Characterization of Construction Materials
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Lecture -66
Electrochemical testing (Corrosion) using EIS - Part 1

Good evening, I am Sripriya and I have recently finished my PhD in the area of corrosion. Today I will be handling the class with the electrochemical testing using EIS.

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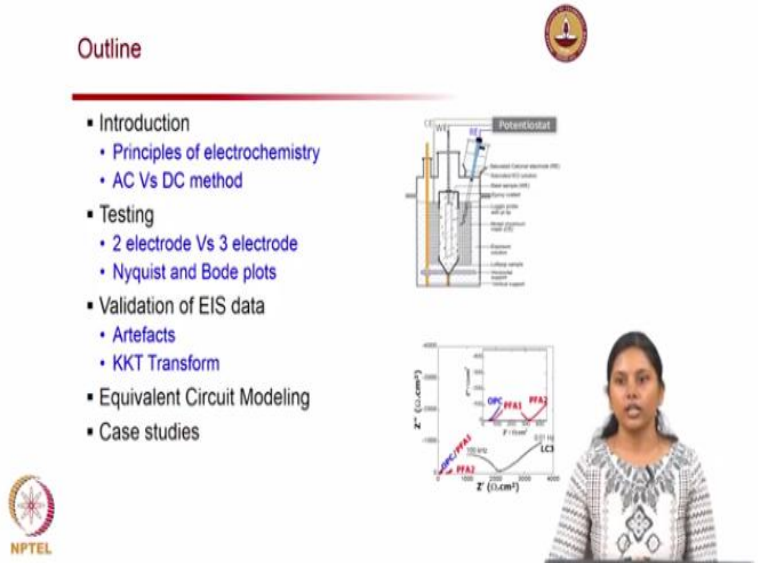

This is the brief outline of my presentation. First I will be going through the principles of electrochemistry; AC versus DC method. Then the actual testing: 2 electrode system vs. 3 electrode system. The different EIS plots we get Nyquist plot and Bode plots; Validation of EIS data using different techniques and then formulation of Equivalent Circuit Modeling followed by case studies.

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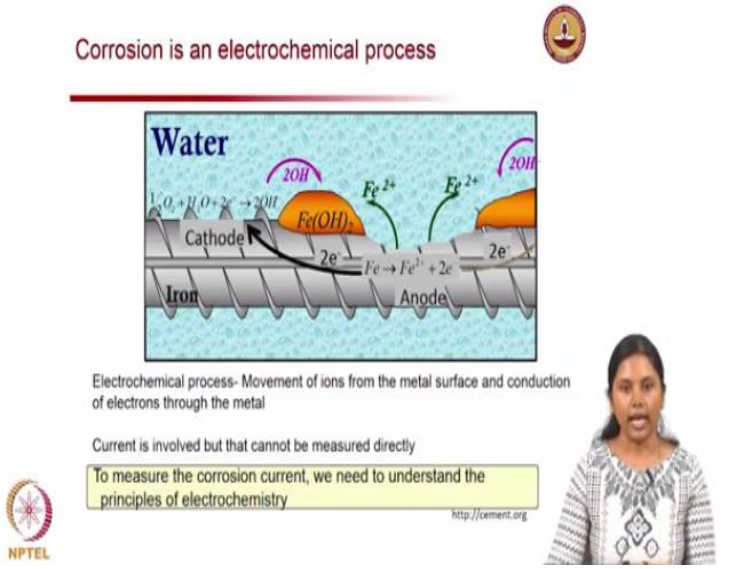

Corrosion is an electrochemical process, so it involves movement of ions and electrons. So if there is a movement of electrons we know that that is current, this current is called corrosion current. But this current cannot be directly measured as it is in the equilibrium state. So to measure the corrosion current we need to understand the principles of electrochemistry.

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What happens when a metal is immersed in a solution? So when a metal is immersed in an electrolyte there will be a reaction, and because of the reaction there will be a surface charge formed on the metal. Due to the surface charge, ions from the electrolyte will move towards the surface and gets adhered to the surface. This adherent layer is a fixed layer and surrounding that

layer we have another layer called diffuse layer, where there will be dispersed ions and then there will be the electrolyte.

