω tends to infinity and that is called charge transfer assistance written as R_t or R_{ct}.

When you see complex plane plots like this (27:46), usually although sometimes it is possible for 2 capacitance loop to merge together, but I am going to assume that these are well separated loops. The point where it fix the real axis first is going to be the charge transfer resistance. I can estimate the charge transfer resistance with this, this part tells the value when ω is not tending towards infinity. We can substitute for dθ/dE and write the expression here.

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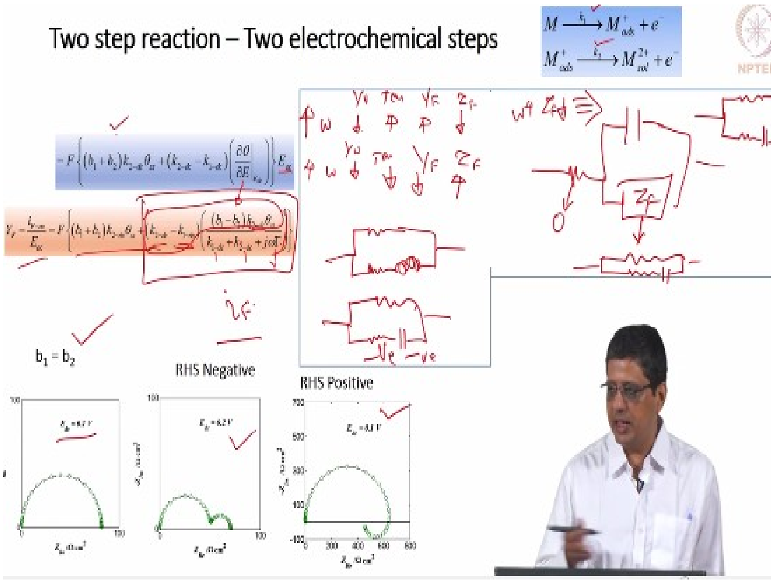

Two step reaction – Two electrochemical steps

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

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

$$-F\left\{(b_1+b_2)k_{2\text{-}dc}\theta_{ss}+(k_{2\text{-}dc}-k_{1\text{-}dc})\left(\frac{\partial\theta}{\partial E}\right)_{E_{dc}}\right\}E_{ac}$$

$$Y_F=\frac{i_{F\text{-}ac}}{E_{ac}}=-F\left\{(b_1+b_2)k_{2\text{-}dc}\theta_{ss}+(k_{2\text{-}dc}-k_{1\text{-}dc})\left(\frac{(b_1-b_2)k_{2\text{-}dc}\theta_{ss}}{k_{1\text{-}dc}+k_{2\text{-}dc}+j\omega\Gamma}\right)\right\}$$

$b_1 = b_2$

RHS Negative

RHS Positive

I brought it from the previous page and I have substituted for dθ/dE and rearranged it (28:25). All that I have done is, this expression is brought from the previous page, this is a substitution for dθ/dE and bring the E_{ac} to the denominator here, and I get faradaic admittance. Now if $b_1=b_2$, [in this case I can tell the first step and the second step as such that $b_1=b_2$ for particular example particular], then this term (b_1-b_2) will go to zero. Therefore, dθ/dE will go to zero when $b_1=b_2$ in this type of reaction. When $b_1=b_2$, faradaic impedance is going to be independent of frequency. Therefore, for a set of parameters [I have chosen some parameters and simulated this impedance], if we say $b_1=b_2$ and take the impedance, it is going to show me a semicircle. I can go to different dc potential I will always get a semicircle. Because this entire business of faradaic impedance can be modeled using a resistor and this (solution resistance) of course [we are saying it] is zero. Therefore, the circuit is going to be a capacitor and parallel with resistor, and that is going to just give me semicircle. High frequency limit is going to be 0, and low frequency limit is going to be whatever that fixed number is. This right hand side when I say RHS here I mean $(k_{2dc}- k_{1dc})$ multiplied by everything in the bracket which is $(b_1-b_2)k_{2dc}\theta_{SS}/ k_{1dc}+ k_{2dc}+ j\omega\,\Gamma$.

Now b_1 may be or may not be$>b_2$, that we are not making any assumption. We are just saying the entire term that is negative, meaning leave alone the ‘jω’ part and look at the other part. If $b_1>b_2$, but k_2 is$< k_1$, [or I should probably say more precisely the numerator there is negative or numerator there is positive]. Denominator k_1 is going to be positive, k_2 is going to be positive this number (Γ) is going to be positive and this ($j\omega$) is anyway complex number.

