Electrochemical Impedance Spectroscopy
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Lecture – 01
Electrochemistry, Double Layer, 3 Electrode

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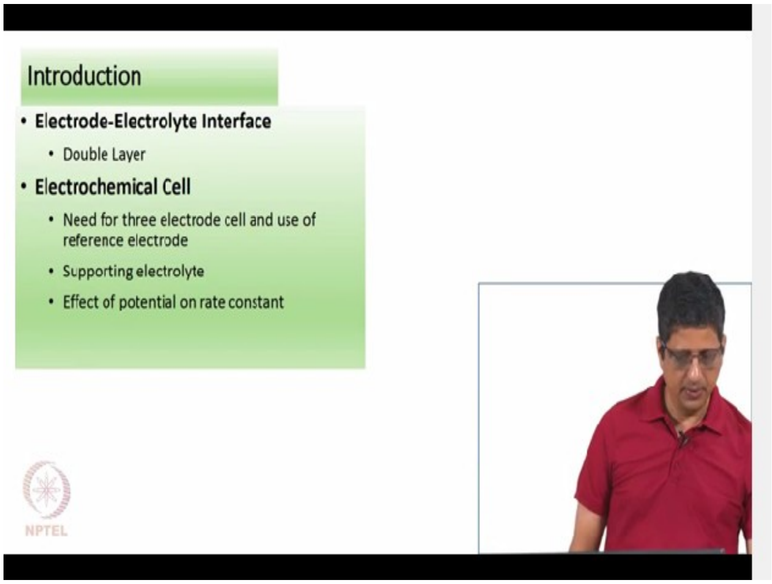

Introduction

- Electrode-Electrolyte Interface
  - Double Layer
- Electrochemical Cell
  - Need for three electrode cell and use of reference electrode
  - Supporting electrolyte
  - Effect of potential on rate constant

So in this class first I want to describe electrode-electrolyte interface. It forms what is called double layer; I want to describe that and then we also want to see why often times we use three electrode system and what is the role of what is called supporting electrolyte. And if time permits, we would see how the rate constant in an electrochemical system will vary with potential.

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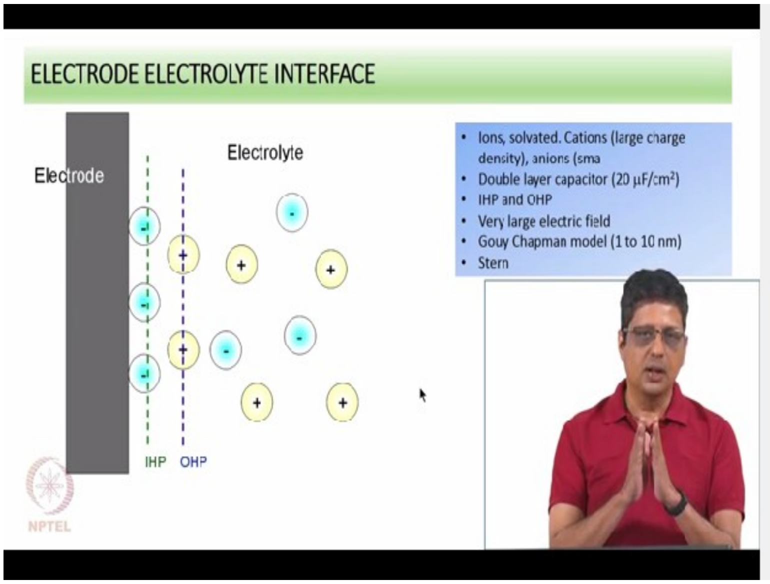

ELECTRODE ELECTROLYTE INTERFACE

- Ions, solvated. Cations (large charge density), anions (sma
- Double layer capacitor (20 μF/cm²)
- IHP and OHP
- Very large electric field
- Gouy Chapman model (1 to 10 nm)
- Stern

If you imagine, you have metal electrode on one side and water based electrolyte on the other side. The moment we put a metal into the liquid, ions in the liquid will come and adsorb on the metal. So this can be visualized as follows: you have one layer of ions adsorbed on this electrode and that forms what is called inner Helmholtz plane or IHP, that is given by the green colour line here.

Once you have many ions adsorbed on the surface, ions of the other polarity, positive ions here for example, would come close to this. So this forms what is called double layer. Normally ions in the liquid or water will be solvated, that means water dipoles will be surrounding this ions. I am not showing them here for simplicity. If you have a positive ion, like sodium, Na^+, that is a cation and chloride, Cl^-, is an anion.