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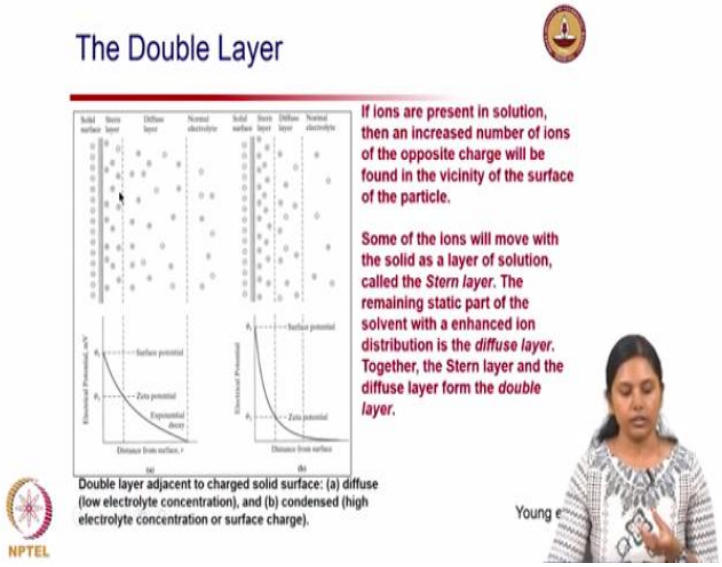

So this is the typical representation of a double layer; first we have a surface layer with some ions on it and then stern layer which is the adherent layer followed by a diffuse layer. And the stern layer and the diffusion layer together forms the double layer. And then we have a normal electrolyte.

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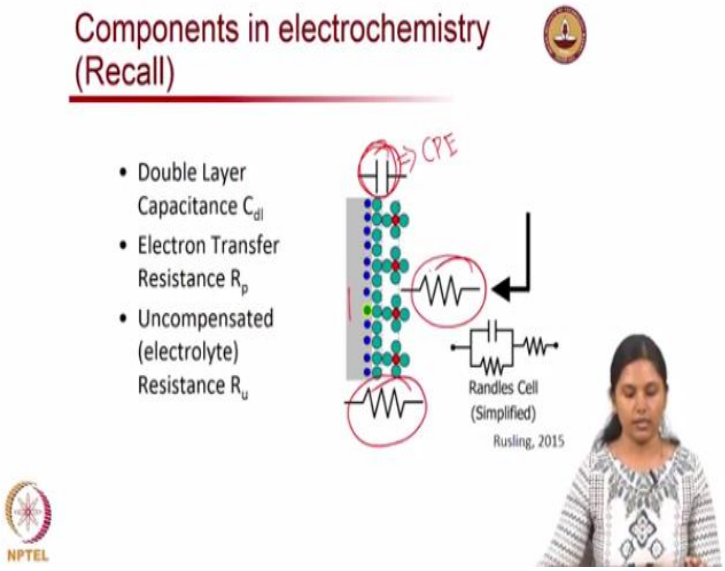

So the components can be represented as the metal (as shown in figure) and then electrical double layer which is represented by a capacitance and resistance in parallel and then we have a

solution resistance, so this is represented by electrical double layer. This and this (resistance and capacitance) together forms the electrical double layer. Here you can see that the diffuse layer is not a fixed layer, so this capacitance is not ideal in nature and can be represented as constant phase element (CPE). That means it is not ideal in nature. Secondly, this part you have electron transfer resistance (R_p); there are two terms which are used interchangeably that is charge transfer resistance and polarization resistance but they have a subtle difference in their meaning. For now we will represent it as R_p alone and then we have the normal electrolyte solution resistance.

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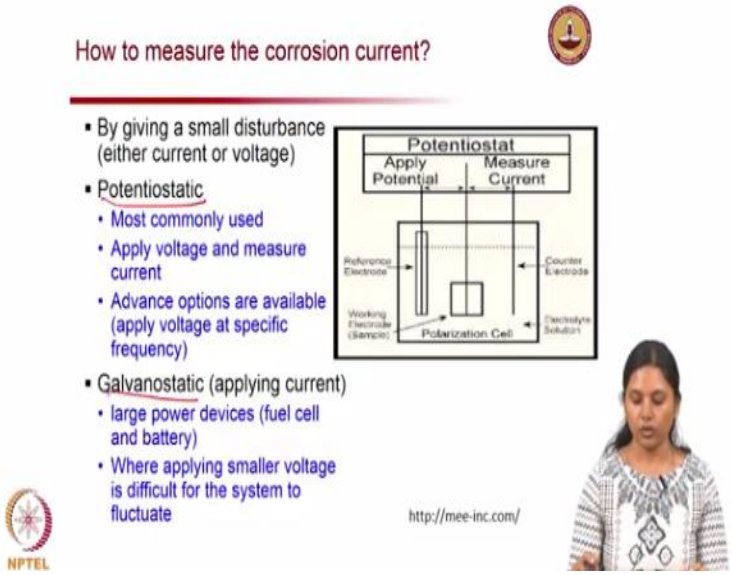

