Electrochemical Impedance Spectroscopy
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Lecture – 05
Introduction to Other Techniques

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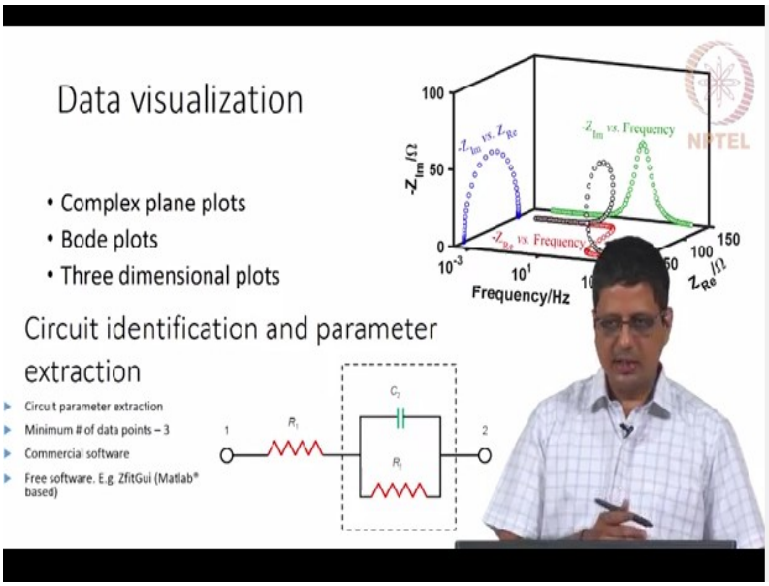

What we saw earlier was that we can plot impedance as Bode plot or as Nyquist plot. Bode plot show magnitude and phase as a function of frequency. Nyquist plot show the imaginary part plotted versus the real part. Once you have the data, can we identify which circuit will be suitable to model this? This is first part. Let us say, we realize that this circuit can be used to model the particular data which looks like a semicircle here in the Nyquist plot.

Next is, can we find the value of R_1, R_2 and C_2? Third, after we get R_1, R_2 and C_2 values, how do we interpret it? What is the meaning of C_2 being 10 μF cm^{-2}, or 20 μF cm^{-2}? What happens when R_2 is 1000? If we do another experiment with slight change in conditions, and R_2 becomes 1010, how do we interpret that? That is one set of analysis. Here, we have to get circuit parameter extraction and we can use commercial software, free software, you can get it.

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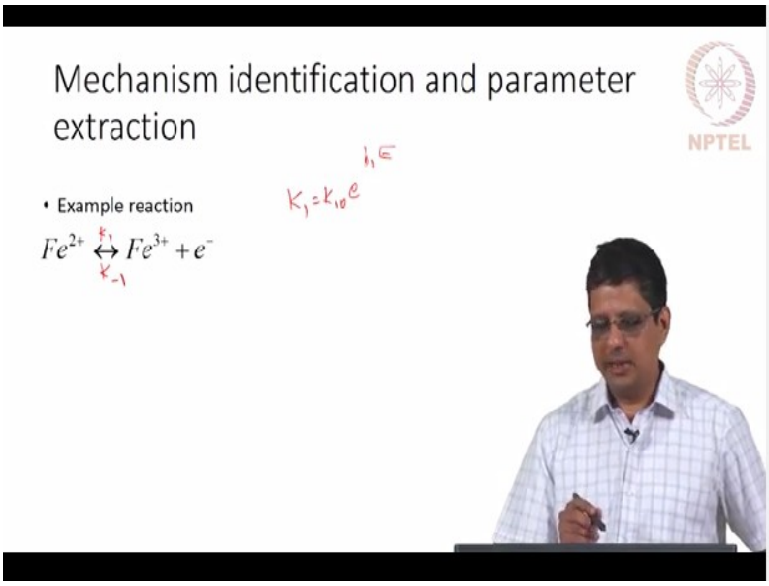

Another aspect is, can we say this impedance has come from this reaction? Can we identify a reaction which will give rise to this impedance? We can say this impedance would have come from this circuit. Similarly, we should be able to say this impedance can arise from this reaction. An example is Fe^{2+} becoming Fe^{3+} with an electron, this is one of the simplest reactions that is used. Second, If the forward rate constant as k_1, and reverse rate constant as k_{-1}, can we find the values of k_1 and k_{-1}?

