Electrochemical Impedance Spectroscopy

Prof. S. Ramanathan
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture 50
Frumkin and Temkin Isotherms

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Previous class

Today

- KKT

- Frumkin & Temkin isotherms (instead of Langmuir isotherm model)

So in the last class, we have seen how we can use KKT. They looked at different cases with large amplitude perturbation and another with drift, potential drift. Now what I want to describe is the following. So far, we have said whenever there is an adsorption involved, we said that Langmuir isotherm model is applicable. The main reason we have done that is so that we can get analytical expression.

When we expand the expressions in Taylor series and truncate after the first term, we could do all these easily when Langmuir adsorption isotherm model is used, but there are other models, which might be more appropriate. They are a little more complex, but if you want analytical solution; it is not easy and in some cases, it is not possible to get the analytical solutions. However, the last three classes we have seen that when we go to NLEIS.

Most of the time, we end up using numerical methods. I want to show some examples where instead of using Langmuir isotherm model, how we can handle Frumkin or Temkin isotherm.

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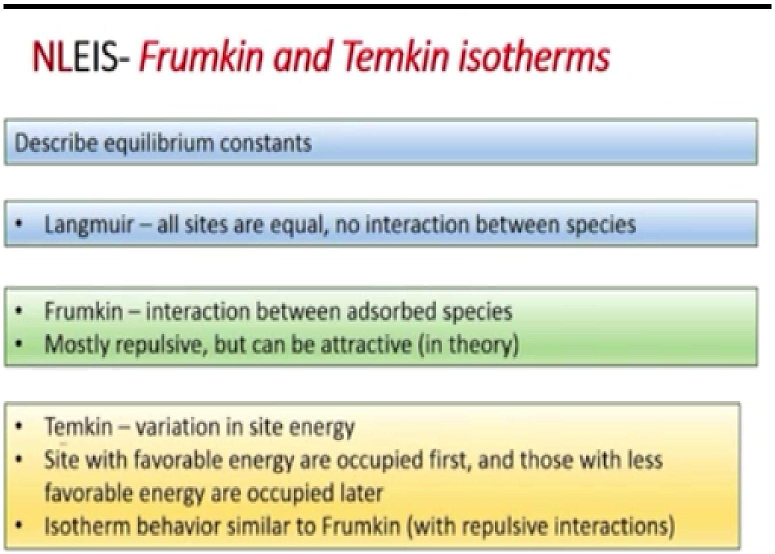

NLEIS- *Frumkin and Temkin isotherms*

Describe equilibrium constants

- Langmuir – all sites are equal, no interaction between species

- Frumkin – interaction between adsorbed species
- Mostly repulsive, but can be attractive (in theory)

- Temkin – variation in site energy
- Site with favorable energy are occupied first, and those with less favorable energy are occupied later
- Isotherm behavior similar to Frumkin (with repulsive interactions)

Now all these isotherms describe the equilibrium constants. In case of Langmuir adsorption isotherm model, this assumes that the equilibrium constant is independent of the coverage, fractional surface coverage. It assumes that if you have n number of sides, the probability of adsorption occurring in a place. In our case, a metal becoming metal adsorbed species. That is not dependent on the location of the site.

Whether it is here or here, or whether it is near the center or at the edge, if it is vacant, the probability of adsorption is equal for all those sides, all the vacant sides. It does not matter whether the neighbor is an adsorbed species or a vacant site. It does not matter whether this location is at the center or at the edge, okay. So there is no interaction between the species. So in the Langmuir, all sides are assumed to be equal and there is no interaction between the species.

Another adsorption isotherm is called Frumkin isotherm. This says that there is an interaction between species. Sometimes presence of one species will reduce the probability that adsorption will occur at the neighboring site compared to site where all the surrounding sides are also vacant. This is repulsive interaction. If you already have a species here, then if you look at the chance of adsorption happening right next to this versus an adsorption happening in these sites, this site has a lower probability.

Basically the presence of an adsorbed species reduces the probability because there is a repulsion. In theory, you can also say that presence of a species enhances or increases the probability of adsorption happening right next to that. That is because of attractive interactions. This is one scenario. Another way to look at that is to say that we have n number of sites, not all sites are equal.

So if I have certain number of sites here, in the very beginning adsorption will occur only at certain sites; preference is given to those and then it would occur at certain sites and then third probably here and fourth here. These are described by the energy levels. In certain cases, it is easier to adsorb. In certain sites, it is harder to adsorb and whichever is harder, it occurs later. Temkin adsorption isotherm basically assumes that all the sites are not equal and there is a variation in the site quality.