So now we know that we have a system with different components, but how to measure the current that is happening in the system. Since it is in equilibrium, we need to give a small disturbance by applying either current or voltage. If we are applying a small current and then measuring the voltage, that is called Galvanostatic. But if we are applying a small voltage and then measuring the current, then it is called Potentiostatic. This Potentiostatic is the widely used mode because it is applicable to lot of applications and it is flexible also. There are different advanced options available; that is you can apply voltage at specific frequencies in different systems like Solartron. Galvanostatic is usually employed for large power devices, that is, fuel cells and batteries where applying small voltage will be difficult for the system to fluctuate. So instead of applying voltage and measuring the current, we apply current and then measure the voltage. So we now move on to the next thing based on Potentiostatic mode.

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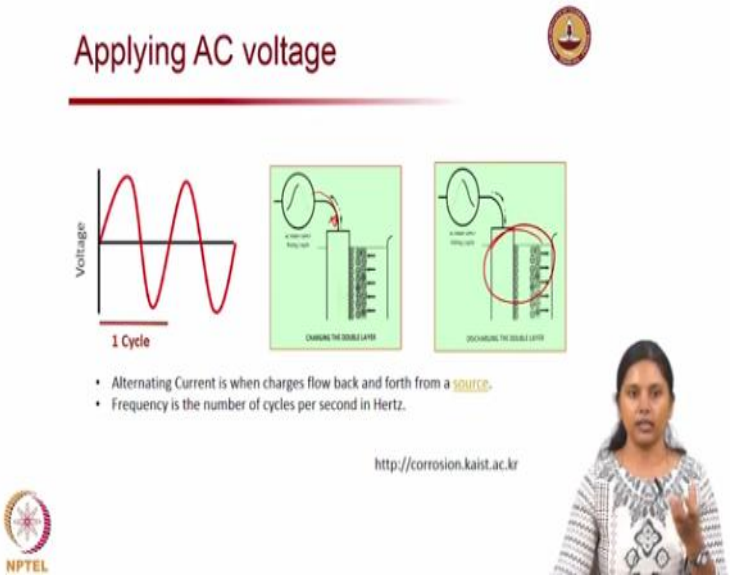

In Potentiostatic mode you can either apply AC voltage or DC voltage. If you are applying AC voltage, you can see there is a charging and discharging that is happening. When charging happens, the electrode surface will have a charge and then the diffuse layer will be pulled towards it and when discharging happens, the diffuse layer move away from it. So this response will yield some data and we will understand about the system, for example if the system has capacitance, if the system has resistance, the response from this kind of charging and discharging will yield us data and we can understand more about the system.

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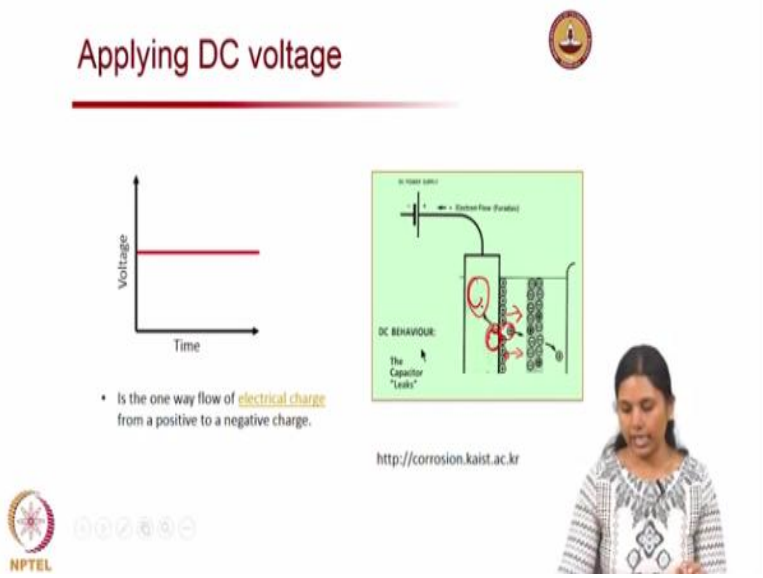

Second is DC voltage: in DC voltage we will apply a unidirectional current, we are charging the electrode. So this charge will push the diffuse layer away from the electrode and because of the constant pushing, there will be a small change in the surface. So the electrode will get roughened. So there is a small disturbance in the system as such. And this layer that is the distance between the electrode surface and the double layer, it is not purely capacitive in nature; there will be a small current flowing and that is what is represented. And this is called a capacitance leak.

