Electrochemical Impedance Spectroscopy
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Lecture - 36
CPE

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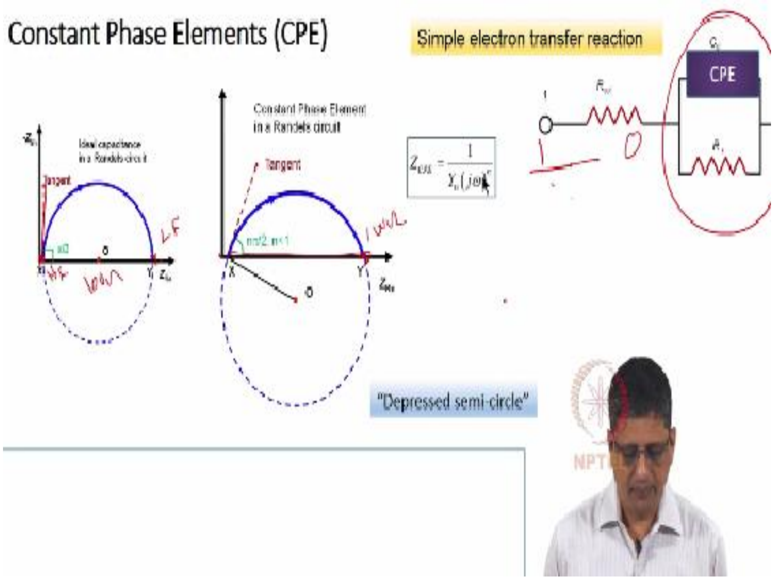

Constant Phase Elements (CPE)

Simple electron transfer reaction

$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n}$

"Depressed semi-circle"

So if you take a simple electron transfer reaction it is little easy to understand therefore I am taking that example. We have C_{dl} which represents the double layer capacitor, we have a resistance to represent the reaction at a particular dc potential, and we have R_{sol} right now I am going to neglect that and say it is very small value or zero value and if I draw the complex plane plot for this circuit I would get a semicircle.

[Please refer to video 0.50] This is high frequency data and this is where the low frequency data will end. I will get a semicircle and that tangent here is going to be at 90 degree, that is π/2 radians because we are assuming solution resistance is zero. And this semicircle has a origin on the real axis, but often when we do experiments we find that even if you take a very simple reaction we do not get a real semicircle.

Instead what we get is only a smaller part of circle. Now look at this the starting point and ending points are still the same. On the real axis it is still zero here and whatever value let us say 100 Ω it is going to be 100 Ω here this is also going to be 100 Ω, but this is as if it is part of a circle which is pushed down the center is pushed down. So sometimes this is called as depressed semicircle. And for this if you look at the tangent even if the solution resistance is zero. you look at the tangent it is going to be little less than 1, $\pi/2$. So we would write it as n $\pi/2$ and less than 1. So the circle radius is not the same as what it was before previously the circle diameter was R_t, now the circle diameter is not R_t it is larger than that. So this is still a fraction or part of a circle, but it is not really half a circle it is less than that. It is not that we are visualizing it as a arc like this, and this is what experimentally seen many times.

And this is represented by an element which is termed as 'constant phase element' so there is a reason for that I will explain that a little later. For this if you calculate the impedance you have to use two parameters. There are different ways of using this sometimes people write it as $Q\ (j\omega)^{\alpha}$ because we use α for charge transfer coefficient we are not using it here we will call it as n.

Sometimes people use Y_0 sometimes people use Y for admittance so we will have to have a compromise right now, I am just going to say Y_0 for the coefficient here and n for the exponent there. When n is the same as 1 this is going to be capacitance. We would write $j\ \omega C$ as the admittance for the capacitance $1/j\omega C$ as the impedance for the capacitance.

Here notice that the $j\omega$is within the bracket, and it is raised to the exponent n it is not $1/Y_0(j\omega)^n$ this case all the values are imaginary just that how it changes with omega will vary. In this case it is generally a complex number where n is not an integer. If $n=0$ is a real value, if $n = 1$, it is a capacitance and the impedance is a imaginary number not a complex number. You can say it is a complex number, but it really a imaginary number.

And if $n = -1$ it is going to be like an inductor it is again an imaginary number for the impedance. n is 0.5 it is going to be a complex number it has real part and imaginary part. In general, it is going to represent a complex number there.

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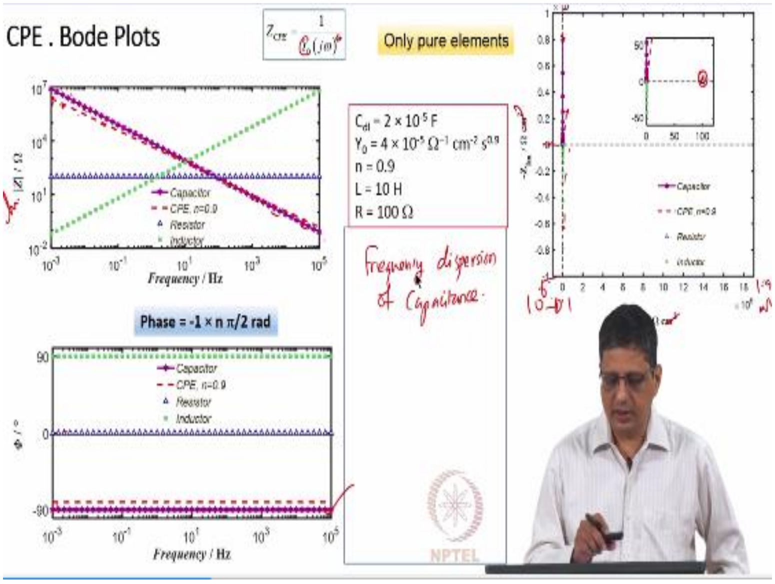