It is actually a function of potential, so we should also be able to tell what is that function. Usually, we would write it as $k_1 = k_{10} e^{b_1 E}$. Similarly, k_{-1}, k_2 if you have multiple reactions, just like you have R_1, R_2, C_2 and you can get the values. Here you should be able to say what reaction can give rise to this impedance spectrum and what are the values of those parameters.

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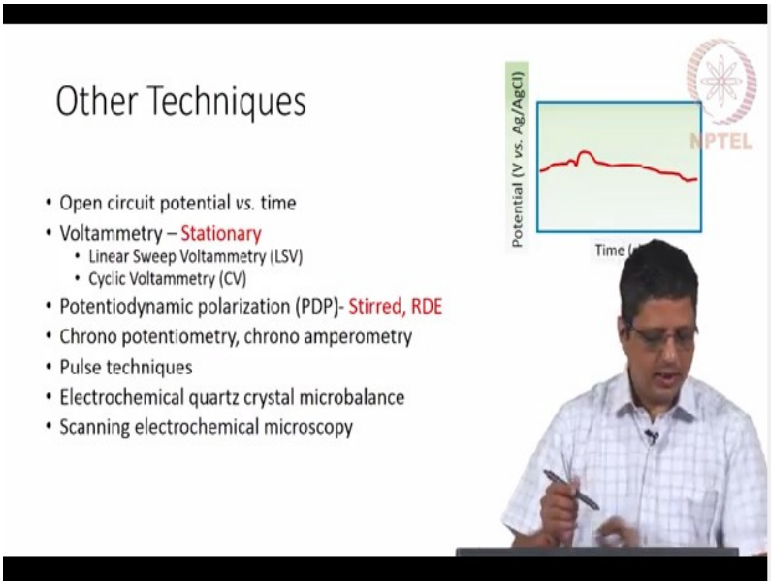

Here I want to discuss few other techniques. EIS is normally referred to as a versatile, powerful technique. If you look at the books, if you look at the publications, they would say it is very powerful. And in some cases, you would also see people writing that all the information about the system can be captured by EIS. It is not exactly true. What they mean is if the system is linear and if you have the information from zero frequency to infinite frequency, then you can reconstruct how the system will behave for any perturbation, any form of change in potential. So, it is essentially saying I know how the system behaves from zero frequency to infinite frequency, therefore if we know that we are going to apply a triangular wave, or a rectangular pulse, then we can reconstruct it using a method called Fourier series.

And in Fourier series, you can add multiple sine waves to reconstruct a particular shape, periodic. Then you can basically say by adding the responses, I can get the result. But then electrochemical systems are usually not linear, and this will not always work. Here I want to pause and give you an idea of few other techniques. There are many techniques and you have some idea of what you get in other techniques.

Normally if you run experiment, you will first measure the open circuit potential. That is without applying any potential, you just measure what is the potential between the reference electrode and the working electrode. You have zero current and it will vary as a function of time. Sometimes it is stabilizes quickly and you get more or less constant value. Sometimes it changes,

because the interface changes.

It is possible that the electrode dissolves. That means electrode's surface area will change. The concentration of the solution species near the electrode will change because it is dissolving, or some contamination from the liquid can adsorb on it. Sometime it may not be a contamination; it may be something you deliberately introduce. It may adsorb on it. So, the potential will change if the electrode surface or the solution changes.

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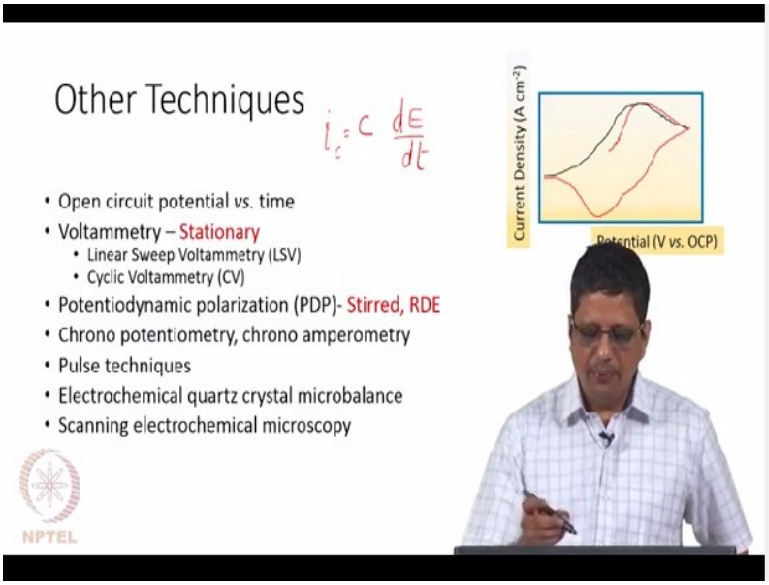