I want you to argue and get this. When ω increases, $1/\omega$ will decrease. If this is negative in the numerator, the term will increase in terms of the actual value not the magnitude (31:12). If this term increases, what happens to the faradaic impedance? Faradaic admittance will increase and faradaic impedance will decrease. When ω increases, impedance decreases. That means it is going to look like a circuit with capacitor in it. The faradaic impedance in this case is going to be represented by a resistor in parallel with a resistor-capacitor. It is one Maxwell element. Using similar arguments, you can say, if the right hand side numerator is positive, ω increases, $1/\omega$ will decrease. This term here will also decrease, because it is a positive term. That means faradaic admittance will decrease, faradaic impedance will increase. You can model that with an inductor like (32:24) this or you can model it with this (capacitor) allowing for negative values for the elements there [after all they are equal]. Same set of parameters I have chosen. I have just taken 2 different potentials so this is completely different set. I use some parameters, synthesize this data or simulated this data.

I use another set of parameters. I have gone to 1 dc and another dc. When I change the dc value, k_{1dc} and k_{2dc} will change, b_1 and b_2 are not going to change, Γ is not going to change. Same system I can super impose ac on top of 0.1 V dc with respect to equilibrium or 0.2 V with respect to equilibrium. I will get quite different spectrum and yet I do not have to use different circuits. I can just use one reaction and model this.

Not only that I can also predict the dc current at these 2 potentials and any other potentials also, and compare with what the experiment shows.

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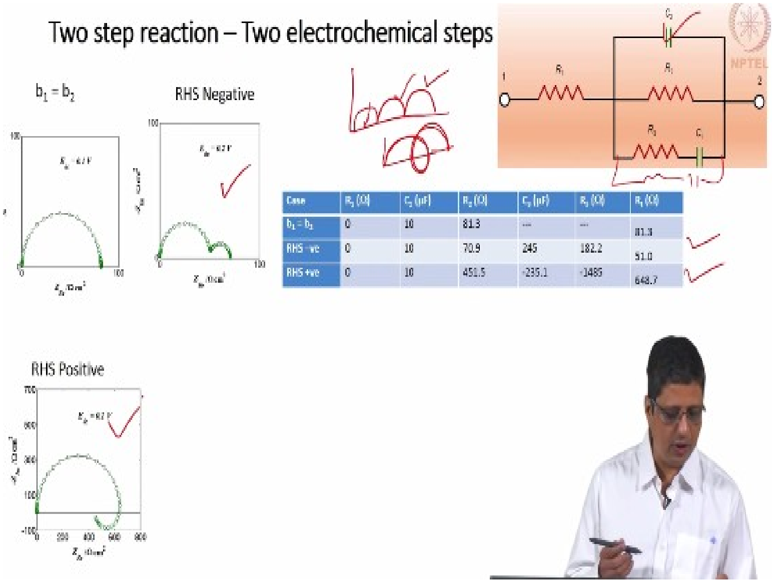

Case	R_1 (Ω)	C_2 (µF)	R_2 (Ω)	C_1 (µF)	R_3 (Ω)	R_t (Ω)
$b_1 = b_2$	0	10	81.3	---	---	81.3
RHS -ve	0	10	70.9	245	182.2	51.0
RHS +ve	0	10	451.5	-235.1	-1485	648.7

(33:49) This two-step reaction, you can model this [I don't know if the circuit is there] you can model it with the same circuit as what you have seen for the previous reaction except that I have moved the solution resistance to be 0 here, the double layer capacitance could be 10 µF cm^{-2}. What you also notice is that, if you have one adsorbed intermediate you get one Maxwell element. It does not matter whether the first and second reactions are charge transfer, or only the first reaction is faradaic reaction second reaction is not; it does not matter as long as we assume that there is no other complexity involved, that there is no film on top of this, there is no mass transfer limitation etcetera. Normally the number of adsorbed intermediate will tell you the number of Maxwell element.

It is possible to get very complex set of reactions where some of the reactions are not linearly independent there is a specific way to get this. That is if you write 3, 4 steps together you might be able to generate the fifth step, in which case it is not really separate step. Those cases you may get fewer number of loops. Generally, for the simple reactions that we look even the reactions we are seeing now few more reactions you can add all those things.