CPE . Bode Plots

$Z_{CPE} = \frac{1}{Q_0 (j\omega)^n}$

Only pure elements

$C_{dl} = 2 \times 10^{-5}$ F
$Y_0 = 4 \times 10^{-5}\ \Omega^{-1}\ cm^{-2}\ s^{0.9}$
n = 0.9
L = 10 H
R = 100 Ω

Phase = -1 × n π/2 rad

Frequency dispersion of Capacitance.

Now I want to show you how it looks like if I take the pure element and generate the impedance for various frequencies and plot it, in Bode plots as well as in complex plane plots. So I have taken this expression that Z_{CPE} as $1/Y_0$ jω^n. I have taken some examples where I am plotting a double layer capacitance with 20 μF is just an artificial calculation I mean artificial element I am calculating it so I am not writing it as per centimeter square.

Even here I should have written this, but it is okay Y_0, the units of Y_0 has to be such that this comes as Ω or Ω cm^2. So Y_0 will have a unit which depends on the value of n, here I am taking n as 0.9. I am also plotting the impedance for an inductor of 10 Henry, impedance of a resistor it is 100 Ω, it is always going to be 100 Ω. [Please refer to video 6.30] If you put it in a complex plane plot this is the imaginary axis and this is the real axis and this is sort of zoomed in version resistance is just going to be there 100 Ω regardless of which frequency we use. This is how the value will look like, if I really measure it is just going to just hover around that because there is going to be some experimental noise. If I take a good capacitor and measure it correctly high frequency is going to be here lower and lower frequency it is going to become more and more in magnitude, but it is still going to be an imaginary number.

If I take an inductor it is going to start at zero frequency it is going to be zero. [Please refer to video 7.16] Inductor has, at higher and higher frequency it is going to have more values and this is given in terms of 10^6, 1 MΩ 0 to -1, 0 to +1 MΩ or actually it is going from I think -0.1 to 1.9 M Ω are M Ωcm^2, let us sort it out. If you look here the red color line corresponding to 0.9 of the CPE.

It is actually going at a slight angle to this, when n = 1 it is a capacitor it is going vertically if n = 0.5 it is going to be go as a 45 degree line, n = 0 it is going to go as, a not as a line here it is just going to settle as a point n = -1 it is again going like this. Not just that notice the value I have used 4 x 10^{-5} for the Y_0 value. I used 2 x 10^{-5} for the capacitance and yet if I look at the magnitude here it is actually smaller at the lowest frequency.

It is a smaller value, that means you cannot just take this value and compare with this value. It would not even give you an idea of how the impedance will be for a given frequency. We will actually have to calculate it with the n value. If we have 2 capacitances, you do experiment you get 3 capacitances values for 3 different conditions, you can compare them and say something about it.

If you get constant phase elements sometimes it is n=1 sometimes it is n=0.95 another time is 0.98 another time is 0.92 you cannot just take the Y_0 values and compare them, it is not a fair comparison. [Please refer to video 9.40] Now if you plot them in Bode plot with log of z, I have put the log scale here with frequency in the log scale a pure capacitance will give me a straight line with a negative slope.

Basically I have to take this and take a log of this I am going to get log Z or if I take the magnitude the j will go away this is what will look like. So it is going to look like a straight line with a negative slope -1. If I take this as 0.9 it is going to look somewhat like that, but with a slightly lower slope. Zero, of course it is going to look like a 0 slope this -1 is going to look like a +1 slope here n = -1.

[Please refer to video 10.30] If you look at the phase here capacitor is going to look like this, sorry capacitor is going to look like this, this is actually 90 ° this is going to be lower than 90, 0 and +90 degree here. This element has a constant phase. Capacitor also has a constant phase, resistor has a constant phase, inductor has a constant phase. This element does not have the same phase as any one of those, but otherwise its phase is constant, although the magnitude is changing. This is the reason it is called a constant phase element. Sometimes, people call this behavior as ‘frequency dispersion of capacitance’. What they mean is, if you take a capacitor and calculate the impedance you can calculate the impedance based on the frequency. And if I tell you the impedance, and tell you the frequency you can calculate the capacitance. That means if I give you various values here, at each value you can calculate the capacitance and if I take the dark pink color line there I would get one value for capacitance. At each of these value, I will get the same value each of this frequencies. If I take this, I can still assume this is a capacitor and using this formula with n=1, I can calculate the value of C, but that will vary as we change the frequency. That is essentially saying if I assume that this is the capacitor and calculate the capacitance based on the impedance value and the frequency value I will get a capacitance but that is a function of frequency that is not identical value everywhere that is another way of saying that it is a constant phase element. So they would call we see a frequency dispersion of capacitance, that means we are not seeing a ideal capacitance everywhere we are seeing a frequency dependant capacitance here and that is essentially a constant phase element.