Another experiment that is commonly used is called Voltammetry. Voltammetry is basically potential and current. We will control the potential as a function of time, we usually vary it and is given at a particular sweep rate for example, 10 mV s^{-1}, 100 mV s^{-1}, 1000 mV s^{-1}, 1 mV s^{-1} and so on. If you scan from one potential to another potential at a particular scan rate, that is called linear sweep voltammetry (LSV). It is linear, you are sweeping the potential and measuring the current as a function of time. It is normally plotted as current versus potential or more commonly current density versus potential.

Now I want you to remember this, if you take an instrument and select LSV or cyclic Voltammetry, the instrument will change the potential, measure the current and plot it in a particular format, usually this format (current density *vs*. potential). If you want to interpret the system, which is, the electrode and the liquid, they have to be stationary for cyclic voltammetric

interpretation. The liquid should not be moving and the electrode is not rotating. It is a stationary electrode. When you change the voltage, let us say some reactant comes from the liquid and reacts with this, forms a product and goes out. Let us say when the potential becomes more and more, one of the reactions, either forward or reverse reaction becomes more and more favourable, then species will come, react and form the product and go out. The concentration of the species at the interface will change. Therefore, in voltammetry if you do either linear sweep or cyclic, the current density would increase and because it becomes diffusion limited, it becomes lower current. And then if you go in the reverse, the current density increases in the reverse direction, becomes diffusion limited and reaches a lower current again. This cycle can be repeated. It is like potential versus time, potential will increase, decrease, come below the original potential possibly and then go up and come down again.

When it is stationary, diffusion will also play a role and most of the interpretations in the book will use that it is stationary. Now it is possible for you to rotate the electrode and click cyclic Voltammetry. You will get the data. It will not look like diffusion limited, because diffusion will not play a role. The software does not know whether you are rotating the electrode and mixing the fluid or not. Therefore, one has to conduct the experiment correctly, then the data can be interpreted using the standard methods.

There is another technique called potentiodynamic polarization. In cyclic Voltammetry, typically you will specify 20, 50, 100, 200, 1000 mV s^{-1}. You can also specify 1 mV s^{-1}, it will still run correctly. In cyclic Voltammetry what happens is, you have potential changing quickly with time. The double layer capacitor will also contribute to the current. Current in the capacitor is going to be given by this function, $i_C = C\frac{dE}{dt}$. If potential is changed quickly with time, the dE/dt becomes a large number. Therefore, the current due to capacitance may become a significant number. Total current is due to the reaction plus this capacitance. The reaction may be kinetics limited or diffusion limited depending on how fast the kinetics are, how slow or how fast the diffusion is.

Now the next technique called potentiodynamic polarization from the software point of view,

you would again specify as scan rate. Potential will change from one to another value at the scan rate given by us. Usually it starts at a potential and ends at another potential. It is similar to LSV, linear sweep Voltammetry. Again here, you have to rotate the electrode if you have the facility at as high rate as possible or you have to mix the solution. Sometimes in corrosion cells, they will not mix the solution. They will have 2 electrodes at a given space and they will run the technique as potentiodynamic polarization and they will interpret the data assuming diffusion is not playing a significant role. It may or may not be correct depending on the system. If there is a significant corrosion, diffusion may play a role. If it is very small, then it may not play a role. So ideally you should be able to move the fluid well either by pumping the fluid or using RDE at a high. Next, in the potentiodynamic polarization, the software will allow you to specify a scan rate. You can specify 100 mV s^{-1}. It will run but it is not going to be correct for interpretation of the data.