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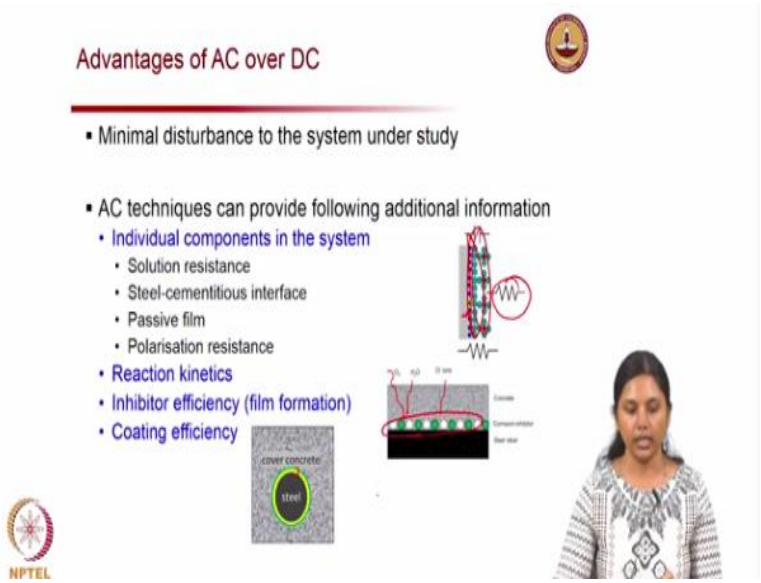

So when we apply an AC voltage over a DC voltage, there are several advantages; the first advantage is there is a minimal disturbance to the system. Then with the help of DC voltage, we will earn only the resistance of the system. But when we apply an AC technique we will be able to identify the individual components of the system, for example, the solution resistance, the double-layer resistance that is steel interface in our case. And then there is a passive film formation in this electrode, if there is a thin film formation whether it is porous in nature or fully adherent**,** that also we will able to know from this AC technique.

Then we can also determine the reaction kinetics, for example, there is a reactive species that is adherent to this layer. So, how fast or how slow the reaction is happening so that there is a change in this layer, that also can be determined with the help of this technique.

Then we have inhibitor efficiency. So if we are adding inhibitor to the concrete we assume that there is a film formation that is happening at the steel-cementitious interface. The formation of the film and the efficiency of the film can also be determined by periodic testing.

Then we have coating; if we have used a coated rebar the efficiency of the coating can also be determined, all this will be discussed in detail later.

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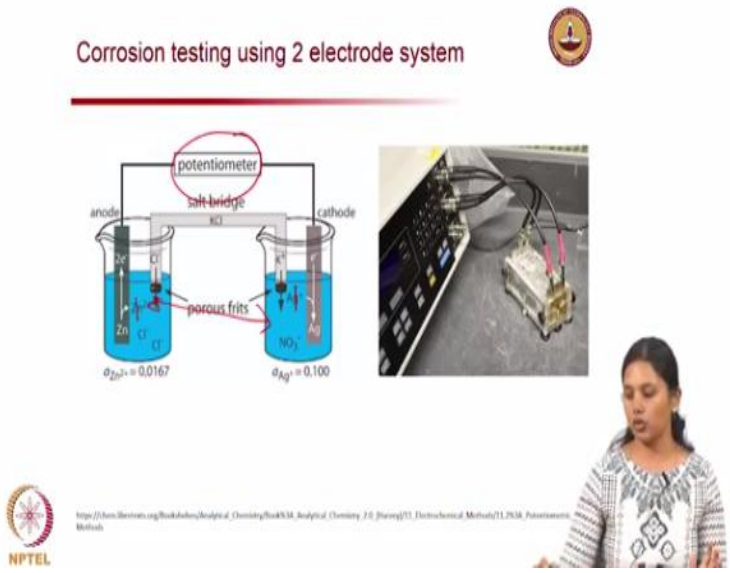

Now we move on to the actual testing. So when we go to the lab we will have confusion whether to use a 2 electrode system or a 3 electrode system. So when we use a 2 electrode system what happens is there are two half-cells here one is here and other is here (shown in figure). So when we connect the two half-cells with the potentiometer, what we measure is the response of the whole system. So if we do not want to differentiate between the reactions and but to only know the resistance between the systems the reactions that is happening, then we can use the 2 electrode system. Otherwise if the working electrode is of too high impedance then in that case also you can use a two-electrode system.

