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

Lecture- 30
Challenges in RMA

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Previous class

- RMA
  - An example with Frumkin Isotherm
  - PEM Fuel Cell . CO poisoning. Springer Mechanism

Today

- RMA
  - Challenges and few remarks

We saw one example where we have taken Frumkin isotherm example and then we have developed the equations. We also just showed you an example with PEM Fuel Cell and said it is possible to derive the equation for that. It is going to be complex so I did not really spend time on that. now I want to summarize and also make some remarks. So far what we have seen is, if you are given a mechanism how to get the expression for impedance, how to get the expression for steady state current values as a function of potential dc potential. How to get the expression for impedance at any given dc potentials for any frequency, we can calculate the impedance.

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RMA. Challenges and few remarks

1. No easy-to-use (commercial or free) software
2. How many loops (in complex plane plots) will we see?
3. Kinetic parameter extraction - Optimization Strategies
4. Number of parameters. EEC *vs.* RMA
5. Multiple solutions: An example of poor analysis strategy
6. Min # of potentials (E_{dc}) at which EIS must be acquired
   - To avoid infinite # of solutions.

But in real life what happens is, we get impedance data. We can get impedance data at different potentials or different dc currents. In certain cases like fuel cell, batteries, people usually use galvanostatic mode, different dc current which corresponds to different dc potentials. Galvanostatically, one can get impedance data potential statically one can get impedance data.

And from that, we want to first identify or propose a mechanism and say that this mechanism is an operation and we are getting the impedance data like this. We also have to come up with kinetic parameters values and say if I use this mechanism and this parameter value this seems to match the impedance spectra at different dc potential. This seem to match the dc current at different dc potential. Therefore, I think this is the mechanism. first, you have to be able to come up with a mechanism, vary the parameter values and see which parameter combination matches this well. If the mechanism you propose and the kinetic parameters you try if they do not match, either we have not done a good optimization, or this is not the right mechanism both are possible right.

Sometimes you should be able to tell this mechanism will not work no matter what, no matter how much optimization I do. That, I think at this level you should be able to tell that, at least in some cases. If we see three capacitive loops you should not try a mechanism with one adsorbed intermediate. Certain mechanism you can eliminate and say this is not possible. Certain mechanism you may not be able to eliminate. You will have to try.

And sometimes we have come to conclusion saying this mechanism, although it has two adsorbed intermediates and impedance shows 2 loops or 3 loops, 2 loops for the faradaic we still cannot predict it with this because certain features in the potentiodynamic polarization, cannot be matched with this. That is one more level just like saying, if the data looks like a curve I cannot use linear, but you have to do with little more care to say can I use quadratic? can I use cubic? or should I use sinusoidal wave? Some more analysis is necessary, some more familiarity with this. What type of expression, what type of mechanism can give rise to what type of impedance spectra? That is necessary. The difficulty in using this methodology is, at least I am not aware of any software that can do this. Commercial software or free software where you can download it and click it the way you do it for electrical circuit, commercial software are there. Even free software is there where I can give variety of RC combination, RQ, RL, add those things in parallel, or in series and to a reasonable level, at least for relatively simple data, you will be able to get proper results [proper match]. You do not have something like that equivalent one for mechanistic analysis. You will have to write the code yourself in whichever language or script you want to use. That is a barrier.

The first barrier is whether we are able to write the impedance expression for a mechanism that we give. I think at this level you should be able to do with practice you will be able to do with comfort right now you may be able to do it with some difficulty. But next level is to write a program to do this that is one difficultly. After that I want to show you some of the challenges, some of the points that you should be aware of when you are actually using.

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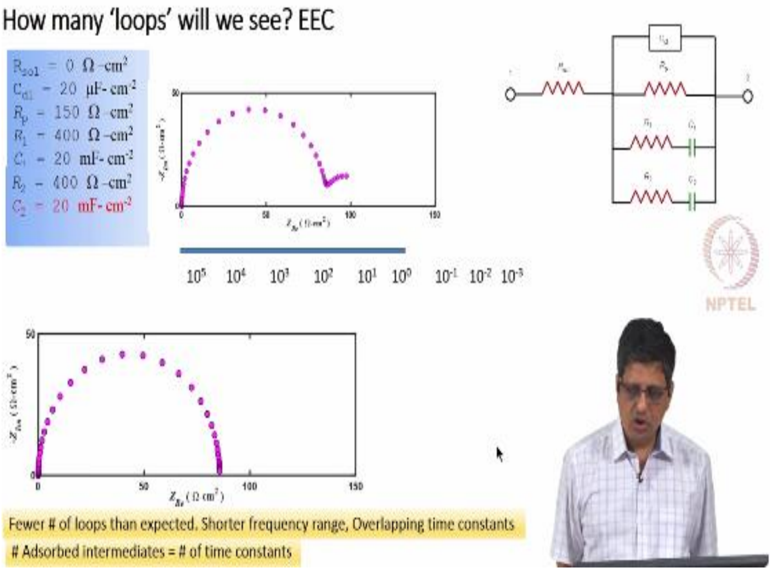

How many 'loops' will we see? EEC

R_{sol} = 0 Ω-cm²
C_{dl} = 20 μF-cm⁻²
R_p = 150 Ω-cm²
R_1 = 400 Ω-cm²
C_1 = 20 mF-cm⁻²
R_2 = 400 Ω-cm²
C_2 = 20 mF-cm⁻²

Fewer # of loops than expected. Shorter frequency range, Overlapping time constants

Adsorbed intermediates = # of time constants

There are few I have listed here. I will go through them one by one. It is easy for us to look for the EEC and learn few points. Let us say we have a circuit shown here. You have one representing R solution, one representing double layer, 2 Maxwell elements Maxwell element R_1C_1, R_2C_2 all in parallel with RP. It is one representation. You can do similar one in voigt. It does not matter. Voigt or the ladder with inductance. Right now, I want to show you what would happen if you have the values given here solution resistance is 0, double layer has some typical value and other values I have made them up. If you have data like element value like this and if you generate the spectrum from 10^5 Hz that is 100 kHz to 1 mHz, you would see a spectrum like this.