And Frumkin adsorption isotherm assume all sites are equal in the beginning and then adsorbed species is present in one place, then the chance of adsorption or the probability of adsorption right next to that is changed. If I look at the variation of the adsorbed species concentration versus concentration in solution for example, the equation which describes the Temkin isotherm is similar to the equation which describes the Frumkin isotherm, when repulsive forces are active.

Now I can give you an analogy. Imagine, you go to a restaurant. You have n number of seats and some seats might be occupied; some seats might be vacant. If we say that a new person who comes in will occupy any vacant seat, okay without worrying about whether the neighboring seat is occupied or not. So if it is vacant, the probability that the new person who enters will occupy that seat does not matter where that is located in the restaurant and whether the neighboring seat is occupied or not.

As long as a seat is vacant, somebody might occupy it. The probability is same for all the vacant seats. That is Langmuir adsorption isotherm. In case of Frumkin isotherm, imagine that you go to restaurant, you go to a table, in that table two are occupied, you are not likely to go to that same table and take the third seat or the fourth seat, right. You are likely to go to a place where it is completely vacant, a table where nobody is occupying there.

So this is equivalent to saying that all sites in the beginning are equal, but if some sites are occupied, then there is a repulsive interaction. That is, you are not likely to go to a place, which is already occupied with few vacancies right next to them. You are likely to go to a place where there is nobody around, okay. On the other hand, if you know the people who are there, if you are friends with them, you are likely to go and join them in the table.

That is similar to saying attractive interaction. So if you do not know them, if they are strangers, you are likely to go to a place where it is completely empty. If you know them and you want to go near them or sit next to them, that is similar to attractive interaction. Now it does not mean the seat is better or the location is better. It just means that location is better because that person is present there or location is worse because somebody is present there.

Now Temkin isotherm, the way you can describe that is this. You have a restaurant. We have n number of seats, but some seats have better view, so anybody who comes in will first occupy those seats, okay. The ones which have poorer view probably could get occupied second. We do not consider the interaction between the species, that is to say if you have a table where it is partially occupied, the view is very good.

This scenario, it says that the third person who enters will go and occupy that table, though it is already occupied by somebody else, it is partly occupied by somebody else, but still because the view is good, the new person will go and occupy that table. This is just an analogy.

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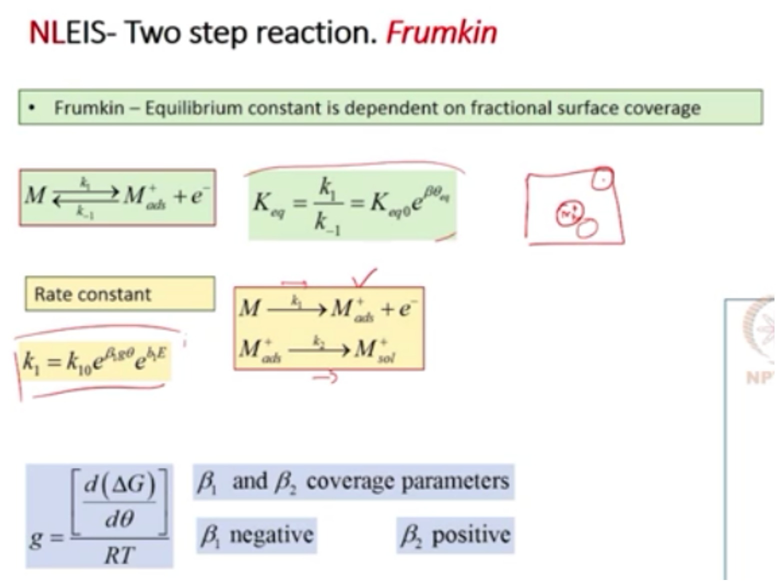

NLEIS- Two step reaction. *Frumkin*

- Frumkin – Equilibrium constant is dependent on fractional surface coverage

$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^+_{ads} + e^-$

$K_{eq} = \frac{k_1}{k_{-1}} = K_{eq0} e^{\beta\theta_{eq}}$

Rate constant

$k_1 = k_{10} e^{\beta_1 g\theta} e^{b_1 E}$

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

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

$g = \frac{\left[\frac{d(\Delta G)}{d\theta}\right]}{RT}$

β_1 and β_2 coverage parameters

β_1 negative

β_2 positive

In case of Frumkin isotherm, it does not tell anything about the rate constant. All that it tells is the equilibrium constant. So if you have a simple reaction, okay, in one step, let us say k1 is the rate constant for the forward reaction, k-1 is the constant for the reverse reaction. Then it does not tell how k1 will vary or k-1 will vary. It just says that equilibrium constant, which is k1/k-1, that is dependent on theta. That is all it says.