If you see actual data showing 1, 2, 3 loops, I am going to claim this (first) loop is coming from the double layer and 2 more loops are present, therefore I need 2 Maxwell elements, that means I need 2 intermediate species. The loop may look like this also (35:28). This is one loop, this is inductive loop, and this is another loop. It does not matter whether it is inductive or capacitance. [I would actually give it you as a homework, where I will give you the kinetic parameter. I would ask you to generate these 2 graphs. I want you to convince yourself that it is possible to get an inductive loop and the capacitive loop from the same system. It does not mean something is special about inductive loop or special about capacitive loop. It is just the values can be on the positive side negative side when you rearrange them]. These values can be positive or negative depending on the potentials. That means it can give you inductive loop or capacitive loop. Many times people try to come up with some sophisticated argument for inductive loop. You do not see that frequently, you do see it occasionally. You see capacitive loop more often, but inductive loop is not necessarily any more special than a capacitive loop. You can get the inductive loop here it does not mean you have magnetism in the system. It is just that this spectrum that is generated by this reaction can also be generated by a circuit with inductance. That is all it means. Likewise, you can model the inductive loop with a negative capacitance [negative resistance it does not mean there is current flowing in the opposite direction].

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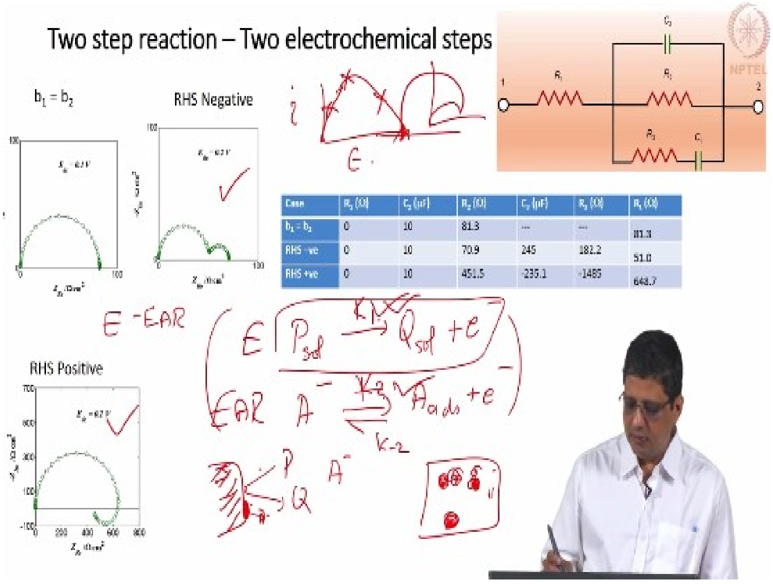

Two step reaction – Two electrochemical steps

Case	R_s (Ω)	C_d (μF)	R_t (Ω)	C_1 (μF)	R_1 (Ω)	R_p (Ω)
$b_1 = b_2$	0	10	81.3	---	---	81.3
RHS -ve	0	10	70.9	245	182.2	51.0
RHS +ve	0	10	451.5	-235.1	-1485	648.7

[What I want to show you next is, I will start it here, but we will continue with the actual derivation later]. I want you to visualize the scenario: we have an electrode here, the liquid has a reactant P (37:20). It can react on the surface and form Q, that similar to Ferro-Ferri reaction. This is electron transfer reaction. We can consider reversible reaction, but for simplicity I am going to consider only the forward reactions here. In addition, it has a chemical we call it as A^-, it can adsorb on the surface, or the adsorbed species can go back.

When it adsorbs it is actually coming from the liquid and adsorbing, it is not the metal adsorbed that we saw before. When it adsorbs it releases an electron, it can take an electron and go back into the solution. Once this is blocked by adsorbed the reaction here cannot happen on that area. if I look at it from the front of an electrode, this is looking from this side this is electrode, this is liquid. Look from the front, if ‘A’ adsorbed is occupying this area, that area is not available for this reaction. Only on pure metal this reaction can happen. This is called Electrosorption or electroadsorption reaction, together this is called EAR reaction. Qualitatively I describe why I want to choose this and what you expect to get out of this and then we will go into the detail in the next class.

When you go to positive potential we expect this reaction to happen faster. Electron is taken out or consumed. When you go to positive potential, we expect the forward reaction here to happen faster and the reverse reaction here to happen to a lesser level. Current here will increase, current here will also increase (39:10). When you go to very positive voltages, this entire surface will be covered by ‘A’ adsorbed. Almost entire surface will be covered by ‘A’ adsorbed. That means you cannot have more of this reaction, you cannot have more of this reaction. Current start at low potential, if you increase the potential current will increase. After sometime current will decrease. This will give rise to a spectrum which goes like this (39:40). I want you to be able to derive the equation for this, and for given set of parameters generate the current potential curve and the impedance curve at various potentials.

Then also explain what is meant by this negative impedance? Why is it physically okay to have this? We will stop here today.