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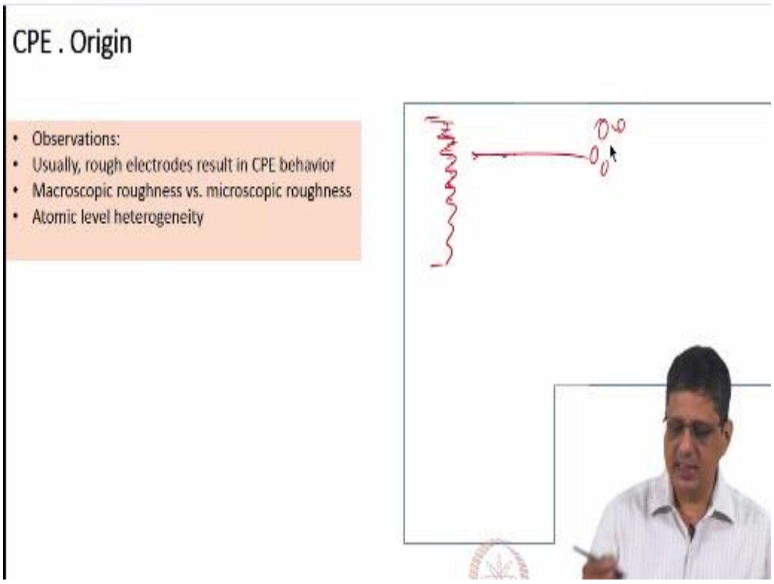

CPE . Origin

- Observations:
- Usually, rough electrodes result in CPE behavior
- Macroscopic roughness vs. microscopic roughness
- Atomic level heterogeneity

Now where do we see this, and how does it occur. Usually this is seen when the electrode surface is rough and initially researchers thought that is because you have a rough surface, the double layer capacitance and the resistance keeps varying across the surface to a significant level, that is you have millimeter level or multiple scales of roughness, millimeter level micron level or nanometer level. People used the thing that it may be caused because of rough electrode in millimeter level or 100s of micron levels roughness. Microscopic roughness means the electrode appears to be more or less smooth even if you look in micron level scale, but individual locations have different energy levels. Energy level means for a reaction to occur if they have an alloy surface let us say one of the element promote the reaction other element does not promote the reactions or it promotes the lesser level.

And if I have atoms surrounded by different atoms it may promote a particular level, but the surface may look flat. If I just use an AFM and measure the roughness it may look flat, but this energy levels are different means the reaction is catalyzed to a different level, that is a possibility. If I take a pure element and roughen it again I will get a different crystal plain and they may again have different energy levels for promotion of reaction.

So now the thinking is that it caused by atomic level heterogeneity, not by macroscopic level heterogeneity. Although generally if you introduce macroscopic level heterogeneity meaning if you make a rough electrode the atomic level heterogeneity will also be there in general that is true.

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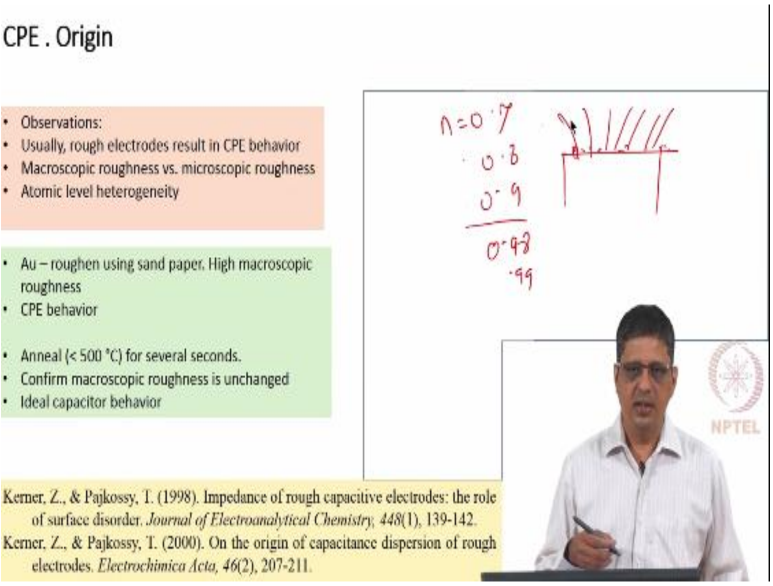

CPE . Origin

- Observations:
- Usually, rough electrodes result in CPE behavior
- Macroscopic roughness vs. microscopic roughness
- Atomic level heterogeneity

- Au – roughen using sand paper. High macroscopic roughness
- CPE behavior

- Anneal (< 500 °C) for several seconds.
- Confirm macroscopic roughness is unchanged
- Ideal capacitor behavior

$n = 0.7$
0.8
0.9
0.98
$.99$

Kerner, Z., & Pajkossy, T. (1998). Impedance of rough capacitive electrodes: the role of surface disorder. *Journal of Electroanalytical Chemistry, 448*(1), 139-142.
Kerner, Z., & Pajkossy, T. (2000). On the origin of capacitance dispersion of rough electrodes. *Electrochimica Acta, 46*(2), 207-211.