And the dependence on the theta equilibrium, fraction of surface coverage at equilibrium is given by this expression. So k equilibrium 0, exponential of beta, theta equivalent, although it does not tell anything about k1 or k-1, we can get this expression for equilibrium constant if we say that k1 or k-1 for the reverse reaction is given by an expression like this. K1 is given as k10, earlier we would have said k10 exponential b1e, right.

Because we said this is Langmuir isotherm model, but now because it is Frumkin isotherm model, it also depend on beta 1G theta. Now G is the ratio of variation in del G that is Gibbs free energy with respect to theta. That is in the numerator. The ratio of that to the factor RT, R is of course the universal gas constant, T is the temperature. Now beta 1, beta 2 are called coverage parameters. In this case, beta 1 is for the first reaction, beta 2 is for the second reaction.

And we say both these reaction rate constants are going to depend on theta. Now we are going to assume that repulsive interaction is likely if part of the surface is occupied by n + adsorbed, site here is more likely to become n + adsorbed compared to this site, because these two are charged species. It is quite likely that they will have repulsive interaction. Because of that, we are going to say, if theta increases, if this becomes more, this reaction will slow down.

But if theta is more, it is more likely that this reaction will happen faster. That is to say k1 will decrease with theta and if k1 has to decrease with theta, G of course is a positive number here, beta 1 has to be negative, beta 2 will be positive, then we can say when theta increases, k2 will increase, k1 will decrease. So that is more realistic scenario.

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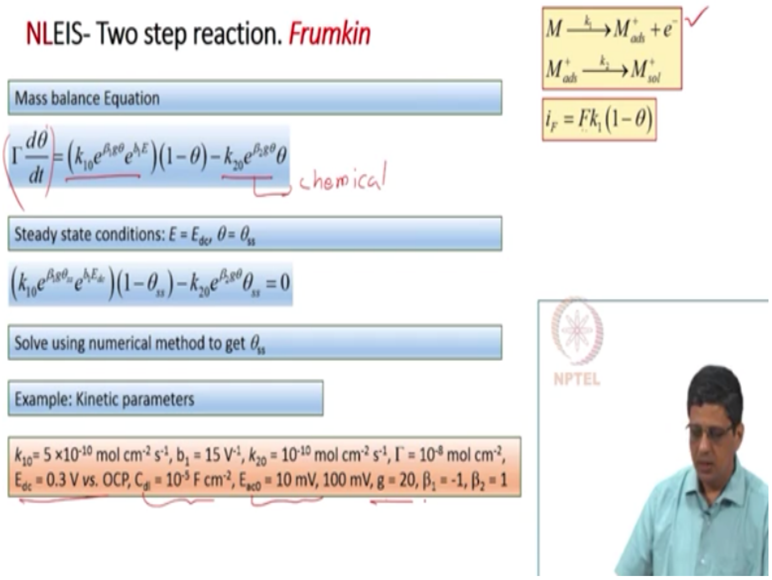

NLEIS- Two step reaction. *Frumkin*

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

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

✓

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

Mass balance Equation

$$\Gamma\frac{d\theta}{dt} = \left(k_{10}e^{\beta_1 g\theta}e^{b_1 E}\right)(1-\theta) - k_{20}e^{\beta_2 g\theta}\theta$$

chemical

Steady state conditions: $E = E_{dc}$, $\theta = \theta_{ss}$

$$\left(k_{10}e^{\beta_1 g\theta_{ss}}e^{b_1 E_{dc}}\right)(1-\theta_{ss}) - k_{20}e^{\beta_2 g\theta}\theta_{ss} = 0$$

Solve using numerical method to get θ_{ss}

Example: Kinetic parameters

k_{10} = 5 ×10^{-10} mol cm^{-2} s^{-1}, b_1 = 15 V^{-1}, k_{20} = 10^{-10} mol cm^{-2} s^{-1}, Γ = 10^{-8} mol cm^{-2}, E_{dc} = 0.3 V vs. OCP, C_{dl} = 10^{-5} F cm^{-2}, E_{ac0} = 10 mV, 100 mV, g = 20, β_1 = -1, β_2 = 1

Now we can write the mass balance equation, charge balance equation, as we have done before. We would normally write. For this, the mass balance equation will be k1 1-theta-k2 theta that would tell us gamma d theta/dt. Instead of k1, we expand this and write it as k10 exponential beta 1G theta exponential B1e. That second reaction is a chemical reaction. Therefore, it is independent of potential, but it is dependent on theta anyway.