It is easy for you to do this in Matlab or any other programming language. Calculate this or use commercial software you will get this. Right now trust me when I say you will get a loop like this. Now with this, you can tell I need a circuit with three time constants, one time constant comes from Cdl and R_P, other two time constant comes from R_1 C_1, R_2 C_2, or an equivalent representation in any other form or L maybe with negative values. Maybe in voigt circuit, ladder circuit you can get this. If we chose that we are going to use, if we decide that we are going to use Maxwell circuit with capacitor, this will do the job. Now the same circuit, if I have taken data only until 1 Hz. let us say below that for whatever reason it was noisy or it was scattered so we decided we are not going to look at this. Our spectrum will show only this.

What it means is, from this you would come to a conclusion saying a circuit with 1 Maxwell element can model this adequately. That is probably correct. It does not mean the spectrum was generated from a circuit with 1 Maxwell element. It is generated from a circuit with 2 Maxwell element. But, we have a limited range of data [for whatever reason I see data or instrument capability whatever this is one example].

If I use other values you might see even up to 1 mHz. I will see only one and half loop to get the second loop or third loop I will have to use it till maybe µHz. I may not have enough time to do the experiment. I may not have enough quality of data. Even if I have time it may be noisy, or scattered. I cannot really see anything our points are all over the place. You may get fewer number of loops than the number of time constant in the actual system, because we have limited frequency range that is a possibility.

Similarly, this is easy to see here because it is easy to generate here. If we have 2 adsorbed intermediate, 2 Maxwell element will be suitable, but you may not see 2 additional loops or 2 loops for the faradaic process because we have limited frequency range. Second, I want to change the number. So instead of 300 µF, I have given values like R_1 is 400, C_1 is 20 mF, R_2 is 400 Ω-cm^2 because it would be corresponding to an electrode. If it is pure resistance it is going to be Ohm and µF or mF. C_2 was originally 300 µF, but now it changed it to 20 mF. Now look at R_1 C_1 and R_2 C_2 they are matched R_1=R_2, C_1=C_2. This case the time constants are identical. If this close enough it will overlap. And when you measure data there will be some noise. If I use identical values here I can go till 1 mHz, I will still say only 2 loops. There is no way, I look at this data and say this comes from a system with 2 Maxwell elements or 3 time constant. Because the time constant overlap even if I go to 1 µHz I will not get any difference. I will get only 2 loops there.

So adsorbed intermediates will give you time constant, different dc potential they will give rise to different time constants and it is possible that at some specific dc potential 2 time constant are overlapping maybe identical that may or may not happen that easily, but they overlap and within noise level you may not see a difference. Even if you go to low enough frequency you may not see all the time constant manifesting as different loops in the complex plane plot.

So generally if you see certain number of loops, here if you go to 1 Hz, I will say only 1 loop. If I see fewer number of loops than what I should expect in theory that basically means time constant may be overlapping, or the frequency range may be limited and both effects may play a role. When we say either a shorter frequency range or overlapping time constant we will get to a number of loops than expected. Expected meaning, what I would expect in the maximum number of loops from this system.

So if you see certain number of loops you should say one loop is meant for the double layer in parallel with polarization resistance in Maxwell representation. Other loops represents how many number of adsorbed species are there, but this tell you minimum number of adsorbed species that is necessary. It does not mean the system has only that many number of adsorbed species.

So if I get a spectrum like this, for example, I can get 1 dc potential I may get spectrum like top another dc potential I may get spectrum like this. It means I need minimum one species as per this, but I might actually require more number of species to really model this data. the number of time constant is based on the number of adsorbed intermediates and this is assuming there is no mass transfer, there is no solution resistance etcetera.

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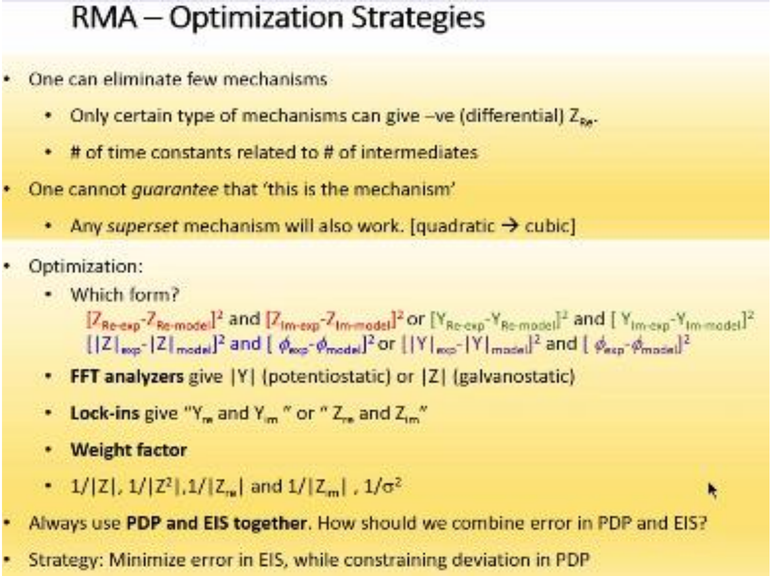

RMA – Optimization Strategies

- One can eliminate few mechanisms
  - Only certain type of mechanisms can give –ve (differential) Z_{Re}.
  - # of time constants related to # of intermediates
- One cannot *guarantee* that 'this is the mechanism'
  - Any *superset* mechanism will also work. [quadratic → cubic]
- Optimization:
  - Which form?
    $[Z_{Re\text{-}exp}-Z_{Re\text{-}model}]^2$ and $[Z_{Im\text{-}exp}-Z_{Im\text{-}model}]^2$ or $[Y_{Re\text{-}exp}-Y_{Re\text{-}model}]^2$ and $[Y_{Im\text{-}exp}-Y_{Im\text{-}model}]^2$
    $[|Z|_{exp}-|Z|_{model}]^2$ and $[\phi_{exp}-\phi_{model}]^2$ or $[|Y|_{exp}-|Y|_{model}]^2$ and $[\phi_{exp}-\phi_{model}]^2$
  - **FFT analyzers** give |Y| (potentiostatic) or |Z| (galvanostatic)
  - **Lock-ins** give "Y_{re} and Y_{im}" or "Z_{re} and Z_{im}"
  - **Weight factor**
  - $1/|Z|$, $1/|Z^2|$, $1/|Z_{re}|$ and $1/|Z_{im}|$, $1/\sigma^2$
- Always use **PDP and EIS together**. How should we combine error in PDP and EIS?
- Strategy: Minimize error in EIS, while constraining deviation in PDP

We can use RMA to eliminate few mechanisms. For example, not all mechanism will give you a negative resistance. If you see negative resistance, if you see polarization data, I am going to draw it here increasing with potential and then decreasing after sometime current increase and decreases then you can say certain mechanisms will never give that type of polarization. you can eliminate those.