Normally you have sodium that loses an electron and becomes Na^+, that has a small volume. It has unity charge, so it is having a large charge density. Chloride on the other hand will have a small charge density compared to the Na^+. By and large anions have small charge density, cations have large charge density. There are exceptions to this, but by and large this is true. So this is one description where within 1 nm you have one polarity for the metal, adsorbed ions right next to that, and then in the outer Helmholtz plane, another set of ions.

This can be visualized like a capacitor and this is often called double layer capacitor. And a typical value is between 10 to 30 μF per unit area. Unit area here means per ~~unit~~ square centimeter. If you visualize, you might be supplying 1 V across this interface. 1 V in 1 nm is about 1 GV/m. So it is a very large electric field occurring in a very short range.

There is an another model called Gouy-Chapman model which says that from the electrode for about 10 nanometer or so, the charge distribution occurs. So it is not occurring in 1 nm but it actually occurs over a 10 nm distance. And there is a model called Stern model which combines the inner Helmholtz plane, outer Helmholtz plane and Gouy-Chapman model which says lot of discharges are lined up right next to the electrode but some charges are distributed further away from the electrode.

So it is a combination of the Helmholtz plane as well as the Gouy-Chapman model. If you have electrolyte concentration in the range of 1 M, then pretty much all the charge separation or charge distribution occurs right next to the electrode and you do not have to use the Gouy-Chapman model. If the concentration of the electrolyte and water is about 1 mM, then probably it is better choice to use Gouy-Chapman model.

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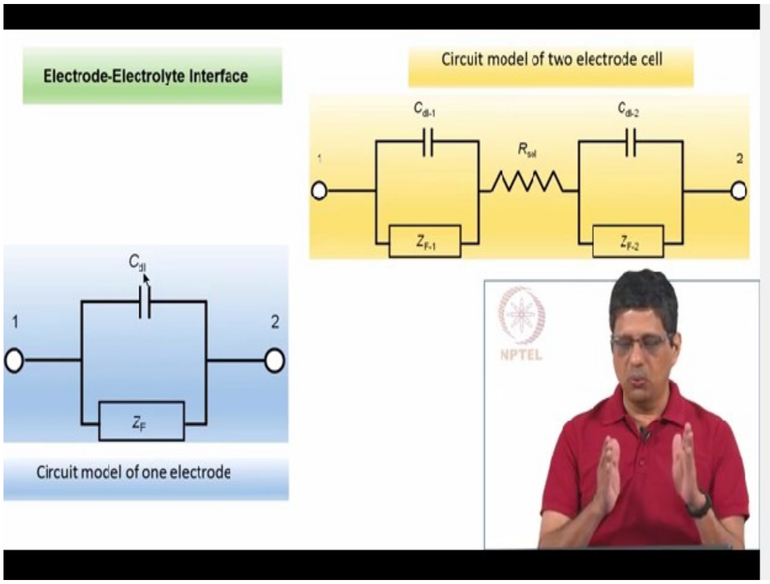

Electrode-Electrolyte Interface

Circuit model of two electrode cell

Circuit model of one electrode

Now if I have one electrode, right next to that is the electrolyte. I have shown that, you can describe that by a capacitor and we call that as a double layer capacitor and we represent that by C_{dl}. So on the left hand side picture in the blue colour diagram, you have got C_{dl} but this assumes that there is no moment of electron or any material across the interface. But at sufficient potential, you may have a reaction happening. That means you have metal here, you have electrolyte here. Electrolyte may take an electron or give an electron. The material can come out and dissolve or some material in the electrolyte can go and deposit. If any of this happens, this type of reaction is called electrochemical reaction.

There is a chemical reaction but in addition to that, there is an electron transfer. This reaction, electrochemical reaction would also give rise to current. And this gives rise to, you can think of a resistance or a generalized resistance. We call that as impedance. I will give you a better description of impedance later. But right now, we can take impedance can be represented by the letter Z and we give a subscript F to indicate it is a faradaic impedance that means it is associated with the electrochemical reaction. So I have a capacitor; if current passes because of the capacitor, we call that as a capacitor based impedance.

If the current passes because of a reaction, we call that as a faradaic impedance. In one electrode you may have a reaction or you may not have a reaction. If you do not have a reaction, we just represent by the double layer capacitor. If we have a reaction, we say there is a capacitor, in parallel we have an impedance given by the Faraday process. At the minimum in an electrochemical cell, you will need two electrodes.