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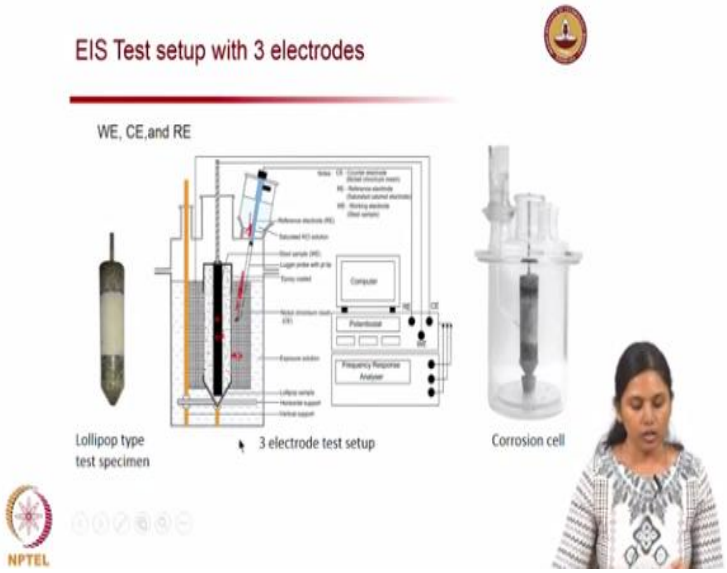

This is a typical example of the 3 electrode system. Here you can see this is the working electrode - working electrode is always the system under study. Then there is a counter electrode where we apply current or we measure the current from the Potentiostat and then we have a reference electrode. The reference electrode is a standard electrode where we know the potential of the electrode. So we measure the working electrode potential with reference to this reference electrode and then we apply a small potential and then observe the differences that happens in the response. Also, the counter electrode, working electrode, and reference electrode - all the three together forms the corrosion cell.

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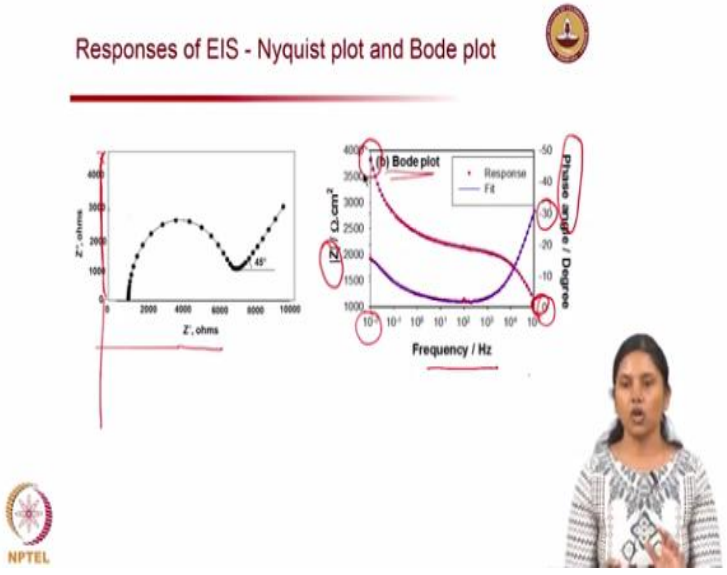

Once we connect the corrosion cell to a potentiostat and start the testing, we get two types of curves: one is called Nyquist curve, the second is called Bode plot. So the Nyquist plot is real versus imaginary - the real component is the resistance that is in the system. The imaginary component if it is here (left plot), then it is capacitance. You have to note that Z'' represents the negative imaginary component just for ease and our sake of understanding we always mention the capacitance in the top and the inductance in the bottom.

But if you see this carefully you will understand that this curve does not tell anything about the frequency - at what frequency we yield this type of graph. So for that we need to have this Bode plot. This plot is represented as a function of frequency. So here you can see that the frequency starts from 10^5 Hz to 10^{-2} Hz. And this phase angle represents the lead or lag by the current. So if it is negative, then that means it is capacitive in nature that is the system is lagging; if it is positive, then it means that it is leading the current. Then you have the $|Z|$, here if you see, this portion (bottom-right curve portion in graph) represents the solution resistance and this portion (top-left portion) represents the solution resistance plus polarization resistance. But you can directly take these values only in case of metal aqueous system. For a system like steel-cementitious interface or what we do for steel corrosion in concrete, this is not straightforward and you cannot take it like this simply, you have to formulate an equivalent circuit modeling for extracting the parameters.