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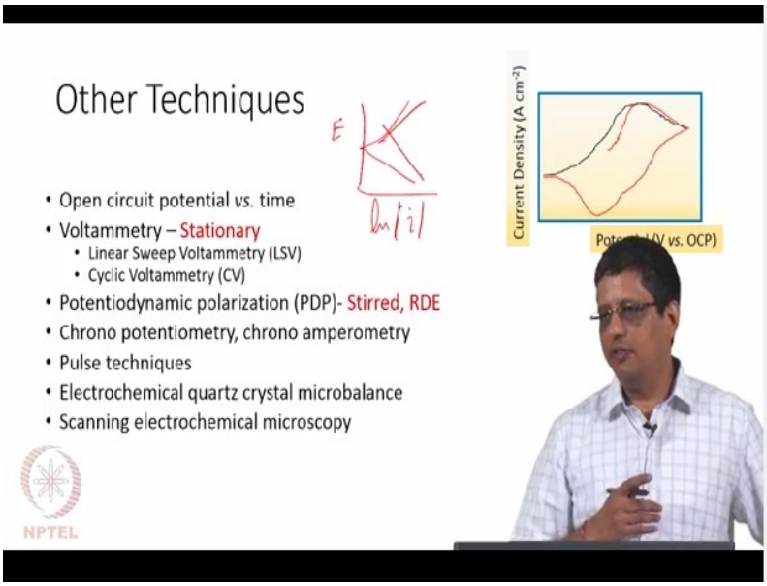

Because in the potentiodynamic polarization, usually people will take this and do a particular analysis where E is plotted against log of that absolute value of the current and they would do a particular extrapolation called Tafel extrapolation. That analysis assumes that all the current comes because of reaction. That means there is no contribution from the double layer capacitance. This is correct only when you scan at a low rate. If you scan at a fast rate, software will do this. Our final calculation will not be correct. Because the assumption that double layer capacitance does not contribute to this, that has to be confirmed by us choosing the experimental setup correctly and running it correctly. If you want to do the experiment fast, click, a larger scan

rate can be chosen and the software will run it fast but the results you get will have contribution from double layer capacitance. Therefore, you should run it at a slow scan rate. What is low? Typically, it is 1 mV s^{-1} or less than that. If you have a significant corrosion current, significant current from the reaction, large current from the reaction means very fast dissolution, then you might be able to go at a slightly faster rate and still get the correct results. This is because the double layer capacitance will not contribute that much current to the final value. For example, if we do experiments at 2 mV s^{-1}, it will shorten the experimental time by half. And if your dissolution is very fast, large dissolution occurs, you do not want to conduct the experiment for long time because the electrode will dissolve fast. Therefore, one has to conduct the experiment for a short time and at that condition, it is okay to have little faster scan rate. Because you are dissolving fast, the total current is mostly going to be reaction current, very little will come from double layer. These are the things that you have to know. It is not that the software will force you to do it the right way. You will have to do it the correct way. Only then the interpretation will become correct.

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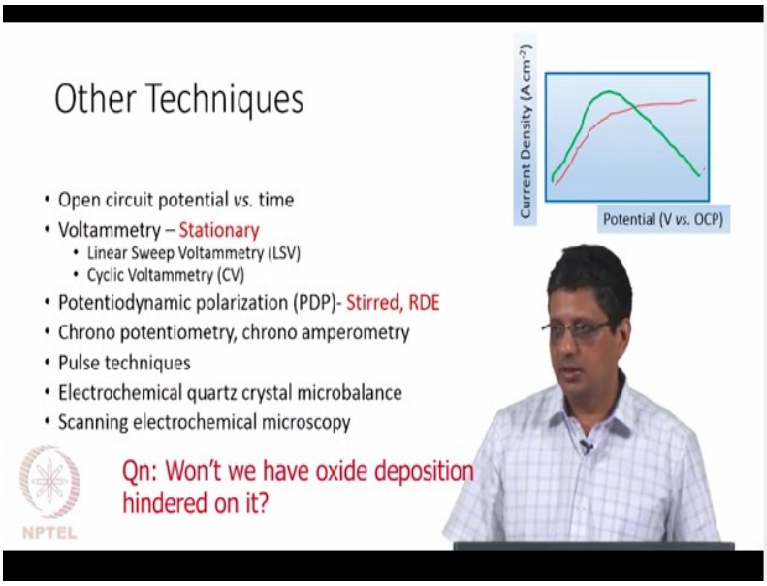

There are other techniques. In the potentiodynamic polarization, this is an example. You can have current increasing and then stabilizing after sometime. You can have current increasing and decreasing after sometime. For example, you can have a reaction where you have a metal which dissolves and also forms an oxide. The oxide may also dissolve at a particular rate in the solution. When you go to higher and higher potential, the oxide formation rate may be more than

the dissolution rate of the oxide. In which case, the surface becomes passivated as a result the current comes down. At a superficial level, it will appear like current increases and decreases. This is similar to cyclic voltammetry (CV). But it is not similar to CV. The reason current decreases in cyclic Voltammetry if you conduct the experiment correctly, is because it is diffusion limited. The reason current value is decreased here is because it may be getting passivated. So, the interpretation will differ, although the appearance is the same for these two types of experiments.