And the way its concluded is like this. So you take a gold electrode, make it rough clean it with acid, alkali, hydrogen peroxide these things will usually remove material it would not remove gold, but it will remove any other contaminant that may be present there, and conduct a simple electrochemical reaction and see how it behaves and it will behave like a constant phase element, it would not give you a pure capacitance.

Next you can anneal at moderate temperature not very high temperature. If you go to high temperature gold will melt, you go to less than 500 gold will not melt, but it will anneal meaning some of the stress will be relieved and to some level very small fluctuations, roughness will go away, but the major roughness will not go. So if you take a SEM or AFM before annealing and after annealing structural change in terms of physical morphology will not be significant.

But if you do a electrochemical experiment at least they report that it behaves more towards an ideal capacitor that means initially if we say the roughness leads to a n of 0.7, 0.8, 0.9 somewhere in this range depending on how rough the surface was, not really depending on how rough in physical sense, but in terms of the variation in the energy levels. After annealing and maintaining the same physical roughness they get close to 0.98, 0.99 somewhere in that region.

And that leads to a conclusion that what you see here is because of energy level variation, energy level variation is one way of saying that another way of saying that is that the current distribution is not uniform. If the reaction occurs at the same rate everywhere in the electrode, current will also occur at the same rate; assuming of course potential is also distributed evenly.

If the rate is different at different locations the current passing through at each of this region if we imagine that these are different islands, that is also going to change and the proposal is that this is causing a CPE behavior. Of course none of these are like really agreed upon by everybody it is proposed that this is one possible reason.

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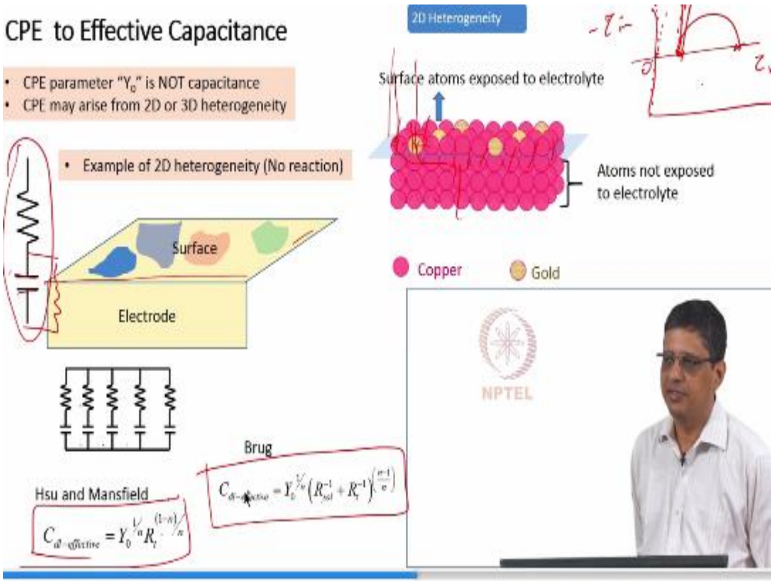

CPE to Effective Capacitance

- CPE parameter "Y_0" is NOT capacitance
- CPE may arise from 2D or 3D heterogeneity

- Example of 2D heterogeneity (No reaction)

2D Heterogeneity

Surface atoms exposed to electrolyte

Atoms not exposed to electrolyte

Hsu and Mansfield

$$C_{dl-effective} = Y_0^{1/n} R_t^{(1-n)/n}$$

Brug

$$C_{dl-effective} = Y_0^{1/n} \left(R_{sol}^{-1} + R_t^{-1}\right)^{\left(\frac{n-1}{n}\right)}$$

The other thing that one needs to notice the Y_0 value is not a capacitance, the CPE behavior can arise from different causes. In one case it is heterogeneous surface it is 2D distribution. So I just tried to plot it here or picture it here, you have a surface this is hidden from the solution only this top surface is visible to the solution and I just shown it in different color to say that it is a flat surface, but these are actually behaving slightly differently in terms of electrochemical reactions.

If it is identical, then I would just represent it by one capacitance here and a solution resistance here that is all there is no reaction here and this is just another pictorial, to say this is the surface atom these are all below the surface and out here, they are not of the same color they are different color just to indicate that the pink color may be copper, the yellowish color may be gold so that is actually a heterogeneous surface.

Although it is a flat surface now if I model this, I should probably model this with many different capacitance and resistance.[Please refer to video 18.35] This has a capacitance, and this has a solution resistance this is the capacitance with solution resistance. So various capacitance values here and solution resistance, that is a possibility. So I should actually model it with many capacitance and resistance in parallel, I mean capacitance resistance unit in parallel that would say when I sent electron down here it is going through a multiple paths here, and then it will be collected and pass through the potential straight at the other end. You may have a simple transfer reaction in which case you would get R_{sol}, R_t and of course Y_0 and n here. So there are different proposals, in one proposal solution resistance was not considered and you can extract an effective capacitance from this, so you obviously cannot use Y_0 as a effective capacitance.