Certain mechanism can give an increase and decrease. you should evaluate those. EAR can give you, catalytic mechanism can give you, there are few other mechanism which can give. We do not have time to go through everything so we are leaving it out, but once you become familiar and try a few mechanism you would know which can give you a polarization curve which can match the data.

Now I cannot guarantee even if I find a mechanism under kinetic parameter set which matches with the experimental data. I cannot guarantee that this is the best mechanism just like if a quadratic equation works cubic equation will definitely work. Likewise, any mechanism you find a superset of that mechanism will always work. Meaning, I will find a mechanism I say first reaction is reversible second reaction is irreversible, it matches. If I say second reaction is also reversible definitely it will match.

If I add one more step definitely that should be able to give me a match. I can always say this is a mechanism that can describe this data. It is possible. I need to come up with other reasons to say why it cannot be something else. Maybe I will use surface characterization and say only these intermediates are found so another intermediate may not be necessary to describe this. I do not find any evidence for other intermediates I should not use other intermediates. I cannot use impedance data and polarization data and mechanistic analysis and guarantee that this is the mechanism. I can say this is the possible mechanism.

Now when I say I match the experimental data what I would do is predict data, find the difference between the experimental data and the model data. And when I minimize, it I will say this is a good match. Ideally it will be zero error. Now I have to decide what form to use. Impedance comes in the form of Z real and Z imaginary. That is one. It comes in the form of magnitude and phase that is another representation. It comes in the form of admittance again real and imaginary magnitude and phase. should I minimize the error between the real parts and imaginary parts? Should I minimize the error between the magnitude and phase? Should I minimize the error between admittance or should I minimize it in the impedance form? Ideally what you should do is prediction you can predict in any form and change it, it is not a problem. We can predict as impedance and then convert it admittance or the real and imaginary you can convert into magnitude and phase.

In what way do we measure it? If we are using FFT analyzer in potentiostatic mode usually that means, we are measuring magnitude and phase of Y [that is admittance]. We are applying a potential; we are getting a current. The transfer function is admittance. That is why in potentiostatic mode ideally you should use KKT in the admittance mode. But many times impedance mode also seems to work because it is stable under galvanostatic condition so we typically use impedance.

Similarly, if you are measuring in galvanostatic mode, you should find the error between the magnitude of the impedance in the model and experimental. Likewise you should do the difference in the phase. If we are using lock-in amplifier or any instrument that user’s cross correlation technique like the Solartron FRA, you would be getting real and imaginary parts. That is how it calculates.

And again in potentiostatic mode it will calculate admittance in galvanostatic mode it calculates impedance. Having said that, typically, most researchers including our group end up finding the difference between the real model and real experimental impedance. And likewise take the imaginary part of the impedance and find the difference between the predicted and model values predicted and the experimental values and minimize that.

You can also use a weighing function, weight factor. High frequency data gives you information on the solution resistance, high frequency data gives you information on the double layer capacitance and that usually not that difficult to find. The low frequency mid frequency data contains information about the reactions. We have to give weight for this. If you give no weights that is unity. We will just minimize the error between Z real and Z imaginary, give equal weight to all frequencies or all impedance values. Usually the low frequency impedance will be large value and that has more scatter and that will dominate. Because a large difference in even 1% difference in the low frequency model will be here, experimental point will be here and in case of the high frequency data even 100% difference will make it only slightly off.

So you need not always give unit to weight factor that may not be appropriate. Again, ideally what one should do is to repeat experiments 3 experiments, 4 experiments, 5 experiment and at each impedance value find the standard deviation [we call it a sigma]. Take the inverse of sigma square that is variance, and if we have very low sigma you have more confidence in the data. If you have a large value of standard deviation you have poor confidence in the data. Take the inverse of sigma square that should give you how much weightage you should assign to that data. That will be the ideal weight to do that. You can say that I can use inverse of impedance mode, inverse of impedance square inverse of real part for the real error imaginary part for the imagine error people have tried variety of these things, various methods have been used.

But this is something you have to choose when you write the code. You have to say how much weightage I am going to assign for each point. Sometimes at lower dc potential with respect to open circuit potential data, will have lower scatter because the dc current will be low. Corresponding impedance will have relatively better quality. When you go to potential which is farther away from the open circuit potential, there will be large current and associated will be large noise.

So you may have poor confidence in that data. You may not want to give a weighing factor only based on the frequency. You may also want to say, at this dc I have more confidence in the data at that another dc potential have less confidence in the data so I will assign less weightage to that. Because you are going to fit all the data using one set of kinetic parameters using one algorithm.

So you have to choose the weight factor correctly. Always you should use potentiodynamic polarization and impedance data. You have data of potentiodynamic polarization, if we imagine we have one column of dc potential and dc current then we have few spectra. At one dc you have frequency real imaginary impedance. Another frequency, real, imaginary, I have 2 types of data. One is dc current and potential, another is impedance which is a coupled quantity. For each frequency I have one, and for each dc I have one. How do I combine all these errors? I cannot just find the model impedance error that is in Ω-cm^2 at different dc potential and different frequencies. I can calculate the error, I can assign weight factor for this and then I cannot sum up that error with this error; this is a completely different type of data. what we end up doing there are different strategies of using it.

What we end up doing is to minimize the error in EIS and we give up a constraint saying vary the parameter, minimize the error here in the impedance data as per our weight factor, while maintaining the current within certain percentage of deviation 5%, 10% you have to choose that. Ideally you want to say 1% but then you may not be able to find any fit here. You will have to loosen it a little and see if we can get a good fit here.