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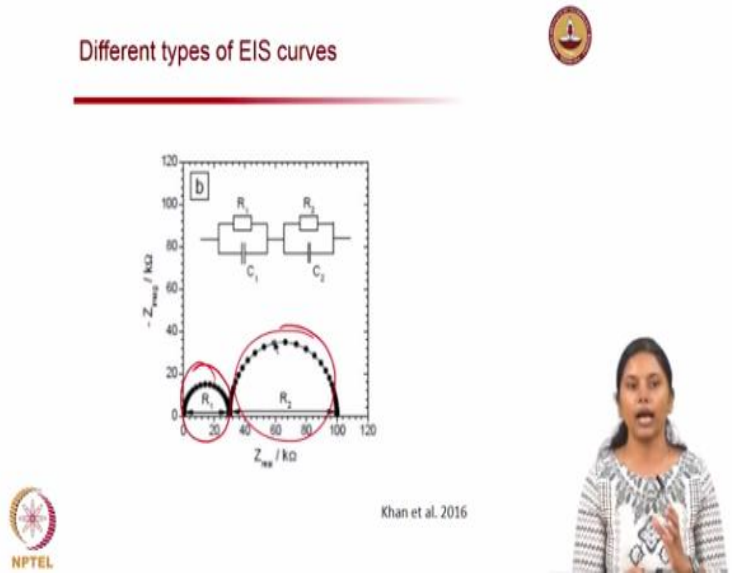

These are the different types of EIS graphs you can get. If you get only one element, that is RC element that means, you have only one kind of double layer that is forming and if you have different RC elements that means your system is behaving differently. So, depending on the system only, nature of EIS curve will differ.

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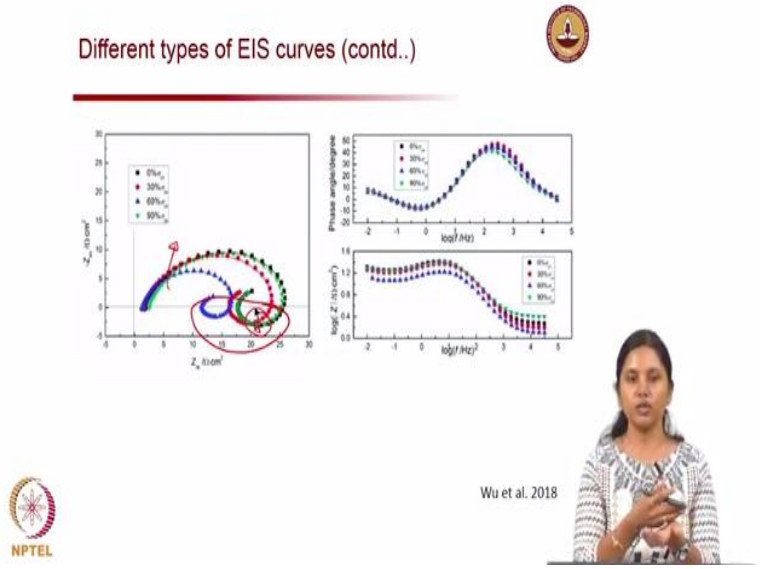

So this is another typical example, here (left graph) you can see that it is coming in the negative region. So if it is coming in the positive that means it is RC - that is resistance and capacitance in parallel; if it is coming here (negative) that means RL - that is resistance and inductance in parallel. This means that there is some reactive species adherent to the electrode surface and within the ions it is having an inductance nature. It does not mean that there is an inductor there, it means that the arrangement of ions near the surface of the electrode interact within each other and induce an inductive nature.

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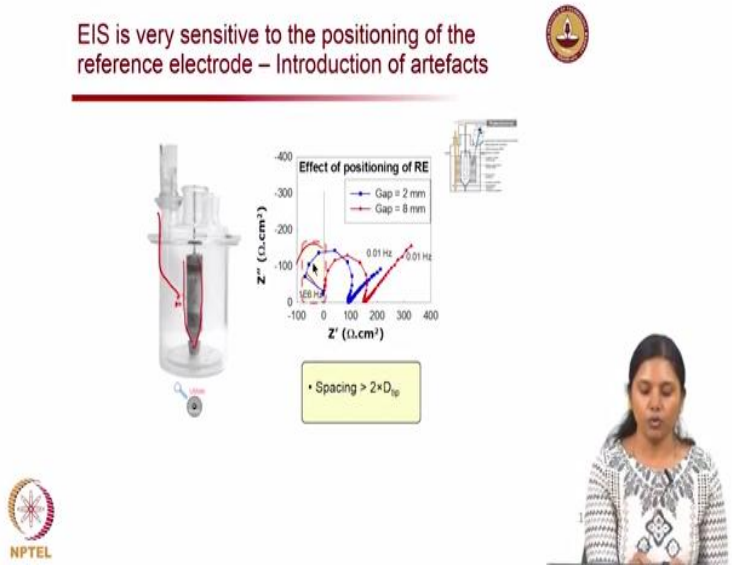

Now we will move on to the different types of artefacts which we get. Artefacts are nothing but distortion of EIS curve. Why this kind of distortion happens is the distortion can happen in two levels; one is due to the arrangement of the electrochemical cell, that is the arrangement of working electrode, counter electrode, and reference electrode. If your arrangement is very complex it will distort the distribution of current and cause distortion in the EIS curve.