But you can use this formula to estimate the effective capacitance. How do we get the formula? I have not told you that yet. It is another proposal to say that if solution resistance is zero of course this two are going to be matching, but when it is not zero you have a slightly different formula yeah go ahead. Which graph no this graph is for a case where you have a resistance. [Please refer to video 20.00] So what I showed you earlier I will just extend it a little more I will say this is the origin this is Z real, and -Z imaginary.

Pure capacitance high frequency will start here low frequency will go here. It is in the imaginary axis pure inductance will go like this except that low frequency have low impedance high frequency have high impedance. Pure resistance will just have one on the real axis, one point. A constant phase element with n slightly less than 1, will look like a capacitor but it is going to be an angle it is a complex number. If I say there is a resistance and then a capacitance or resistance and capacitance will start here and will have value like this. A constant phase element under resistance will have starting point here, because even if

I go to infinite frequency I will get zero impedance from this capacitance or from the constant phase element, but the resistance will be there, it is not going to be zero.

So resistance plus a constant phase element, resistance plus a capacitance will have lines here. It is still going towards infinity when I go to low frequency. This in parallel with resistance will give me this and in those cases I can use these two formulas to extract an effective capacitance. Sir like you discussed in the previous slide that if we have different current at different points so we consider as a non-homogeneity existence there will be CPE will exist. So can we say with this also like copper and gold they have different conductivity, different resistivity, so maybe we get it. At this level the conductivity difference is not very significant, meaning we are measuring few Ω few mΩ etc. Yes, there is a difference in conductivity, but that is not causing when we have copper wire, aluminum wire, little longer wire, shorter wire by and large you would not see much difference in the impedance measurement.

Only in special cases even that it is not that it is pure copper or mixture of copper and aluminum any of those causing the problem. When it exposed the solution it is not the conductivity of this and this causing the difference, it is the reactivity that is causing the difference.

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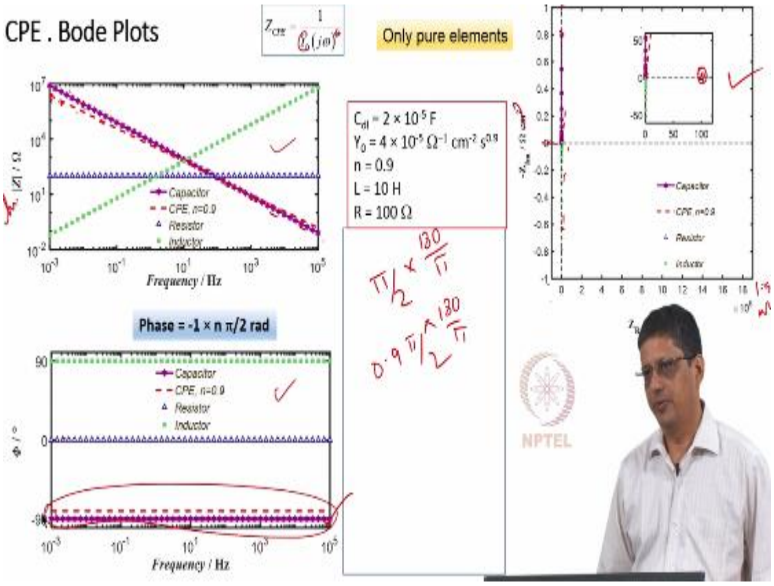

CPE . Bode Plots

$Z_{CPE} = \frac{1}{Q_0(j\omega)^n}$

Only pure elements

$C_{dl} = 2 \times 10^{-5}$ F
$Y_0 = 4 \times 10^{-5}\ \Omega^{-1}\ cm^{-2}\ s^{0.9}$
n = 0.9
L = 10 H
R = 100 Ω

Phase = -1 × n π/2 rad

$\frac{\pi}{2} \times \frac{180}{\pi}$

$0.9\frac{\pi}{2} \times \frac{180}{\pi}$

Which one the one on the complex plane or the one on the bode plot? Complex plane, the red color dash line is the CPE, the violet or dark pink color is the capacitance. Of course I wanted to show you in equal scale therefore I have plotted like this if you zoom in more and more you would see a difference. No, one is at a slight inclination look the dark pink color line is a straight line vertical line.

Both are straight lines that is correct, but both are not vertical lines. This red color line is a straight line, but at a slight angle to the vertical. In fact that is what given by the previous slide. The vertical line is at $\pi/2$ this is 0.9 $\pi/2$. Of course you can get into degree $\pi/2$ is in radians this is at a slightly lower angle if you put it in equi-scale this may not appear that well if you zoom in and put different scale you might see the difference better.

Another way to look at it is this, look here you would see a difference. Magnitude of course there is a difference, but magnitude I can chose a different value of Y_0 and make it come closer even closer than this phase value will not change.

So these are obtained using the following method. [Please refer to video 24.50] If you take a regular Randles circuit and plot this in complex plane plot you can relate them, peak value here meaning not the imaginary and real value and at what frequency do we get the maximum here from that you can calculate the capacitance.

If I change the capacitance you have done this in the exercise. If you change the capacitance without changing the solution resistance and charge transfer resistance, the points here will move although the line entire line will not appear to change. Points there will move and if I mark the frequency at which the maximum occurs, I can find capacitance from there so there is a way to extract the capacitance by looking at the maximum value here.