So you have one electrode described or modeled by the circuit on the top left called C_{dl-1} and Z_{F-1}. You have another electrode which is given by the subscript 2, and in between, you have the electrolyte, we call it as solution and the resistance offered by the solution is called solution resistance or R_{sol} here. So this is a model for a simple two electrode system with electrode on 1 side, electrode on the other side and electrolyte in between these two .

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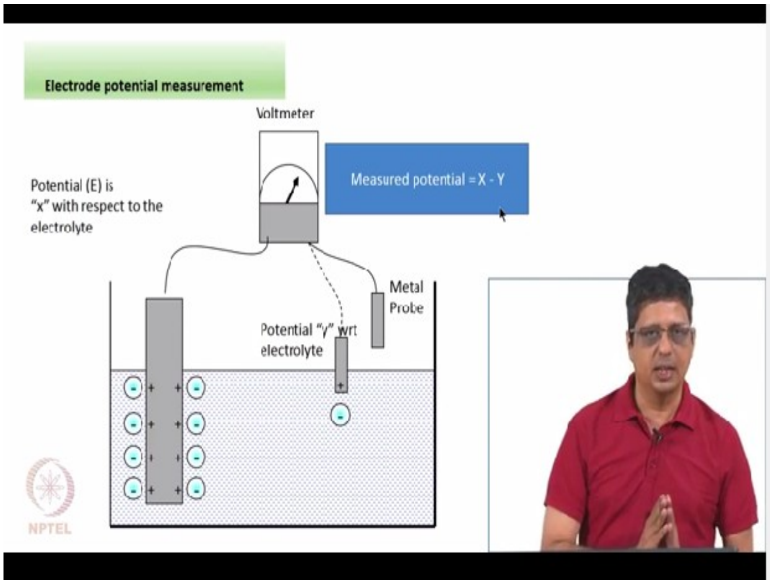

Electrode potential measurement

Measured potential = X - Y

When we put an electrode or a metal in solution, it develops a potential. Can we measure the potential? There is a difficulty associated with that, so I want to describe that here. We cannot measure the potential of a single electrode. The moment we immerse the electrode; it forms a double layer, there is a potential. We want to know the potential difference across the double layer, across the electrode-electrolyte interface. In order to do that, we will connect it to a multimeter.

The other side of that wire which we call as ground, normally call as ground, (and) we want to connect to the liquid. The moment we connect to that liquid, that probe will also form a double layer. It is not going to have zero potential difference between the metal probe that is a ground probe and the liquid; liquid or solid whatever (be) the electrolyte, that is there. So that potential, let us say it is *y* and let us call the actual potential between the metal and the liquid across this double layer as *x*. All that we can measure is "*x-y"*. We cannot measure the exact value of *x*, because the *y* value is comparable to *x*, it is not negligible compared to *x* value.

So we will always be able to measure only the potential drop across one electrode, , any potential drop that can occur in the solution~~.~~(and) we will have to take into account, that there is 1 more electrode; we do not mean it (the probe) as an electrode, but the moment you insert a probe into this (electrolyte), that becomes an electrode. So we cannot measure the potential across a single electrode. Not just that, there is an additional problem.

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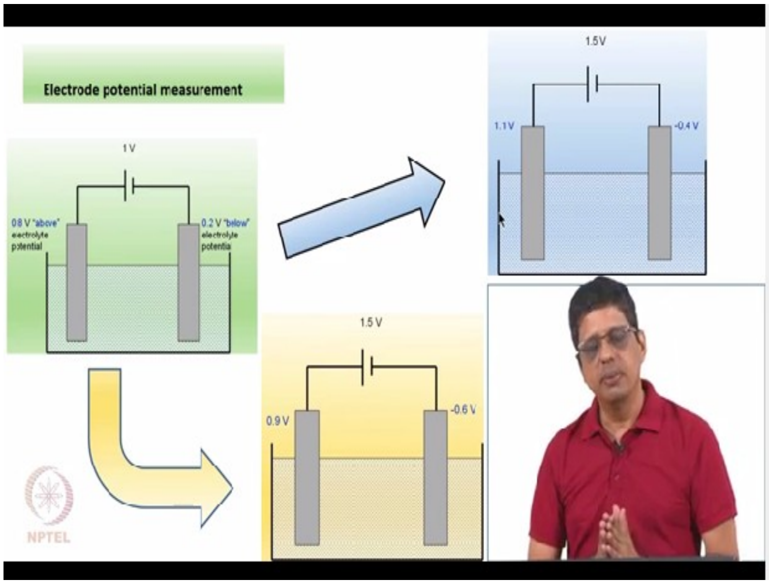