So if you have a cell like this, this is the luggin probe (in figure) and then this is the working electrode. So if I keep the luggin probe very close to the working electrode, then there will be a current cut off that happens between the working electrode and the tip of the luggin probe. So this may induce the distortion like the blue curve. So if you do not want a distortion like this, what you should do is, you should simply keep the luggin probe slightly away from the working electrode.

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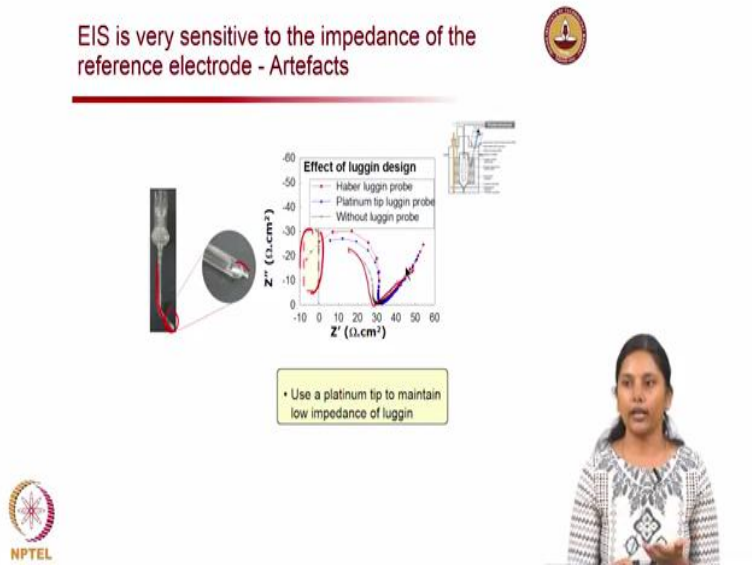

Then there are other kinds of artefacts that are induced because of the impedance of the luggin probe. So if your luggin probe is narrow or if your luggin probe has some bubbles or if your luggin probe has some crystallization that happened in the solution, all this will create high impedance inside the tube and because of this there will be a non-uniform conduction and this will distort the curve in the high frequency region. You may note that all the distortion that happens are in the high frequency region so you can easily identify whether this is a distortion or not.

This kind of distortion can be eliminated by simply adding a metallic tip at the bottom. So one may argue that here by looking at this graph, you may need not include a luggin probe to avoid this artefact, but there are some cases where the reference electrode while keeping it in the electrolyte, may contaminate the electrode and cause instability of the reference electrode. We do not want that kind of instability, that is why we introduce the luggin probe and then, when the luggin probe has some issue we can eliminate with the help of metallic tip.

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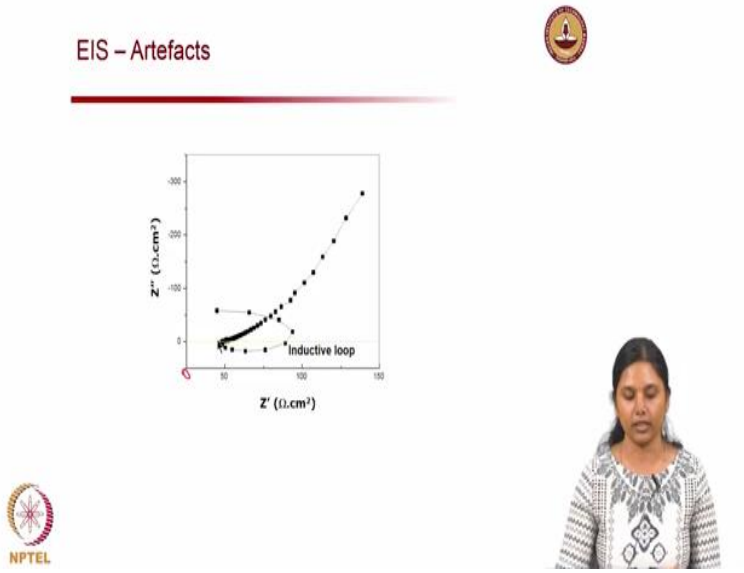

So this is another interesting graph I got. One may look at this and think that this is a very good graph, it does not have any distortion in the high frequency region. For example the zero is here (marked in graph), so it is not in the negative side of the impedance. But this kind of graph I got it in a new system, so I thought it is because of the species that got adherent to the surface.