I can do similar things in impedance I mean I can do the same thing in admittance format also meaning admittance it is going to look like it is going to if it is a fixed value here it is going to be fixed value here another fixed value slightly here and I can look at the maximum value, maximum or minimum whichever that is and then say that can be used to relate to the capacitance.

In case of CPE, obviously it is not a semicircle, but you can still take the maximum and if you say in CPE, the maximum can be related and you can extract the capacitance this is how you would get the capacitance value. In admittance form, one of the equations would come in the impedance form the other equation would come, but basically these are taken by using the procedure which we normally used to take peak value and extract the capacitance from there.

Of course now we do not do right, we can fit it using the software. Previously what people would do is when they do not have access to such program they would plot it get the R_{sol} by extrapolating in the graph get the R_t by marking, where this points will go and then go to the center, center meaning the peak value note which frequency that point is and from that they would calculate the capacitance.

Now we would use the software use optimization and then get the value because we can fit it to many types of circuits, but this is the origin of this equation.

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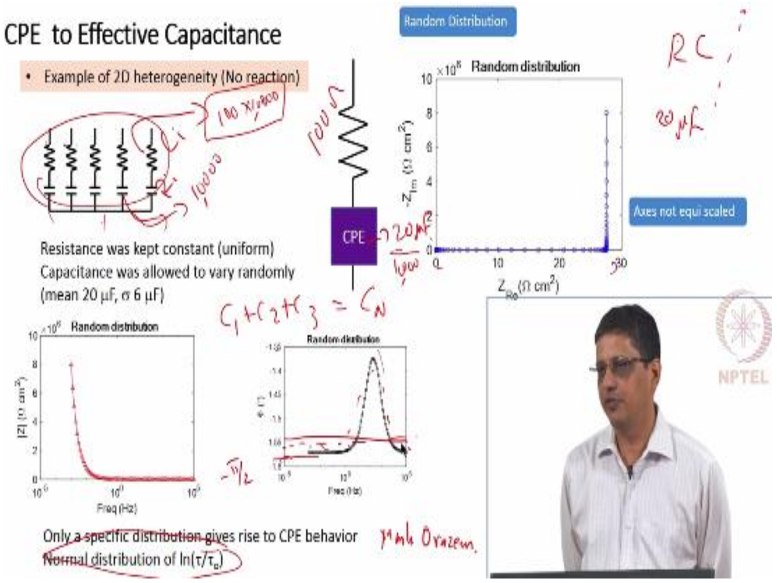

CPE to Effective Capacitance

- Example of 2D heterogeneity (No reaction)

Resistance was kept constant (uniform)
Capacitance was allowed to vary randomly
(mean 20 μF, σ 6 μF)

Only a specific distribution gives rise to CPE behavior
Normal distribution of ln(τ/τ₀)

However, I also want to note the following if you just take many resistance, capacitance in this form and randomly assign values, here what I have done is I used the fixed resistance value everywhere, but randomly change the capacitance value. Randomly meaning I have taken it such that it varies between 20, so I have taken a standard deviation of 6 μF average of 20 μF and 3 σ stress the limit.

So I have allowed it to very randomly. So what I have done is taken one unit divided by 10,000 units. Resistance also of course changes it becomes much larger so that they are in parallel it will still give you the original resistance more or less. If I use the random distribution and plot it first of all note that these are not equal scale, this is 0 to 30 this is 0 to 10 MΩ.

If it is a pure simple resistor with a simple capacitor this is how, it has to look it has to start at 30 Ω and just go as a vertical line. A CPE behavior would go like this, here you would see it actually goes like this. It moves to the right and then goes out. What that means is, if I have random distribution of resistance and capacitance here I will not get a CPE behavior. So when we say atomic level heterogeneity is there and the resistance and capacitance vary they are not identical.

Therefore, we are getting a CPE behavior, we are not going to really get that because if I look at the phase here I generated the spectrum and then look at the phase it is not, this is supposed to correspond to $-\pi/2$, $-\pi/2$ if it is pure capacitance. If it is CPE it is going to be little less than that but it is going to be flat everywhere. [Please refer to 29.20] Instead I get the distribution like this; it is varying from -1.6 to -1.35, and that does not give me a CPE behavior.

So there is a proposal, Orazem-Tribollet book tells that a particular type of distribution gives rise to CPE behavior, and that is basically a Gaussian distribution not in terms of the capacitance but in terms of $\ln(\tau)$. τ here is the time constant corresponding to each R and C. So the resistance and capacitance can vary and that together is called variation in τ and that τ distribution has to be in a particular form only then you would get a CPE like behavior.

So we cannot just say that randomly these vary and then they will get that or uniformly they are varying you cannot assume any particular distribution other than what is proposed there because only that I have not tested it, but I am just taking it on face value that only a particular distribution will give you the CPE behavior. Of course when we experimentally prepare we see this we are not somehow preparing in that distribution.

So that is a proposal to say that can give rise to that CPE behavior. What it means it there is no universal clean explanation universally agreed upon by everybody to say you get CPE behavior because of this there are proposals, there are some cases where you can eliminate the possibility. We can eliminate the possibility that a random distribution of capacitance and resistance will give rise to CPE behavior. And with experimental error that might appear somewhat similar to this, but it is not going to look like a clean CPE if you are preparing it in a random manner.