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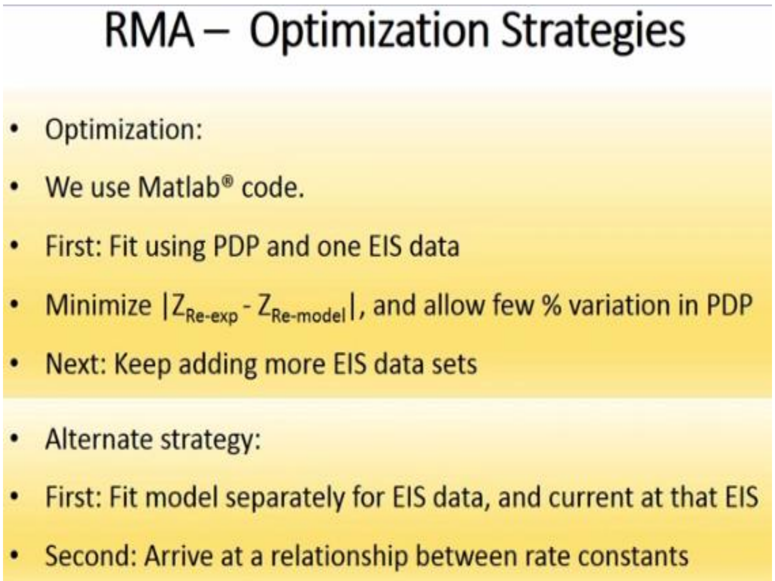

RMA – Optimization Strategies

- Optimization:
- We use Matlab® code.
- First: Fit using PDP and one EIS data
- Minimize $|Z_{Re\text{-}exp} - Z_{Re\text{-}model}|$, and allow few % variation in PDP
- Next: Keep adding more EIS data sets
- Alternate strategy:
- First: Fit model separately for EIS data, and current at that EIS
- Second: Arrive at a relationship between rate constants

So we write it using Matlab code we sometimes get initial values using C++ code. We try like few billion combinations and then see whether any of them give any data which looks like the experimental data. That if you do it in Matlab it takes lot of time. Initial values are important. After getting some reasonable initial value what we do is fit 1 EIS data using Matlab code and give a constraint here. You should not give this as a final choice. Meaning you cannot use one EIS data to model as system. Because, you will get infinite number of solutions, in theory. In practice, because this program does not know this is a non linear system with infinite number of solutions, it may converge to some solutions and give you a solution. Since you are using potentiodynamic polarization data also along with this.

But you should use a minimum number of dc potentials, you should have certain number of spectrum and I will also describe how to get that information after this. But in the beginning we use one spectrum, then we get initial values we get the fit here, used that as initial value for the next iteration where we had the second spectral data also and say fit both of them with the constraint, add the third spectrum data also.

And likewise we do it for in theory I can give all the spectrum data, potentiodynamic polarization data, give it to the program and say find the best fit here within 5% of variation here. But it does not seem to work it will not converge properly. We will have to take step by step. we minimize the error in real, experimental and model allow few percent variation in PDP and keep adding more EIS data.

Another strategy people have tried this or used this or published with this. For each EIS data, they would get a parameter and they would find a current value at that parameter, at that dc potential for those parameter. If I have a current like this, I have taken spectrum here, spectrum here, spectrum here just fit this alone, this alone, and this alone along with these 3 points for the current. Then see if I can find a relationship between these 3 parameters. I will not fit it for k_{10}, b_1, k_{20}, and b_2 instead, I will just fit it for k_1, k_2 etc., and then see if I can relate this with an exponential form or any suitable form. But I do not think it is a good idea because you do not know you are not predicting the current at the intermediate values. In one case, if I predict only 3 points it may go like this, it may go like this also. Just be fitting 3 points I am not able to say with confidence that the entire curve will match correctly.

And getting 3 k values and expecting that all of them will go through an exponential form or even fitting them with 3 points I should not fit it to k_{10} exp(b_1E). Because it is basically doing regression with 3 points you will get a value, but it is not necessarily good. If you want to do a regression you should do with many number of points. Similarly k_2, k_3 all those kinetic parameter in my opinion it is not a good idea to do.

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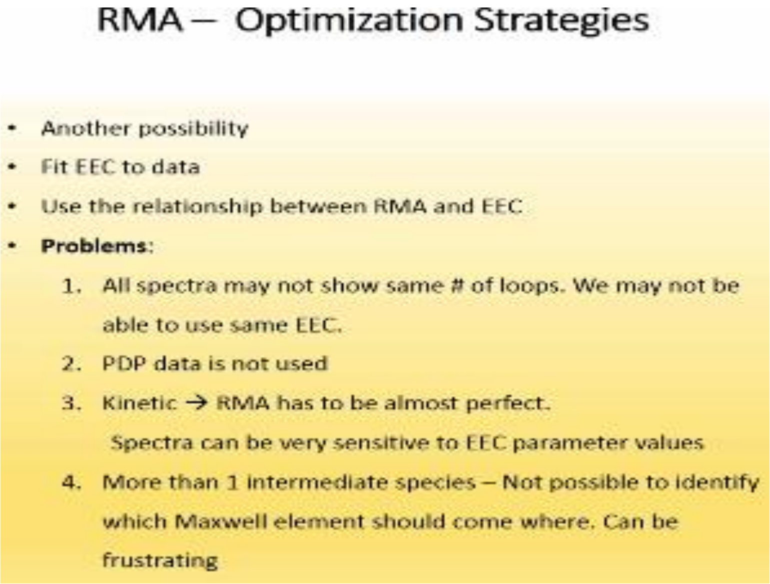

RMA – Optimization Strategies

- Another possibility
- Fit EEC to data
- Use the relationship between RMA and EEC
- **Problems:**
  1. All spectra may not show same # of loops. We may not be able to use same EEC.
  2. PDP data is not used
  3. Kinetic → RMA has to be almost perfect.
     Spectra can be very sensitive to EEC parameter values
  4. More than 1 intermediate species – Not possible to identify which Maxwell element should come where. Can be frustrating

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The third possibility is, it is easy to fit the impedance spectrum to EEC and it is possible to relate the kinetic parameters through EEC parameters R_1, R_2, R_0 etc. We can write the equation and if you look at it, it is very elegant. You can take a spectrum it has 50 points, 100 points whatever number of points, we have 3 spectra, fit to Maxwell elements so you get only 5 data points from there you have 50 points you are reducing it to 5 with 2 Maxwell elements.