Electrode potential measurement

Let us say we apply a voltage. We apply 1 V, we have two electrodes; we apply 1 Vand on the left side, let us say it is 0.8 V *above*, meaning positive compared to the liquid. On the right side electrode, it may be 0.2 V below. That means, I have total of 1 V between these 2 terminals but 0.8 V potential drop occurs in the first electrode-liquid interface and in addition, compared to the liquid, this is - 0.2 V, the metal is 0.2 V below (the liquid). So if you take the algebraic sum, you will get 1 V. We do not know whether it is 0.8 V (and) -0.2 V but let us just imagine that this is the case. If I increase, the potential from 1 V to 1.5 V, can I guarantee that increase will occur evenly? Can I guarantee that the increase will occur only near one electrode? Can I get anything about the distribution of the increase?

So I cannot measure the potential across one interface, fine. I do not know the potential but if I increase a little, if I increase the applied potential a little, can I at least say that increase will go into this or it will be going 50:50 or in some given ratio, can I guarantee that?

It may go like the example given here. If it changes from 1 V to 1.5 V, the electrode on the left side can increase with 0.3 V, the potential on the electrode on the left side may go from 0.8 V to 1.1 V, and the potential across the interface for the electrode on the right side may go from -0.2 V to -0.4 V.

That is a possibility. It can also happen that for the same applied voltage, on the left side the electrode might have changed slightly but the potential across the electrode might have gone from 0.8 V to 0.9 V and on the right side, it might have dropped from -0.2 V to -0.6 V. This are just 2 examples. There are many possibilities.

So basically when I apply a potential, I cannot tell how much is the potential drop from the electrode to this liquid. When I change it, I cannot tell how much increase has gone here. So basically that means, if I have an electrochemical system, I can apply voltage, I can measure the current. I can increase the voltage, I can measure the current. I can say this much is the increase or change in the current but I cannot tell, this is the potential change here, this is the potential change here. So you can imagine in this scenario, it is very difficult to come up with any interpretation of the results.

So to overcome this difficulty, we introduced something called *reference electrode*. Reference electrode is a particular type of electrode, where the potential drop across the interface from the metal to the liquid, is a constant. We still cannot measure what that potential drop is. But we know it is a constant. So in that scenario, it is beneficial to use the reference electrode.

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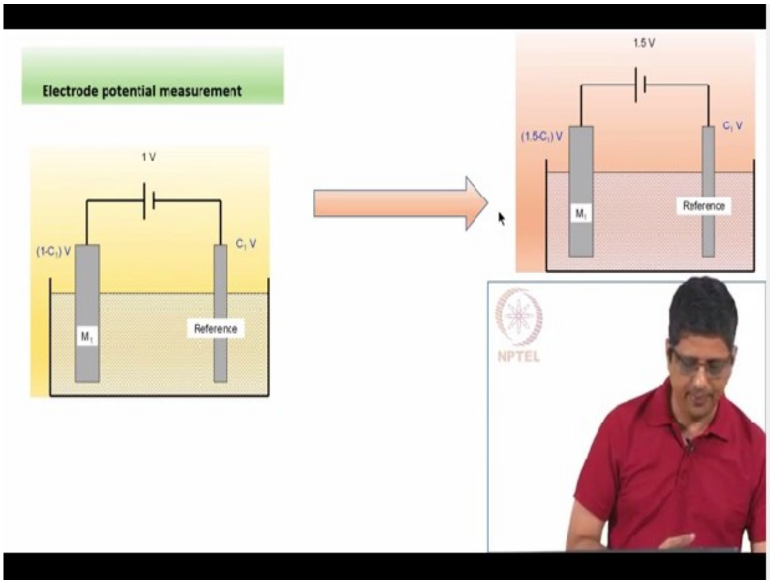

Electrode potential measurement

Let us say that C_1 is the potential drop across the metal liquid interface. It usually consists of multiple interfaces. From the metal to the electrolyte liquid, let us say the potential drop is C_1. It is fixed number. That means if I apply 1 V with the reference electrode here and with the other electrode that is of interest to us, we call it as a working electrode.