“**Professor - student conversation starts**” No see if we take 2 resistance in parallel the effective resistance is going to be half of that right. So it is not going to be same as that resistance. If it distributes it into 10,000 resistances I would say that each resistance is 10,000 times the original final value that I am looking at.

If I say one resistance one CPE is final model right and I think the resistance is for example in this case I have taken it, it is artificial I have synthesized it so I say 100 Ω as the resistance and 20 µF is the capacitance that I am looking at, but it is a CPE so it may be 25 with the proper unit and then 0.95 or so. What I am doing here is to take 100 Ω multiply by 10,000.

So each resistance is going to be large resistance, but when I have many large resistance in parallel, I am going to add the admittance of these to get the effective admittance right in this case of course I am going to add the admittance of this unit, not just the resistance, but each resistance is not going to be the, if this is the value I will say this 100 Ω and I have taken in this example I have taken 10,000 such elements. [Please refer to video 33.10] I would start with 10 MΩ for each or 1 MΩ for each. So this is one MΩ, this is one MΩ and so on. If I have 10,000 such elements assume just right now imagine the capacitance is not there. I will have to use much larger rate, I cannot use the same number.

I have taken up resistances many resistances and taken up many capacitance values, but assuming I want to get around 25 or 20 or 30 Ω and I am going to prepare n number of them I decide how many numbers I am going to use.
So I chose 10,000 numbers. I am actually recalling from memory I do not remember exactly what number I chose, but somewhere around that 20 or 25 Ω for the final value that means I have to choose 25x10,000. Capacitance values, you can again calculate right? For the capacitance if I want if I am expecting 20 µF here or something equivalent to that in the CPE now I would not expect 20 µF in the CPE.

I will expect some equivalent value there. I would divide this into 10,000 so 2 µF by 1000, 2 nF each if I use exactly 2 nF each then there would not be any CPE distribution because resistance is uniformly distributed, the capacitance is also uniformly distribute so all that I need to do is, this is 1 MΩ -+ 2 nF, take that element and then say that is I will calculate the impedance or admittance add the admittance or multiply that by 10,000 times I will get the final admittance.

So that is going to be a proper resistor plus a capacitor, that is all, whereas if I say either the resistance or the capacitance is distributed or both are distributed, meaning on the average I am going to use 2 nF, but I am actually going to go from 0.22, 3.8 nF. Randomly I am going to vary that on the average it is still going to be 2 nF then what I get is this.

Yeah it is okay we will get the same result. No not very different if I use 2 elements versus 20 elements there is going to be a difference. If I use 100 elements or 1000 elements, you are not going to see much of a difference. I used use 10,000 because for sure that is large enough number of distribution. Can we say that by doing this calculation we get a different value from we are going to measure it manually we are going to measure that point.

The point of this exercise was to show a random distribution of R and C will not give you CPE behavior. So if you use 10,000 or 1000 I do not think it is going to make a difference. [Please refer to video 36.30] If you use 1000 or 100 it will look little more grainy, if you use 100 or 10 probably there will be more grain in that in the sense this looks smooth right. It will probably look somewhat like this if I use for your elements if I use five elements it will not be that nice.

But then five elements is not really a good way to say it is very heterogeneous surface for the picture it is okay I have to draw some pictures so I show 3 or 4 islands, but that is not what I really mean when I say it is heterogeneous I mean there are many and they are not randomly distributed that was the point. If you use actual measurement you will get a CPE behavior all this information here is to see whether we can get the CPE behavior by using some circuit.

Then we can say this probably this is the origin of the CPE behavior and the general idea is yes this seems to be the origin of the CPE behavior, but this is not coming from random distribution. Now I have not created this distribution and verified it yet that is why I am not able to tell with confidence that if you have many such elements, but where the RC values are distributed in this particular way you will get a CPE behavior
In order to that I should create it, simulate it and then it show that it goes like this. I have not done that yet, but that is what is proposed in literature so I am showing it to you informing you that this is the proposal. It is probably correct but I cannot say with confidence, but definitely the random one will not give you that I can say with confidence. It is also possible to get the CPE behavior with what is called 3D heterogeneity.

Imagine you have a film, from one location to another location you may have a difference in the film or you may not have a difference. In the film itself when you go from the electrodes to the solution the properties can change, composition can change.