Question: So we will not have oxide deposition be hindered on it?

Explanation: Oxidation of the electrode, for example, if you have titanium and it is immersed in HF solution. Titanium will get oxidized by water and form TiO_2. And if you rotate it, more and more water and HF will come near this. Water is anyway going to be present all the time. Oxidation can happen because of water or because of dissolved oxygen. You may have some other oxidizing agent in the solution. I do not have to assume that the oxidation will get hindered because of rotation. It depends on the situation.

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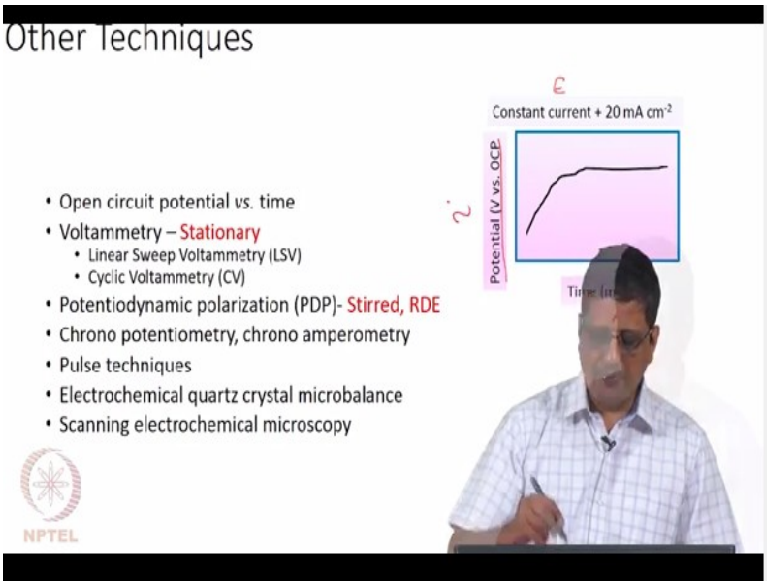

There are other techniques like chrono potentiometry. Chrono is for time. You can have a control current; as an example (you can specify) +20 mA cm^{-2}, positive sign indicates oxidizing. It can be a negative (value). You can give (negative value), for example deposition of some material can be (achieved using) negative current.

European convention would take that anodic is negative. American convention will take anodic as positive. You will have to notice that point correctly. In some of the software, they will also give you an option of selecting one convention. Some of the manufacturers will specify the convention (and you won't be able to change it while using their software).

If the electrode is held at constant current, potential may increase and then become constant, or may decrease and become constant, depending on the situation again. If you go at zero current and suddenly jump to a constant current, the value of potential may increase slowly and then stabilize at value in some cases. Other cases, you might form an oxide on the top of the surface by giving a constant current. Oxide thickness will increase with time; therefore, the potential needed to maintain the current will keep increasing. So, by looking at the potential as a function of time, here I am giving you one example qualitatively but you may have other responses. Based on that, you can interpret as to what is happening in this system.

Likewise, chrono amperometry is for a constant potential. Here a constant potential is given and the response current is monitored.

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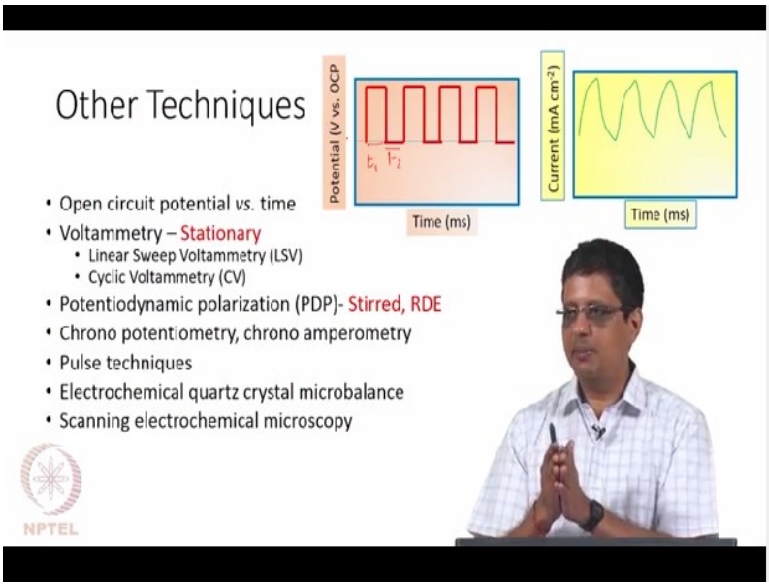