If the potential is applied, and if it is 1 V, I do not know what C_1 is but I know the other electrode has 1-C_1 as the potential drop. Now this is not very useful. However, if I apply a slightly different voltage, if I change the voltage and make it 1.5 V across these two electrodes, I can guarantee that the additional 0.5 V, that drop will occur only at the working electrode. So this is useful. Although I cannot tell exactly how much is the potential drop across an electrode. When I change the potential, I can say this is the change in the potential across this electrode. Therefore, any change in the current, I can assign it to that change in potential. So now I can make some sense out of this system.

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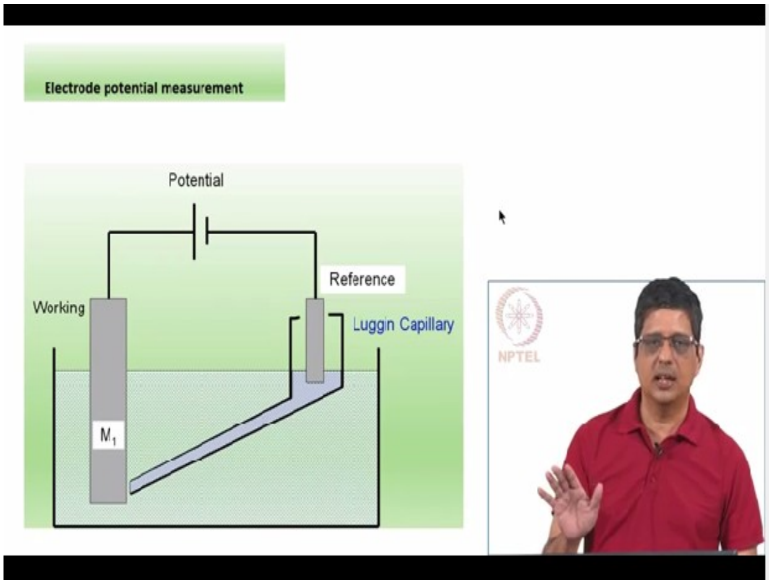

Electrode potential measurement

Lot of times, we use what is called *Luggin capillary*. Basically we want to minimize the resistance, solution resistance between the working electrode and the reference electrode. So if you are able to place the reference electrode close to this working electrode without affecting anything else in the system, it is well and good. If you have some difficulty, we can fill this, fill this entire system with the normal electrolyte, and then place the reference electrode within this Luggin capillary system and place the tip of the capillary right next to the working electrode. This way we always report the potential of the working electrode with respect to a reference electrode. It is not correct to say potential of this electrode is 1 V. We have to say this is *with* *respect to this reference electrode*. There are different types of reference electrodes available.

One is called standard hydrogen electrode, SHE, another is called standard calomel electrode or SCE, another is called silver-silver chloride or Ag-AgCl immersed in various concentrations of KCl. As long as you report it correctly, you can translate from one reference electrode to another reference electrode. So if you do experiment at 1 V with respect to Ag-AgCl, to do the same experiment with another reference electrode, you have to apply a constant offset. These are available in literature.

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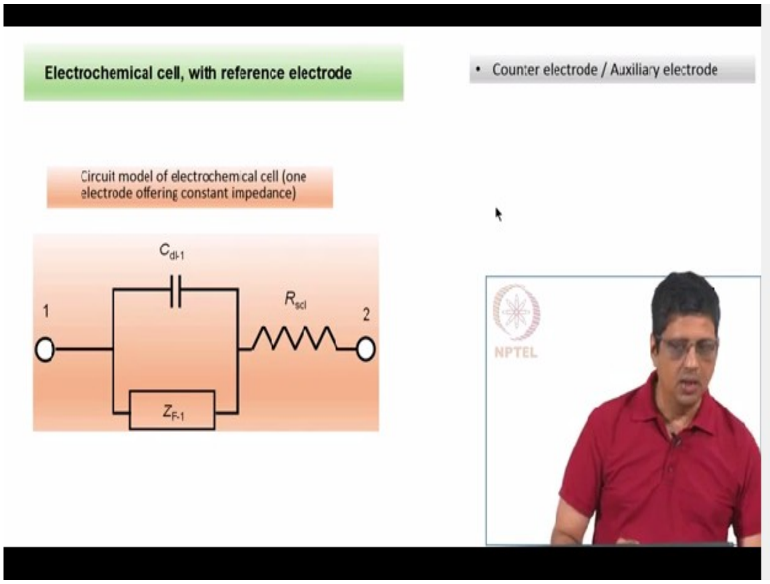

Electrochemical cell, with reference electrode

- Counter electrode / Auxiliary electrode

Circuit model of electrochemical cell (one electrode offering constant impedance)

Now if you make the impedance of the reference electrode as very small, so the re- should have constant potential drop. It should ideally also have very little impedance. Then I can describe the entire system, that is two cells with this circuit. On the other side, the impedance of the reference electrode is very little, then I can just look at the system and say only the working electrode has double layer capacitance and significant faradaic impedance, and you can possibly have solution resistance.