And the current is of course given by first step, Faradaic constant, k1 (1-theta), second step does not contribute to the current, therefore it is not shown here. Now, under steady state condition, if you apply a DC, the fractional surface coverage will also give you a steady state value. We call it as theta FF. We can get that by setting these terms to 0. However, in the earlier case, when we have Langmuir adsorption isotherm, it is easy to rearrange and get a solution for this.

In case of Frumkin isotherm model, you cannot get an analytical solution. So you can set this to 0, that is straight forward, but you have to use numerical method to solve this and get a value for theta FF, okay. I want to show you an example. Let us say the k1 value b1 value, k20, b2 is of course 0 here, gamma value and at a DC potential of 0.3 volts versus OCP, AA capacitance is not relevant for this, but when we calculate the total impedance, we need that value also.

And in that case, we need to look at different AC perturbations, 10 millivolts or 100 millivolts. G value is taken as 20. Typical values would vary between 0 to 20. It is a dimensionless number. So we will keep it as 20 here. Beta 1 as I said theta is -1, beta 2 I said theta is +1.

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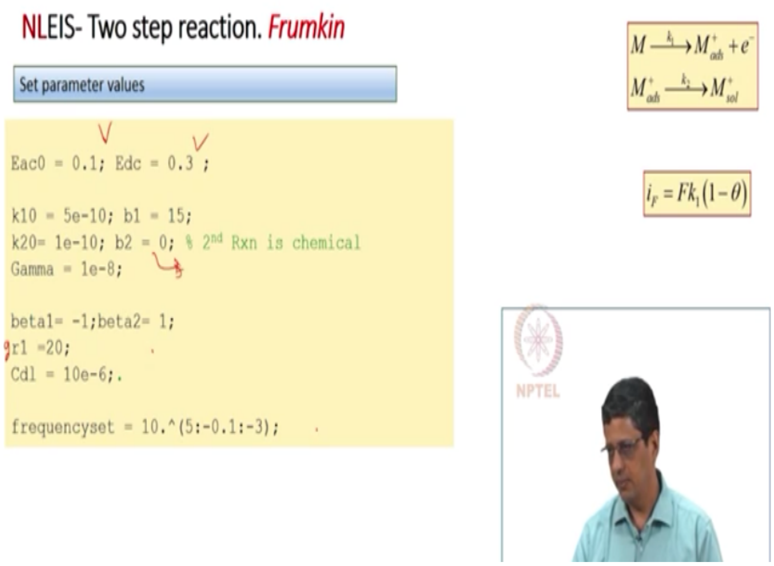

NLEIS- Two step reaction. *Frumkin*

Set parameter values

```
Eac0 = 0.1; Edc = 0.3 ;

k10 = 5e-10; b1 = 15;
k20= 1e-10; b2 = 0; % 2nd Rxn is chemical
Gamma = 1e-8;

beta1= -1;beta2= 1;
gr1 =20;
Cdl = 10e-6;.

frequencyset = 10.^(5:-0.1:-3);
```

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

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

$i_F = Fk_1(1-\theta)$

Those cases are of course; this is in voltage sinusoidal perturbation. K10 b1, b2 is set to 0, still b2 is not necessary, but it is already in the court, so we set it to 0, because second reaction is chemical reaction and this is actually G. For some reason, it is written as R1 in the code and we calculate the impedance, we will look into the value of frequency going 100 KHz to 1 millihertz, 10 frequencies per decade, logarithmically spaced.

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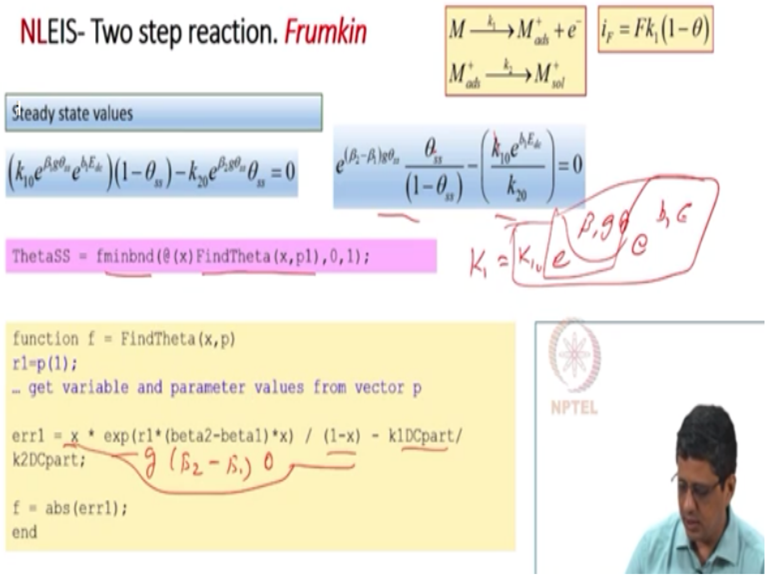