There are other techniques such as pulse techniques where you may control the potential as a function of time. Potential may be at zero, jumps up, comes to zero after a few milliseconds and

this is of course periodic. You specify this time and this time, t_1, t_2 and then this is one cycle, total number of cycles can be specified. The resulting current will not instantaneously go up. Current will actually go somewhat like an exponential function. When you switch off the potential, it will not instantaneously come to zero, but will decay gradually. Based on that you can interpret it is actually sometimes used in industry for a particular way of depositing material.

You can even go to high potential, (and then) come down to *below zero*. You may deposit something, remove some of it, again deposit something, remove some of it, and continue to do this. In some cases, it will give us a benefit. Normally, we want to deposit a material, and to some thickness. We want to finish it fast and then move on to the next sample. But the quality of deposit may not be good. You can run it at a constant potential. You can run it at a constant current. In both cases, many times you would get a sufficiently good quality. (Then) It is fine. Sometimes you may not get a good quality, because diffusion may be slow. If a pulse is given, it deposits something, then give a pause for the material to come by diffusion, and again deposit. This is one way. *(Please refer to video to follow this section)* During that time, it will deposit. Then pause for few milliseconds, diffusion happens, again deposit, the concentration is more or less same as what it was before. The quality of deposit may be better in this way. The reverse sometimes will remove the material. The hope, or expectation, is that it (reverse pulse) will remove the material that is not sticking well, that (poorly adhering material) will go first. Material that is deposited and stuck well to the surface will not come out in the short time. So net deposition rate will be lower but you will get a good quality material. Of course, you have to optimize this by trial and you can see. You do not want to give a large and long reverse pulse because you are going to remove everything. But occasionally it is beneficial to give reverse pulse also. [Occasionally meaning, whenever it is beneficial].

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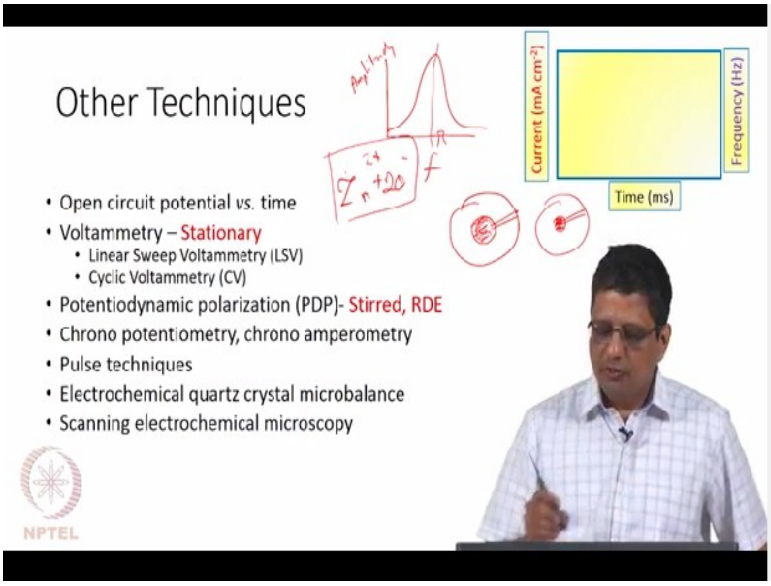

Another technique is called quartz crystal microbalance. I think many of you may be familiar with what is called piezoelectric material. If you apply a potential to the material, it will deform. So certain materials like quartz if you cut in a particular orientation, they have an inherent or natural frequency and when you apply an AC potential at that frequency, it will show a resonance. It will have a maximum amplitude of movement. If you move away from the resonance, the response will be less. So if you plot frequency and amplitude of the movement, it would appear like a bell shaped curve and the frequency of maximum amplitude is the resonance frequency. If you take a material like quartz and make a disc, like a coin, and gold is coated on top of it. You can coat other materials as well. The other side of the disk is again coated with gold. Leads are provided to take them out and connect. If an AC potential is applied the disc will oscillate, vibrate, and the equipment will can measure that. Now if a material is coated on top of it or if some material is removed, the mass will change and the resonance frequency will shift.