Then kinetic parameters can be related to these very easily. But when you actually try this, you will face problems. One, all spectra may not show same number of loops. So in one case you will fit it to one Maxwell elements in another case you fit to 2 Maxwell elements. Same system at different dc potentials it may have 2 arcs here and 3 arcs there. Now it is going to be a problem because your equations relating kinetic parameters to Maxwell elements, It will expect I have 10 kinetic parameters I am going to map it to 3 or 5 Maxwell elements in some I have only fewer numbers in some I have full set. That is going to be a problem. Second, let us say you have actually same number of loops everywhere and you are fitting it to same number of Maxwell element. We are not using potentiodynamic polarization data or you will have to alter it and put it as a constraint.

The actual problem is in the Maxwell element. If you change the values slightly the spectra may change a lot. Very slightly instead of 1.5 mF we use 1.6 mF, it may change a lot. So, you might think that I am using kinetic parameter mapping it to Maxwell element reasonably well within few percentage, but the spectrum predicted by that kinetic parameter can vary or can be very different from what is experimentally measured.

So I have experimentally measured data, fit it to a circuit, kinetic parameter map to circuit and I am mapping it almost correctly. It does not mean I will map the kinetic parameter to the spectrum almost correctly. Because it is very sensitive, slight changes here can alter here. That means I have to get a perfect match here and that is not going to happen. We have tried that method we have not been successful and these are the problems we faced.

And this seems to work [if at all it works] it will work when you have one intermediate species. If you have 2 intermediate species, you will get a headache.

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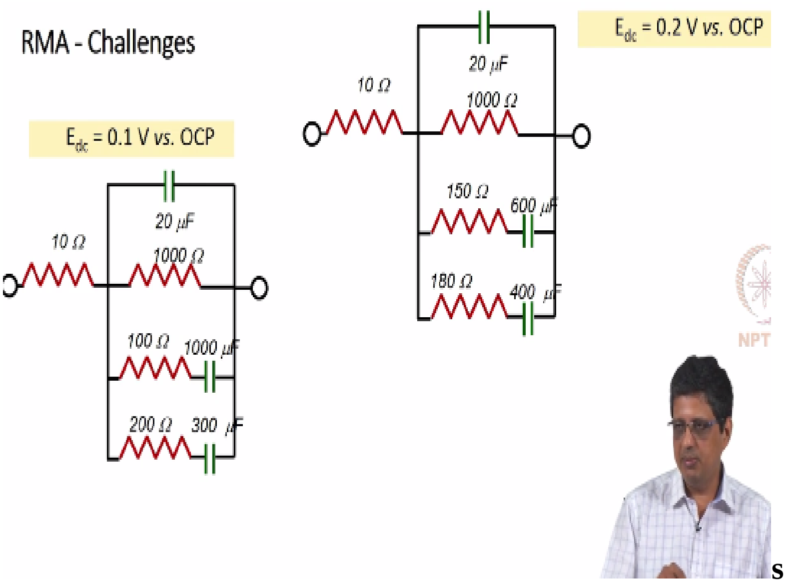

RMA - Challenges

E_{dc} = 0.1 V vs. OCP

E_{dc} = 0.2 V vs. OCP

Let us say, we are able to map the data very well. The experimental data is matched exactly with this spectrum and with circuit on the left hand side. Experimental data at point 2 is matched exactly with the circuit on the right side. Now I have to describe this R_{sol}, C_{dl}, R_P, R_1C_2, and R_2C_2. On the right side I will do something similar except I will say R_1 prime, C_1 prime, R_2 prime, C_2 prime because these corresponds to different circuit.

Now we have seen similar examples before I had just taken the circuit and put it here. When I map the kinetic parameters, I have to say k_{10}, b_1, k_{20}, b_2 are related in a particular way.

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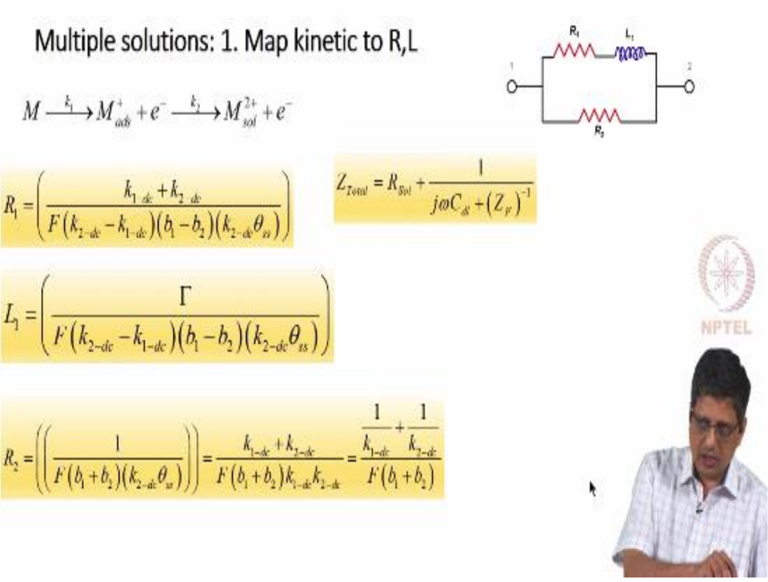

Multiple solutions: 1. Map kinetic to R,L

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

$$R_1 = \left(\frac{k_{1\,dc} + k_{2\,dc}}{F\left(k_{2\text{-}dc} - k_{1\text{-}dc}\right)\left(b_1 - b_2\right)\left(k_{2\text{-}dc}\theta_{ss}\right)} \right)$$

$$Z_{Total} = R_{Sol} + \frac{1}{j\omega C_{dl} + \left(Z_F\right)^{-1}}$$

$$L_1 = \left(\frac{\Gamma}{F\left(k_{2\text{-}dc} - k_{1\text{-}dc}\right)\left(b_1 - b_2\right)\left(k_{2\text{-}dc}\theta_{ss}\right)} \right)$$

$$R_2 = \left(\left(\frac{1}{F\left(b_1 + b_2\right)\left(k_{2\text{-}dc}\theta_{ss}\right)} \right) \right) = \frac{k_{1\text{-}dc} + k_{2\text{-}dc}}{F\left(b_1 + b_2\right)k_{1\text{-}dc}k_{2\text{-}dc}} = \frac{\frac{1}{k_{1\text{-}dc}} + \frac{1}{k_{2\text{-}dc}}}{F\left(b_1 + b_2\right)}$$