NLEIS- Two step reaction. *Frumkin*

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

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

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

Steady state values

$$\left(k_{10}e^{\beta_1 g\theta_{ss}}e^{b_1E_{dc}}\right)(1-\theta_{ss}) - k_{20}e^{\beta_2 g\theta_{ss}}\theta_{ss} = 0$$

$$e^{(\beta_2-\beta_1)g\theta_{ss}}\frac{\theta_{ss}}{(1-\theta_{ss})} - \left(\frac{k_{10}e^{b_1E_{dc}}}{k_{20}}\right) = 0$$

$$K_1 = \boxed{K_{10}\,\boxed{e^{\beta_1 g\theta}}\,e^{b_1 G}}$$

```
ThetaSS = fminbnd(@(x)FindTheta(x,p1),0,1);
```

```
function f = FindTheta(x,p)
r1=p(1);
… get variable and parameter values from vector p

err1 = x * exp(r1*(beta2-beta1)*x) / (1-x) - k1DCpart/
k2DCpart;

f = abs(err1);
end
```

$g\,(\beta_2-\beta_1)\,\theta$

In order to calculate the steady state value, what we have done is first rearrange this. We have this expression, bring this to the right side, you would get k20 e power b2G theta*theta. Then bring this to the denominator, you will get theta/1-theta SS, then divide by exponential beta 1G theta SS, you would get exponential of b2-b1. What is left is k10 exponential b1 eDC, that is one part. On the right side, you would have got k20.

Bring it to the denominator, so you would have one expression A, another expression B. A-B is set to 0, okay. For a given value of eDC, we have to find a theta such that this is satisfied. So what we can do is to write this as f(theta), okay. Find the absolute value f(theta) and that is going to be minimum when f(theta) is 0. It is a real number. It can be positive or negative number, okay and this number when we take absolute value.

That is going to be the minimum when this f(theta) is 0. So what we have done is use a function called fminbnd and say FindTheta. We set the parameters if I want to change the value of k10b1, K20 gamma, or G, well gamma is not relevant here, if I have to change G. Beta 1, beta 2 etc., I can positively using the vector P1. So we can get the variable and parameter values in the first few steps. I am not showing all of them here because of space.

Then, we define something called error. Error is term A-term B. This is theta/1-theta exponential of G beta 2-beta 1*theta. So this does the first term and this is of course k1DC partial because k1 is K10e power beta 1G theta e power b1e. So when e is set to eDC, this entire term will be k1DC, but if I take only k10 and b1e, we will call it as k1DC partial/k2, of course k2 is k20, but does not matter. We can set beta 2 as 0 and that is going to be same as k2DC partial.

We find the absolute value of this and minimize this.

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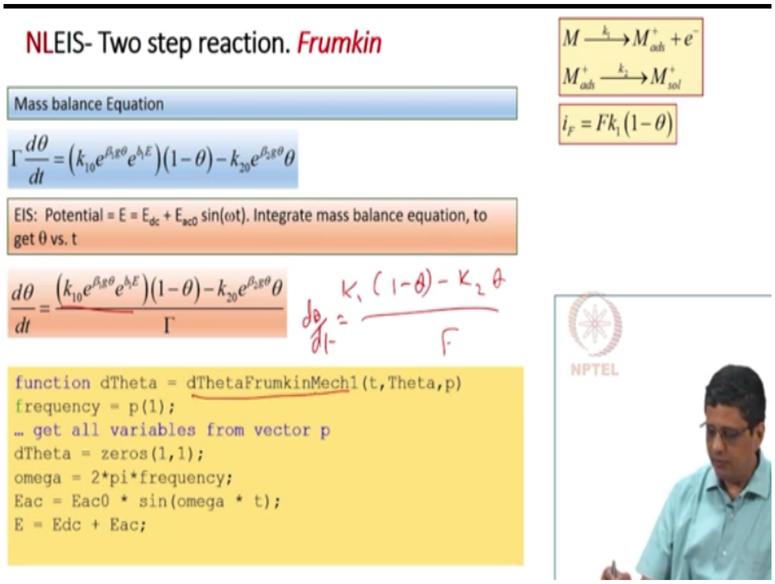