If you coat a material, it is going to be little heavier. If you put in the liquid, it is going to be dampened. So by monitoring the resonance frequency we can measure the amount of material deposited or removed. The resonance frequency can be monitored very fast. The values of resonance frequency is in the range of megahertz. Five megahertz is common, it is possible to get in high frequency range such as 10, 20, and 30. That means the change in frequency can be measured every 100 ms. Every second one can get 10 points, 100 points. At least every second I can get a data which tells this is the mass on this. So if I deposit a material on an electrode, let us

say deposition of zinc on iron [which is used for galvanizing steel]. At a given potential, hydrogen will also evolve on this electrode along with Zn deposition. The current that is measured is the total current. What we want is zinc deposition but when we go to that potential, hydrogen evolution will also happen. We want to know how much is the efficiency of this process; means *how much current goes into deposition*. If I use a quartz crystal microbalance and control the potential or current and change in frequency is measured, I can say how much is the mass change. Hydrogen will evolve as a bubble and go out and will not contribute to the mass. Zinc will contribute to the mass. I know the total current from that I can estimate how much should be deposited if everything were a zinc. There is a constant called Faraday constant which tells one mole of electrons will have this much coulombs. Zinc for example, we expect it to be $Zn^{2+} + 2e^{-}$, one mole of zinc will give us two moles of electrons or two moles of electrons are needed to reduce one mole of zinc from the solution. we know the atomic weight; therefore, we can calculate the mass.

From the current, it is possible to estimate how much zinc should be deposited if all the current has been used for zinc deposition. From the quartz crystal microbalance, you can find out actually how much is deposited to the extent of microgram very comfortably. The manufacturer will claim that you can measure nanograms with this, but you can comfortably measure micrograms, meaning even in presence of noise, you can measure 0.1 microgram with some difficulty. If you want to measure nanograms, it will work only for a few systems, ideal systems.

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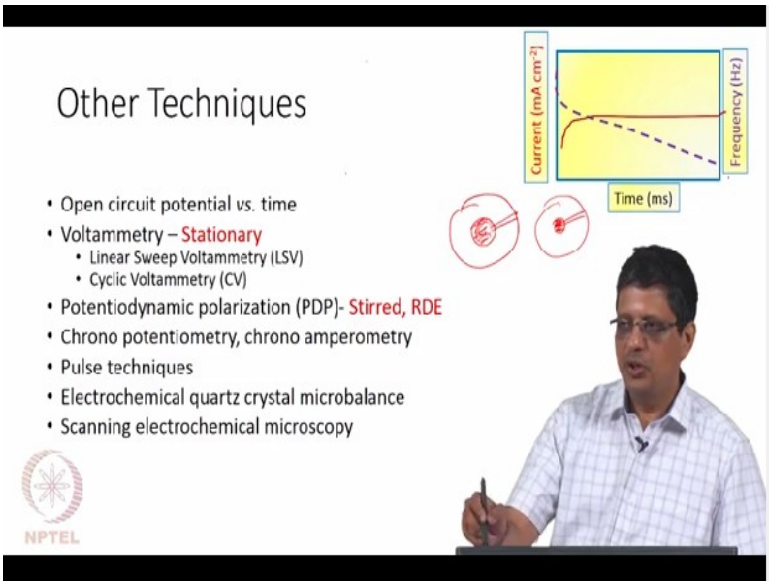

In this case for example, the frequency and current are recorded. initially a potential is applied, and the current is monitored, it jumps up and then it is more or less constant. When current is more or less constant, let us pretend in this case that it is depositing at a constant rate and everything is the metal that is depositing. Frequency will change linearly. Frequency, here is the resonance frequency. You can monitor this and then compare with what you see in the current.

Electrochemical microscopy is where you have a small tip close to the surface in the liquid. One can scan the tip or the sample may be moved using piezoelectric. It can be moved by micron sized steps or even smaller than that depending on the features that are available. The current at these locations can be recorded. You can see how the surface behaves electrochemically at different locations which are spaced by a few microns. If there is a surface heterogeneity one can find that. If you have an alloy, you can say whether there are like metal clusters or it is really completely alloy and it is more or less homogenous. That is one example of how you can use it.