For example, R_1 can be obtained from k_{10}, b_1, k_{20}, b_2 for a given dc. L_1 or C_1 I will have an equivalent relationship that means I need to know R_1 L_1, R_0, R_2, L_2, or C_2 and then fit the values of k_{10}, b_1 etc. Problem here is, how do I know that 150 is R_1 prime and 600 C_1 prime. How do I know that 100 Ω has become 150, and 200 has reduced to 180? That is one possibility or I can just shift this up and down. I can say 100 has become 180 it has increased to 180 and 200 has decreased to 150. You cannot prove me wrong to circuit in parallel I can say this is up, this is down or this is up or this is down both mean the same thing. That means if I have taken data at 3 dc potential I cannot say this resistance capacitance pair has changed to this. This might have changed to this or the other one is also possible.

So I cannot tell with confidence which combination is the correct combination. Which means I cannot really map it that easily. that problem is that. We find it lot easier to what directly with the kinetic parameter and with the experimental data. the strategy we would suggest is to not go by the intermediate step of EEC, although it is tempting to say that this is an elegant way to doing it.

Now lot of people were not familiar we will say RMA, you have so many parameters I can fit anything. Some may claim that EEC is better because you have fewer number of parameters.

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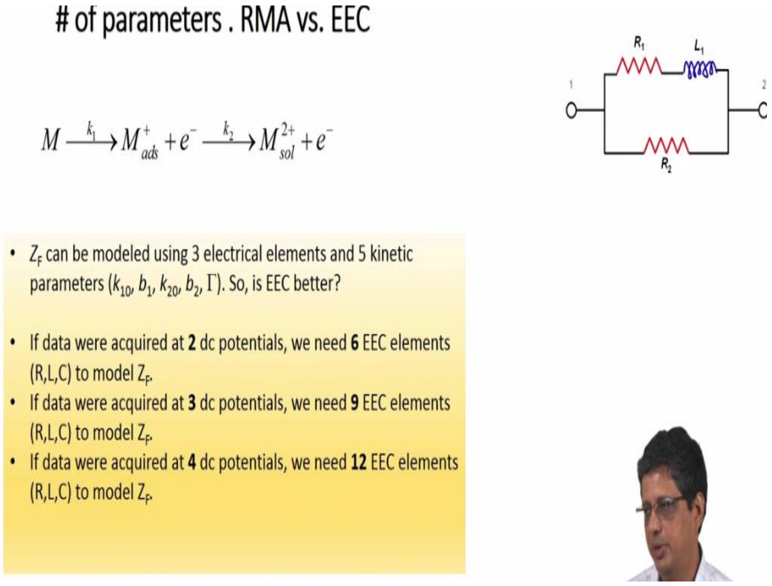

# of parameters . RMA vs. EEC

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

- Z_F can be modeled using 3 electrical elements and 5 kinetic parameters (k_{10}, b_1, k_{20}, b_2, Γ). So, is EEC better?
- If data were acquired at **2** dc potentials, we need **6** EEC elements (R,L,C) to model Z_F.
- If data were acquired at **3** dc potentials, we need **9** EEC elements (R,L,C) to model Z_F.
- If data were acquired at **4** dc potentials, we need **12** EEC elements (R,L,C) to model Z_F.

For example, take this reaction. First reaction is electrochemical and second reaction is also electrochemical. That means you have k_{10}, b_1, k_{20}, b_2, and Γ. And this has one adsorbed intermediate. That means you can represent it by one Maxwell element. Here I have shown you example of R and L. This circuit I have given here is for faradaic component alone. This is going to be in parallel with double layer capacitance and you may have solution resistance. We are going to say that is common for EEC or RMA. So, we can say that you have 3 electrical elements and you have 5 kinetic parameters. If you acquire data or 2 dc potentials you will have to represent using 6 electrical elements 3 here although you will throw one circuit, but when you tabulate it you have to say R_1, L_1, R_2 at this dc. R_1, L_1, R_2 at next dc. those are actually 6 variables. If you have like this 3, 4 the number of EEC element which you vary freely they keep on increasing. We still have the same kinetic parameters so we have 5 kinetic parameters to describe spectra at many dc potentials, the number of EEC element the circuit representation given in a figure can be misleading. You have to look at the circuit, you have to look at the table you will see the number of EEC parameters is actually more. But more importantly the physical insight you get from the reaction is valuable.

But you should not also imagine that it is valuable, but the disadvantage is it has more number of parameters. It is not easy to model many type of spectra with this. You have seen if it comes as negative, negative impedance it can be modeled only with a fewer type of reactions. You cannot just use simple reaction or many adsorbed intermediates, but if it does not have certain characteristics you will never be able to model the negative impedance.

So any mechanism with many parameters cannot model any spectra, that is one thing. Second it does not necessarily use many kinetic parameters. If you have 3 loops which means 2 Maxwell elements, 2 Maxwell elements mean 5 electrical elements R_1, C_1, R_2, C_2, and R_P. If we use 6 dc potentials you will get 30 Maxwell elements. Even if you use 20 kinetic parameters, you are still using fewer number of parameters and you are getting valuable information.

So that is something you need to keep in mind. as I have shown this example before you can map the kinetic parameters to R and L.