NLEIS- Two step reaction. Frumkin

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

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

Mass balance Equation

$$\Gamma\frac{d\theta}{dt} = \left(k_{10}e^{\beta_1 g\theta}e^{b_1 E}\right)(1-\theta) - k_{20}e^{\beta_2 g\theta}\theta$$

EIS: Potential = E = E_{dc} + E_{ac0} sin(ωt). Integrate mass balance equation, to get θ vs. t

$$\frac{d\theta}{dt} = \frac{\left(k_{10}e^{\beta_1 g\theta}e^{b_1 E}\right)(1-\theta) - k_{20}e^{\beta_2 g\theta}\theta}{\Gamma}$$

$$\frac{d\theta}{dt} = \frac{K_1(1-\theta) - K_2\theta}{\Gamma}$$

```
function dTheta = dThetaFrumkinMech1(t,Theta,p)
frequency = p(1);
… get all variables from vector p
dTheta = zeros(1,1);
omega = 2*pi*frequency;
Eac = Eac0 * sin(omega * t);
E = Edc + Eac;
```

When you want to get the impedance, what we have to do is apply a DC on top of the DC, superimpose an AC and then find the response. We find the theta response, we find the current response. We take the current steady periodic results, do the FFT and then we know what to do, okay. So to integrate this, earlier we would have said k1 (1-theta)-k2 theta/gamma. That is going to be d theta/dt and in that case it would have been k10 exponential b1e.

But in this case it is little more complex, does not matter. If you are going to use numerical method, you can just substitute whatever expression we have to. This case, I would have written it as d theta Frumkin for mechanism 1 and we get all the parameter values, variable values and then first set the d theta/dt to 0. We calculate eAC. We calculate the potential e as a sum of eDC and eAC and we will continue in the next page.

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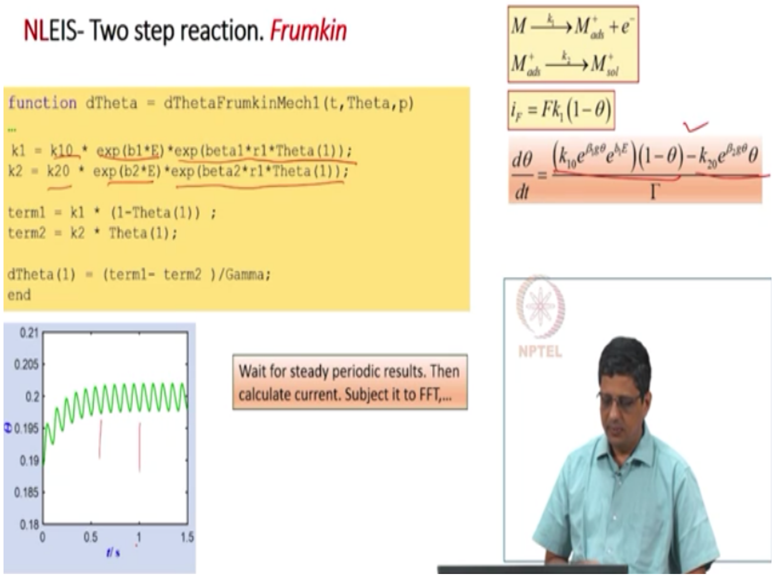

NLEIS- Two step reaction. *Frumkin*

```
function dTheta = dThetaFrumkinMech1(t,Theta,p)
...
 k1 = k10 * exp(b1*E)*exp(beta1*r1*Theta(1));
k2 = k20 * exp(b2*E)*exp(beta2*r1*Theta(1));

term1 = k1 * (1-Theta(1)) ;
term2 = k2 * Theta(1);

dTheta(1) = (term1- term2 )/Gamma;
end
```

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

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

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

$$\frac{d\theta}{dt} = \frac{\left(k_{10}e^{\beta_1 g\theta}e^{b_1 E}\right)(1-\theta) - k_{20}e^{\beta_2 g\theta}\theta}{\Gamma}$$

Wait for steady periodic results. Then calculate current. Subject it to FFT,...

This is the equation that we want to integrate, right. We will set k1 and k2 as k10 exponential b1e exponential beta 1G theta, k20 in this case b2 is 0, so it does not matter and likewise for beta 2 to get the k2. Now I have written this as term 1, term 2. So k1 (1-theta) is term 1 k2*theta is term 2. Term 1-term 2/gamma should give us d theta/dt. So we want to write like this so that it is easier to debug if there is any mistake in the code, it is easier to debug this one.