But when I looked into the literature, two arguments were there for this kind of graph. One was due to the instability of the potentiostat and the next was due to the reactive species adherent to the electrode surface. So to check whether it is an artefact or not, what I did is I went and checked in another potentiostat. When I checked there, I found out that my potentiostat was not working properly and started inducing this kind of artefact. So the main important thing about this is you should understand whether the curve is an artefact or not.

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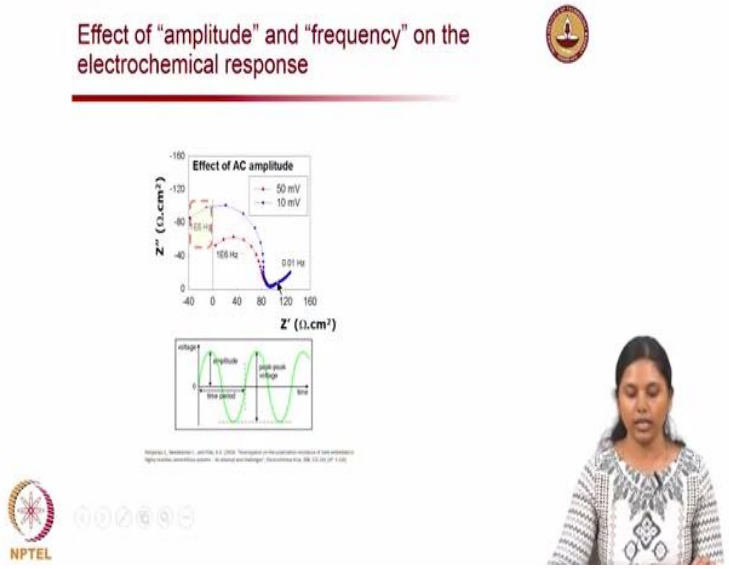

How can you identify that artefact? We will come to that later. So you can have artefacts because of the chosen parameters that you use for testing. For example, if you use an amplitude which goes through the non-linear region, that is, working electrode will have some potential; we want to measure the current, so we apply small potential and disturb the specimen and then we understand the current. But if the disturbance is too high then it may go to a non-linear region and it will not come back easily to the original state. So when that kind of non-linearity happens then we are not able to get the actual corrosion current.

So if you see here the blue curve is 10 mV which is a small perturbation and in the red curve is 50 mV which is a large perturbation. There is a shift between the blue curve to red curve. This indicates that the system has gone to the no-linearity region. If it is in the linear region it will trace back the same curve as that of the 10 mV. So, you can understand that this is a distortion and we should eliminate this kind of high amplitude (shown in bottom graph in slide) when we are using the testing.

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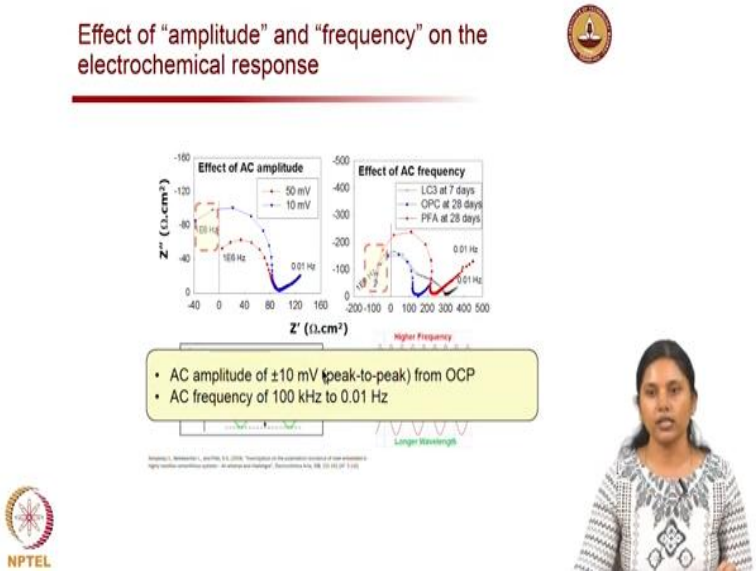

Next is frequency, when you have a very high frequency, the cables will attract noise from outside and this may distort the curve in the high frequency region. So to eliminate that you have to use a low frequency that is 10^5 instead of 10^6 or you can use a Faraday cage which can avoid this kind of noise pick up by the cables.

So there are 3 types of artefacts we have seen: The first is due to the electrochemical cell arrangement, the second is due to the instability of the potentiostat itself and third is because of the chosen parameters.

For steel in concrete, amplitude of ±10 mV from OCP and frequency of 100 kHz to 0.0 1 Hz can be used.