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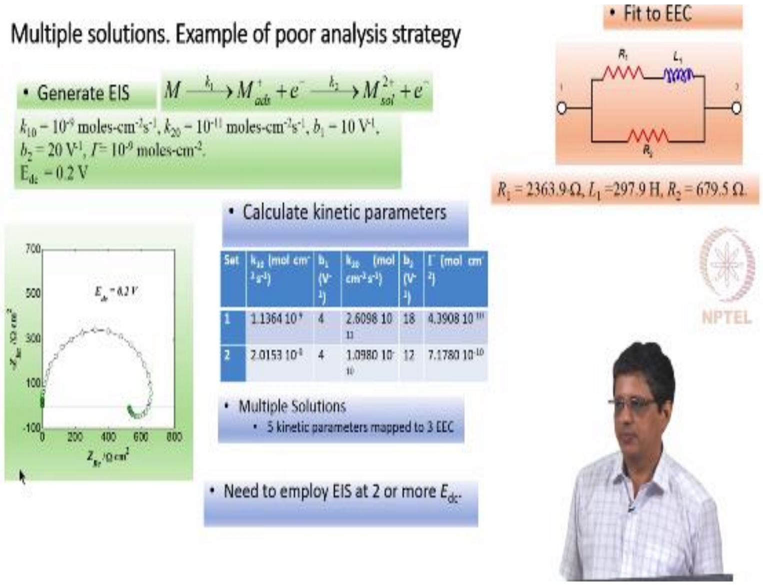

Multiple solutions. Example of poor analysis strategy

- Generate EIS $M \xrightarrow{k_1} M_{ads}^{+} + e^{-} \xrightarrow{k_2} M_{sol}^{2+} + e^{-}$

$k_{10} = 10^{-9}$ moles-cm^{-2}s^{-1}, $k_{20} = 10^{-11}$ moles-cm^{-2}s^{-1}, $b_1 = 10$ V^{-1}, $b_2 = 20$ V^{-1}, $\Gamma = 10^{-9}$ moles-cm^{-2}.
$E_{dc} = 0.2$ V

- Fit to EEC

$R_1 = 2363.9\,\Omega$, $L_1 = 297.9$ H, $R_2 = 679.5\,\Omega$.

- Calculate kinetic parameters

Set	k_{10} (mol cm^{-2}s^{-1})	b_1 (V^{-1})	k_{20} (mol cm^{-2}s^{-1})	b_2 (V^{-1})	Γ (mol cm^{-2})
1	$1.1364\ 10^{-9}$	4	$2.6098\ 10^{-11}$	18	$4.3908\ 10^{-10}$
2	$2.0153\ 10^{-8}$	4	$1.0980\ 10^{-10}$	12	$7.1780\ 10^{-10}$

- Multiple Solutions
  - 5 kinetic parameters mapped to 3 EEC

- Need to employ EIS at 2 or more E_{dc}.

One example to show that you should not use limited set of data to analyze and extract kinetic parameter. I have taken this example reaction M going to M_{ads}, M_{ads} going to M_{sol}, 2+ solution, and I have taken certain kinetic parameter values k_{10}, k_{20}, b_1, b_2, and Γ and at some dc potential and I have generated data. It gives an inductive loop for this kinetic parameters and I can model the faradaic component and of course I have used the solution resistance of 0. I have used some double layer capacitance I do not remember what that is, but let us say that we have model it to your circuit and I had taken only the faradaic component. I get values for resistance, inductance and another resistance here. Now if I model this one spectrum using kinetic expression, I can get infinite number of solutions. obviously the kinetic parameters are used to generate that is one possible solution.

In addition, I have shown 2 examples, but I can get many more example where you can verify if I take this kinetic parameter k_{10} corresponding b_1, k_{20}, b_2, and Γ I have in fact fixed b_1 all of this combination first set, second set, all of them will give rise to the same resistance, inductance, and resistance and we will give rise to the same. Because I am mapping 5 parameters to 3 elements.

So there are multiple combinations which are possible which will give rise to the same set of elements whereas if I take spectra at 2 different dc potentials, then I will not have this problem. Then I still cannot tell you this is going to be unique solution, but I can tell you there is some confidence that this is likely to be the solution. I can tell you at least it is not easy to get infinite number of solutions for the case when you have 2 dc potentials.

When you propose a mechanism, how do I first say how many dc potential should I even take data and then compare.

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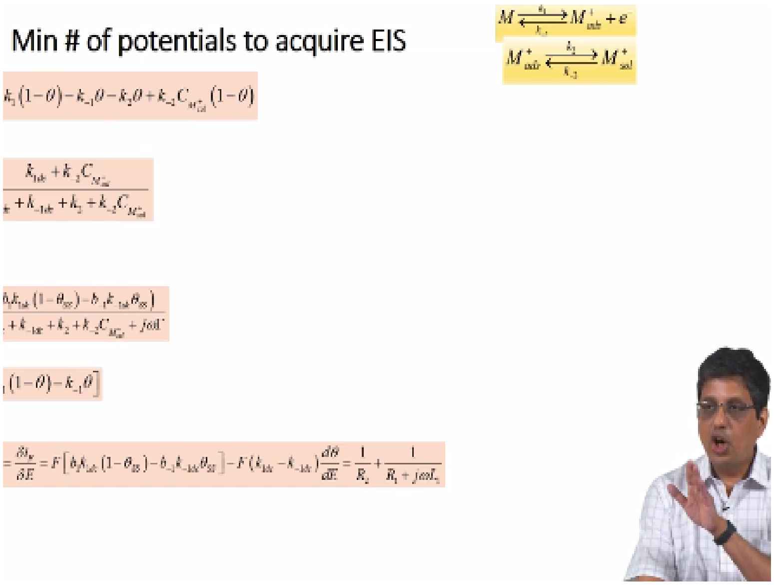

Min # of potentials to acquire EIS

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

$$M^+_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^+_{sol}$$

$$k_1(1-\theta) - k_{-1}\theta - k_2\theta + k_{-2}C_{M^+_{sol}}(1-\theta)$$

$$\frac{k_{1ss} + k_{-2}C_{M^+_{sol}}}{+k_{-1ss} + k_2 + k_{-2}C_{M^+_{sol}}}$$

$$(1-\theta) - k_{-1}\theta]$$

$$= \frac{\delta i_F}{\delta E} = F\left[b_1 k_{1ss}(1-\theta_{SS}) - b_{-1}k_{-1ss}\theta_{SS}\right] - F\left(k_{1ss} - k_{-1ss}\right)\frac{d\theta}{dE} = \frac{1}{R_2} + \frac{1}{R_1 + j\omega L_1}$$

Here I have shown a mechanism where you have metal going to M_{ads}^+, M_{ads}^+ is going into M_{sol}^+. Second step is a chemical reaction, first step is an electrochemical reaction. You can derive this expression. I am not going to derive this I will just say it is possible for you to derive and check that this is correct. Both are reversible reactions. If I propose this reaction, I should take data at certain number of dc potentials, and how many should I take is the question. One adsorbed intermediate means I know that I can model with one Maxwell element in parallel with the R_2 is charge transfer resistance it can be RC it does not matter. I can map all the kinetic parameters to 3.