When you apply sinusoidal potential, this is integrated for about 2 seconds, or 1-1/2 seconds, you can see that it oscillates, it drifts and then achieves steady periodic result after some time, perhaps after half a second, definitely after 1 second, okay. So we have seen this in Langmuir isotherm model. It is going come in Frumkin, Temkin, any of these adsorption isotherm models, we had to look at this. We have ensure the steady periodic system and then we have to take the data, okay.

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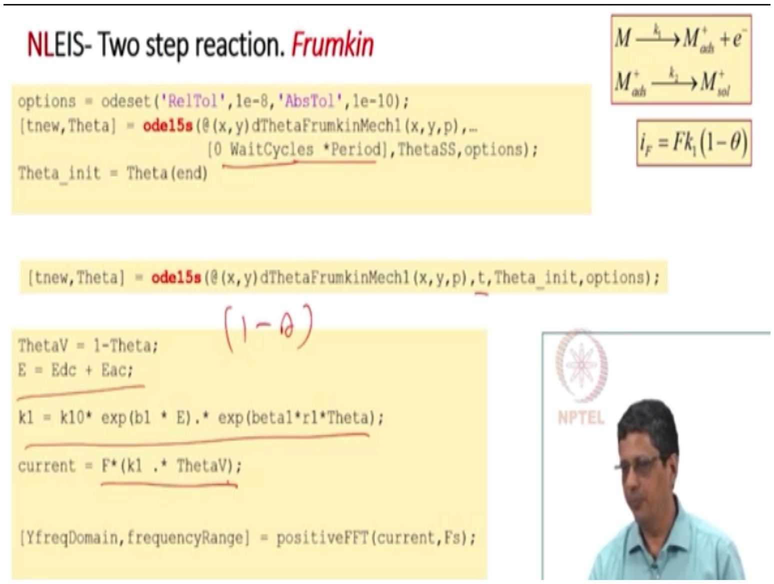

NLEIS- Two step reaction. *Frumkin*

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

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

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

```
options = odeset('RelTol',1e-8,'AbsTol',1e-10);
[tnew,Theta] = ode15s(@(x,y)dThetaFrumkinMech1(x,y,p),…
                     [0 WaitCycles *Period],ThetaSS,options);
Theta_init = Theta(end)
```

```
[tnew,Theta] = ode15s(@(x,y)dThetaFrumkinMech1(x,y,p),t,Theta_init,options);
```

$(1-\theta)$

```
ThetaV = 1-Theta;
E = Edc + Eac;

k1 = k10* exp(b1 * E).* exp(beta1*r1*Theta);

current = F*(k1 .* ThetaV);


[YfreqDomain,frequencyRange] = positiveFFT(current,Fs);
```

So for example, the default tolerance value is 1e-6 if I remember right in the MatLab. If you want a little more accurate value, you have to change that. This integration works well when you use ODE 15S, because the equations happen to be stiff equations, okay. When we are looking at analytical solution, we never had to worry about what type of equation it is. Now when you are going to use numerical method, you have to use the correct solver, ODE solver.

If you have stiff equations, and you use the normal solver, either it will not give you the result or it will take very long time and give you some results, okay. So initially we wait for certain time, we calculate the number of cycles based on the frequency, wait for certain time and then integrate for some more time n number of cycles. I have not shown you all the details. So this first part is for waiting, second part this t is little different.

It is based on the frequency, based on the number of cycles, based on the number of points in a cycle and then of course once I integrate, you get theta, you can get the theta V is actually vacant sites. You can calculate e, you can calculate k1, f(k1) vacant site theta V gives us the current and then you can go through f(t). So process is the same, it is just that you need to get the steady state values using numerical methods here.

You have to do the integration, which is the correct expression for the k1 and k2. Otherwise whatever we have done with Langmuir isotherm model for small or large amplitude perturbation, we have to use the same methodology here. So that way numerical method is pretty much the same. There is no extra difficulty in applying it for a Frumkin or Temkin isotherm model or any other isotherm model compared to applying it for a Langmuir isotherm model.

In case of analytical solutions, it is possible only for small amplitude perturbation. In some special cases, you might get it for larger amplitude perturbation, but by and large it is possible only in the linear regime and that is also relatively easy to do only for Langmuir isotherm model, okay.