(To be precise, one needs to use)one more circuit to describe the reference electrode. But that offers very little impedance, so when I consider the total impedance, I can neglect that. But there is one difficulty in using the reference electrode. If significant current passes through the reference electrode, then it loses the property that it has a constant potential drop across this interface. So that means if you apply voltage, if current comes or current is taken up by this system, then I have to put another electrode and supply that current to the system or take away the current from the system, so that any current that comes from the working electrode is taken up by the other electrode and that is called *auxiliary* or *counter electrode*. Other than taking up the current of giving this current, it should give minimum disturbance or minimum changes to the system.

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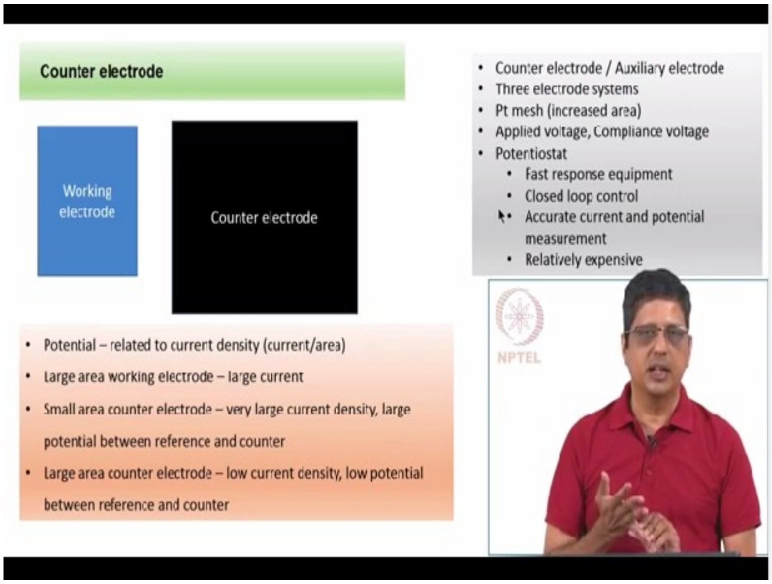

Counter electrode

- Potential – related to current density (current/area)
- Large area working electrode – large current
- Small area counter electrode – very large current density, large potential between reference and counter
- Large area counter electrode – low current density, low potential between reference and counter

- Counter electrode / Auxiliary electrode
- Three electrode systems
- Pt mesh (increased area)
- Applied voltage, Compliance voltage
- Potentiostat
    - Fast response equipment
    - Closed loop control
    - Accurate current and potential measurement
    - Relatively expensive

That is one requirement of a counter electrode. So we end up using three electrode system so that we can have control over the potential drop across the working electrode. So the potential is measured between the reference electrode and the working electrode. If we do the experiment correctly, the current will go from working electrode to the counter electrode, and the potential of the counter electrode will be controlled by the instrument. It will be adjusted so that any current that comes through the working electrode is taken up by the counter electrode. Normally, we want to have a large counter electrode area, large area counter electrode. There is a reason for that.

When we change the potential, what is controlling the electrochemical system, is the current density. If you happen to have a large working electrode, then for a given current density, the current will be large. Now all the current generated here has to be taken up by the counter electrode. In case you have a small area counter electrode, the current density requirement is high. So compared to the working electrode, if the counter electrode area is small, the current density that is taken into the counter electrode or current density requirement for the counter electrode is high. That means it has to be taken to a large potential and possibly you can have problems.

So it is better to have a large area counter electrode, then the load on the equipment, the potential on this counter electrode with respect to the reference electrode and the load on the equipment will be less. So what we end up doing is to use platinum mesh. Platinum because it is inert, mesh because it permits large area for a given geometric area. When you buy an instrument or when you look at the specification of an instrument, it gives you what is called applied voltage range and the compliance voltage range.