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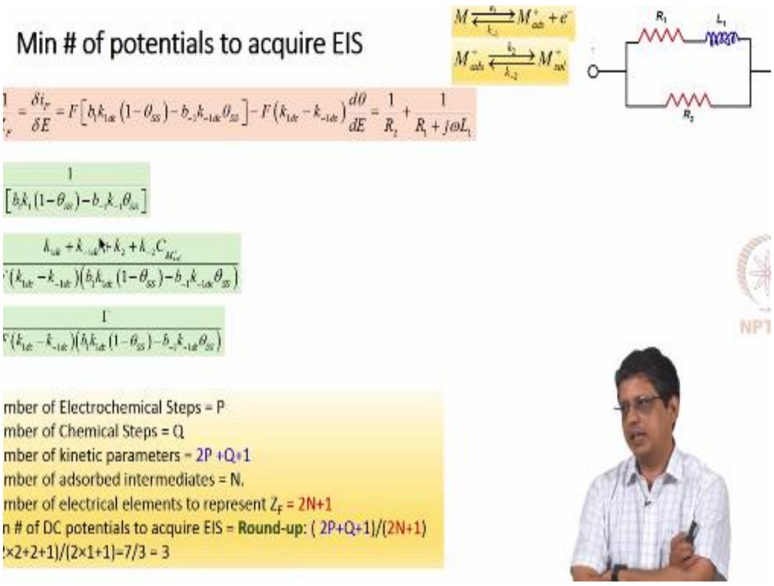

Min # of potentials to acquire EIS

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

$M^+_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^+_{sol}$

$$= \frac{\delta i_F}{\delta E} = F\left[b_1 k_{1dc}\left(1-\theta_{SS}\right) - b_{-1} k_{-1dc}\theta_{SS}\right] - F\left(k_{1dc} - k_{-1dc}\right)\frac{d\theta}{dE} = \frac{1}{R_2} + \frac{1}{R_1 + j\omega L_1}$$

$$\frac{1}{\left[b_1 k_1 \left(1-\theta_{ss}\right) - b_{-1} k_{-1}\theta_{ss}\right]}$$

$$\frac{k_{1dc} + k_{-1dc} + k_2 + k_{-2}C_{M^+_{sol}}}{(k_{1dc} - k_{-1dc})\left(b_1 k_{1dc}\left(1-\theta_{SS}\right) - b_{-1} k_{-1dc}\theta_{SS}\right)}$$

$$\frac{\Gamma}{(k_{1dc} - k_{-1dc})\left(b_1 k_{1dc}\left(1-\theta_{SS}\right) - b_{-1} k_{-1dc}\theta_{SS}\right)}$$

mber of Electrochemical Steps = P
mber of Chemical Steps = Q
mber of kinetic parameters = 2P +Q+1
mber of adsorbed intermediates = N.
mber of electrical elements to represent Z_F = 2N+1
n # of DC potentials to acquire EIS = **Round-up:** (2P+Q+1)/(2N+1)
×2+2+1)/(2×1+1)=7/3 = 3

The way to do this calculation is this. First find how many electrochemical steps are there. We have 2 electrochemical steps, reversible right that means 2 reactions. I will denote that as P. Each electrochemical step will need 2 kinetic parameters k_{10}, b_1, k_{-10}, b_{-1}. If it is chemical step, it will need one parameter each because there is no potential dependency. I will call the number of chemical steps as Q. kinetic parameter is going to be 2 P+Q, plus 1 for the surface site Γ. Each adsorbed intermediate will give me one Maxwell pair and in any case I have one R_P or R_t in parallel with all this. Even if I have 0 adsorbed intermediate, no adsorbed intermediate straight forward reaction one resistance is there. Each adsorbed intermediate will add a Maxwell element.

So if I have adsorbed intermediate it is going to be N, the total number of electrical elements present is going to be 2N+1. So minimum number of dc potential I need is 2P+Q+1/2N+1 and it may not be an integer, we have to round it up. Five parameters to 3 potentials we are going to say 5/3 it is 1 point something, we are going to say 2 potential we need. Here we have 2 electrochemical steps, 2 chemical steps one adsorbed intermediate, how many dc potential do we need it here? 2 point something. Once it exceeds 2 you need 3. If you take data at 3 dc potentials then you do not have to worry that you will get infinite number of solutions. Take it at 2 dc potentials just not try you have to model that data with this mechanism. Then I will just describe it to you. Even after I take a 3 dc potentials I cannot guarantee that this is unique solution. Reason is it is non linear equation.

We get guarantee for unique solution in linear equation with sufficient number of points. If you have a linear equation set of equation I can find the rank of the matrix and I can say that there are so many number of variables, so many equations, therefore I can get unique solutions or I will get infinite number of solutions and of course in some cases where you have inconsistent equation you will get no solution.

Non linear equation may give you a single solution, may give you multiple solution and there is no guarantee. And some of them may be physically meaningful, some of them may not be physically meaningful. If we say e^{-x}, you can visualize if this is Y axis and this is X axis, e^{-x} is going to go like this. If I say e^{-x} - sin x, I will get infinite number of solutions because sin is going to go like this. And this is going to intersect that sin x in infinite number of points. On the other hand, if I say $x-e^{-x}$, y equal to x goes like a 45 degree line. It is going to cut e^{-x} at only one location. It is possible you get one solution. In some cases it is possible you do not get any solution in real that is also there do not worry about that, but it is possible you get multiple solutions.

So I cannot guarantee solution is unique, but I have some confidence that it is not going to be infinite number of solutions. Hopefully, if I have enough number of dc potentials if I take data at more and more dc potentials and fit properly with the model, I have more confidence with the model description is correct. [we will stop here today].