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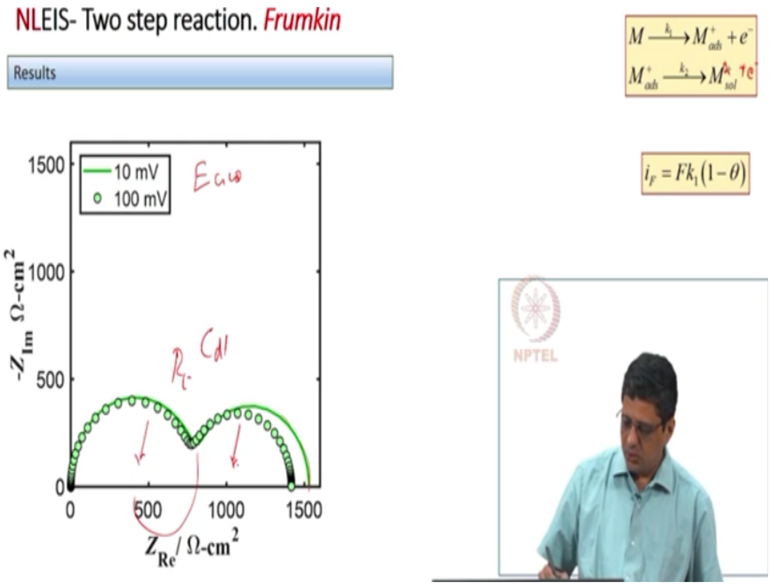
NLEIS- Two step reaction. *Frumkin*

Results

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

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

$i_F = Fk_1(1-\theta)$

Just as an example, see if I set the amplitude eAC0 to 10 millivolts, I get spectrum as shown by this continuous line here. If I set it to 100 millivolt, it is little different, but in terms of the difficulty in getting these results, there is no real difference, okay. For the given set of parameters, it is one adsorbed intermediate, it gives you two capacity loops. One capacity loop is coming from charge transfer resistance and double layer capacitance.

The second capacity loop comes from Faradaic process and of course, if I give two-step reaction, for example with 2+ solution plus another electron, okay, depending on the parameter values, I can also get inductive loop. So even here when I have n adsorbed intermediate, I can get n+1 loop. One loop is for the double layered capacitance in parallel with charge transfer resistance. Every adsorbed intermediate would give me 1 time constant or 1 Maxwell pair.

The rate constant could be described using Langmuir isotherm model or using Temkin isotherm model or Frumkin isotherm model. It can be complex, but we will not get more number of loops because of that. That is also something I would like you to note.

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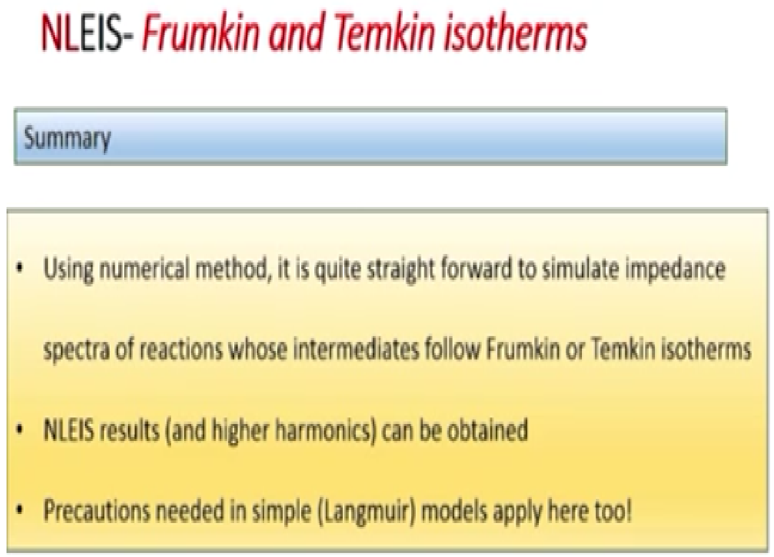

NLEIS- *Frumkin and Temkin isotherms*

Summary

- Using numerical method, it is quite straight forward to simulate impedance spectra of reactions whose intermediates follow Frumkin or Temkin isotherms
- NLEIS results (and higher harmonics) can be obtained
- Precautions needed in simple (Langmuir) models apply here too!

So in summary, using numerical method, it is quite straight forward, okay to simulate the impedance spectrum and to get the steady state values to simulate the impedance spectrum for reactions where the intermediates do not necessarily follow Langmuir's adsorption isotherm and although I have shown only the impedance results here, it is pretty straight forward to extract the second, third and n-th harmonic from this.

And whatever precautions we took in terms of waiting for certain time to get steady periodic results, we have to take the same precautions here also. Otherwise what we get is in the unstable region.