Applied voltage tells the voltage between the reference and working. Compliance tells the voltage between counter and the working electrode. Now you can imagine if current comes through this, the counter electrode potential has to be adjusted very fast, that means you need a fast response system, you need a close loop system. Based on this, the potential has to be adjusted. It cannot exceed a particular limit. If it becomes too high, then too much current will come from this, if it is too little, then sufficient current will not be taken up by this. Either case, you want a fast response system, you want a closed loop control and it has to accurately measure the current. We want to measure current in microamps, nanoamps, possibly picoamps, and the instrument which controls three electrodes, the three-electrode system is much more expensive than a simple dc current or dc potential power supply.

DC potential power supply, you can get it for less than 50,000 rupees, that is less than 1000 dollars, very easily. If you look at *potentiostats*, even a small potentiostat will probably cost about few lakhs, that is few 1000 dollars. One that can supply large current will cost you lot more money. The main difference is that this can handle the three-electrode system, it has to have a fast response with the closed loop without any stability problem.

If you have a two-electrode system, it is very easy to get an instrumentation for that. But then two electrode system is probably useful only in electrical and in some special cases. Electrical circuit analysis and special cases, two electrode system is fine, electrochemical system, it is better to employ a three-electrode system.

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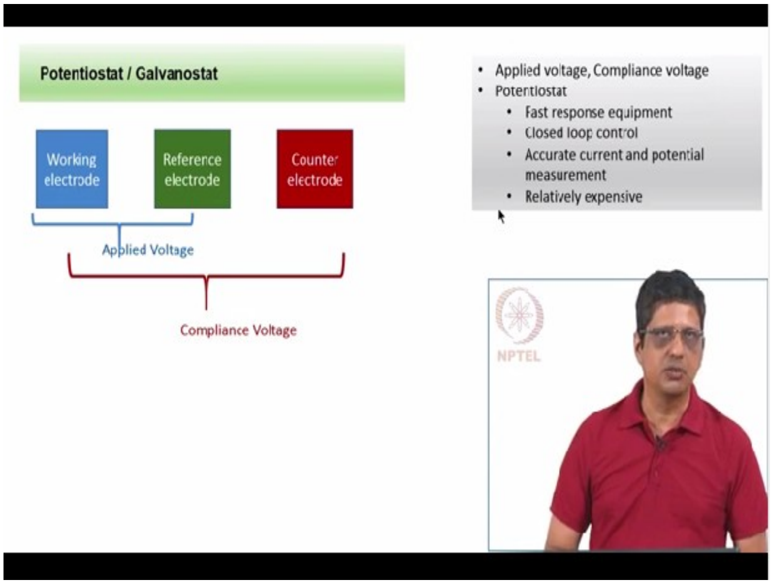

Potentiostat / Galvanostat

Working electrode

Reference electrode

Counter electrode

Applied Voltage

Compliance Voltage

- Applied voltage, Compliance voltage
- Potentiostat
  - Fast response equipment
  - Closed loop control
  - Accurate current and potential measurement
  - Relatively expensive

So this is just a pictorial description to tell you what is the applied voltage, where it is measured and what is the compliance voltage, it is measured across the working electrode and the counter electrode.

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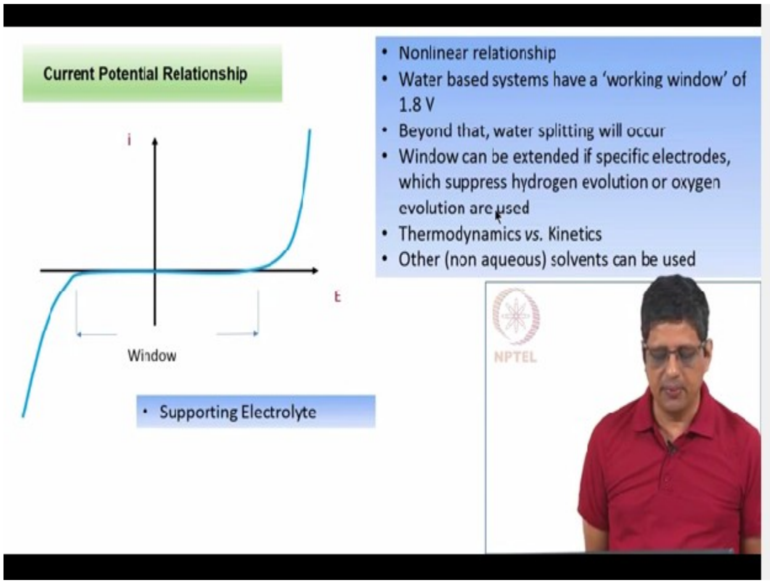