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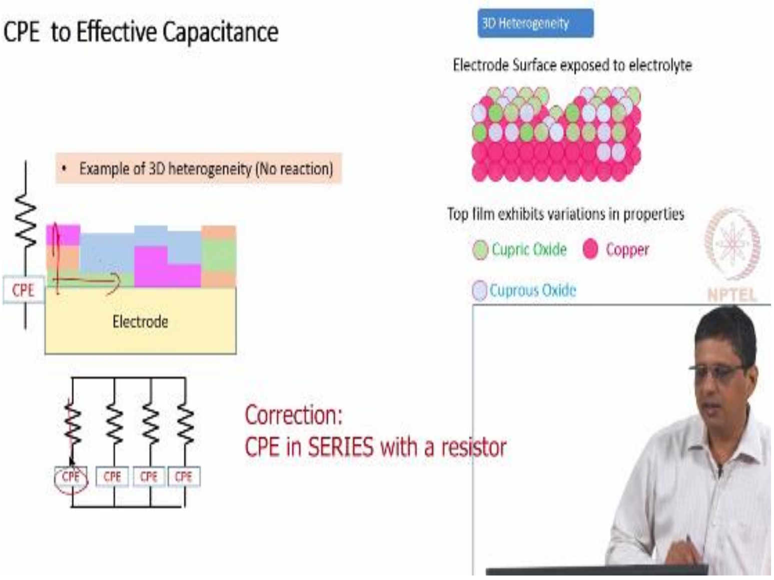

CPE to Effective Capacitance

- Example of 3D heterogeneity (No reaction)

Correction:
CPE in SERIES with a resistor

3D Heterogeneity

Electrode Surface exposed to electrolyte

Top film exhibits variations in properties

● Cupric Oxide ● Copper

○ Cuprous Oxide

So that is what I have tried creating here. One is to say location to location you have difference, that is a possibility, but within a location if it is completely uniform another location it is a different color, but again uniform that is still you can consider it as a 2D heterogeneity because only when you move from one location to another location you see a difference, but if you move vertically the third dimension there is no difference.

But what is shown in the pictorial representation here, is if you go in this direction there is a difference if you go on the surface of course in the picture I will show only one line, but if you imagine there is an electrode on the surface if I move, at a given location in the high still you can see a variation then this itself you have to represent by a CPE in parallel with the resistance and still we are assuming there is no reaction.

So this also gives rise to a CPE behavior, of course you are starting with this so even if you have only one it is going to show you CPE behavior this mixture will show you a CPE behavior and in a pictorial level I have tried representing this by CuO, means there is going to be larger molecule, but here I just showed it like similar sized one with different color. Dark green, light blue and pink color, pink color is copper, one type of oxide another type of oxide. You see a height variation; you see a composition variation, this can also give rise to a CPE behavior. There is one more factor, with that I will stop. The admittance is given by $Y_0\ j\ \omega^n$.

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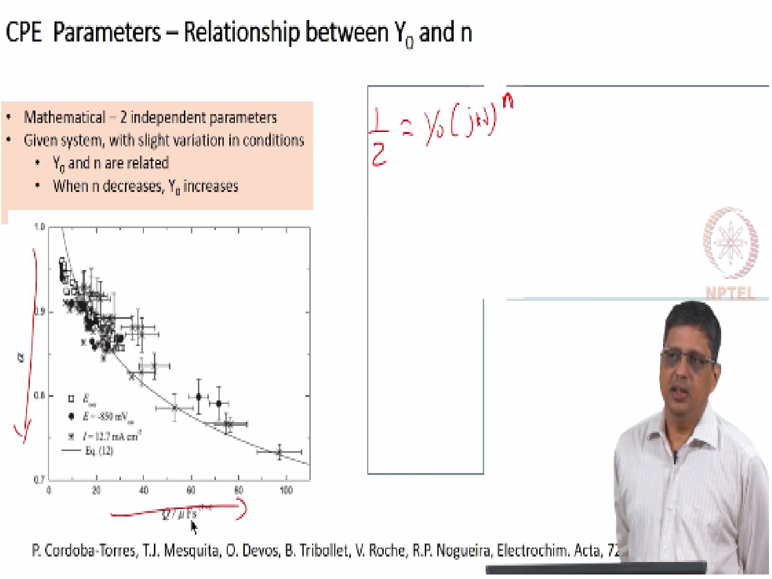

CPE Parameters – Relationship between Y_0 and n

- Mathematical – 2 independent parameters
- Given system, with slight variation in conditions
  - Y_0 and n are related
  - When n decreases, Y_0 increases

$\frac{1}{Z} = Y_0 (j\omega)^n$

P. Cordoba-Torres, T.J. Mesquita, O. Devos, B. Tribollet, V. Roche, R.P. Nogueira, Electrochim. Acta, 72

Mathematically they are two independent values we are fitting it and you are finding Y_0 and n, but actually if we take a system, get the CPE value by doing the impedance spectroscopy fitting it to a circuit, change it slightly may be different dc potential, different solution slightly different solution. You get another CPE value or maybe roughen the electrode and get the CPE value.

You will find that the Y_0 and n values are not completely unrelated, they are not independent. I am not saying take gold electrode in sulfuric acid, take copper electrode in potassium hydroxide and compare them, even there you might be able to compare, but take one system and find some variation there either potential or composition. You would find basically it looks like same electrode, same solution with slight change.

You will find that they are related when n value decreases, Y_0 value will increase Y_0 unit of course should be in similar scale if you write $\Omega^{-1}\ cm^{-1}\ S^n$, centimeter inverse s power n you should write all of them in the same way. If you write it in kΩ we should write it in the same way, but S^n, n will vary it is going to 0.9, 0.95 etcetera depending on what the exponent is.

But if you plot them as the value of what is shown as α here, that is n decreases value of the CPE exponent not exponent the pre-exponent Y_0, what we call Y_0 what they call as Q that increases. That means they are related they are not completely independent. We will stop here today.