Current Potential Relationship

- Nonlinear relationship
- Water based systems have a 'working window' of 1.8 V
- Beyond that, water splitting will occur
- Window can be extended if specific electrodes, which suppress hydrogen evolution or oxygen evolution are used
- Thermodynamics vs. Kinetics
- Other (non aqueous) solvents can be used

- Supporting Electrolyte

Next in a simple electrical circuit, when you have a resistor, you change the potential, you will see a change in current and usually that relationship is linear, that is $\frac{V}{I}$ = R and that is a constant. The R can vary with temperature. Sometimes you would see a slight difference but by and large, it is a constant. There is a huge difference between electrical system response and the electrochemical system response.

This is one curve; I have just drawn it in the PPT here. If you take water and let us say you put some salt to make it better conductor, and then you control the potential and measure the current over a range, you would find that for a wide range, there is no current or there is very little current. So you can go to one potential, measure the current. Go to another potential, measure the current.

So let us say you have a two electrode system, two platinum meshes are there immersed into salt water. If you measure the current and potential, you would find that for a large range, large range here meaning about 1.8 volts, you would see no current at all, and after that, if you go to very positive potential for one electrode, obviously it means negative potential for the other electrode; current will be higher and it is going to be positive because oxygen will come from this electrode and hydrogen will come from the other electrode.

If you go to very negative potential for a given electrode, you will find hydrogen is evolving in that electrode and oxygen is evolving in the other electrode. Basically water splitting happens, and if you want to study any reaction other than water splitting, other than hydrogen evolution or oxygen evolution reaction, then you have to work within this window. If you put water base system and then want to study a reaction, then I have a limited window available for experiments. It is possible to extend this window by using certain electrodes. So for hydrogen evolution, certain electrodes are good catalysts, certain electrodes are poor catalysts. So if you use zinc, if I use mercury, hydrogen evolution does not occur that easily. So thermodynamics tells beyond this potential, hydrogen evolution has to occur. But kinetics tells, at what rate this occurs. So in certain electrodes like platinum electrode, it occurs at a good rate, it is a good catalyst. Some electrodes like zinc, lead, or mercury, hydrogen evolution does not occur that well. So the rate of production of hydrogen is very low, so I can extend the window and still study some other reaction, this is one trick. Another possibility is to use different electrolyte so I can use non-water based or non-aqueous solvents and extend the window. But every solvent will have a breakdown voltage and beyond that window, we cannot use it.

Now, I can increase the conductivity of this electrolyte by using what is called supporting electrolyte. Supporting electrolyte is basically a salt or acid which you can use without causing any change to the system except for change in conductivity. That is it should not undergo any reaction, it should just increase the conductivity.

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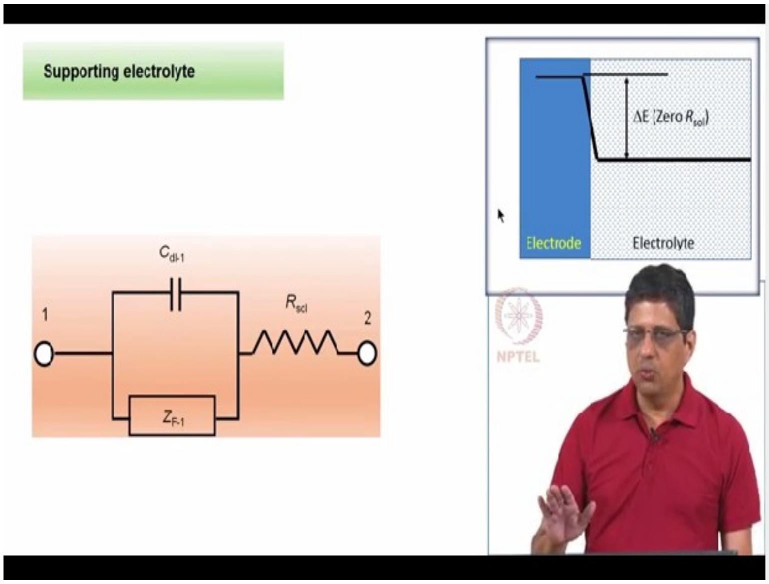

Supporting electrolyte

If you have good conductivity, if you have lot of supporting electrolyte, then you can take this model, this is for a good reference electrode, the model on the orange colour is given for a good reference electrode. Working electrode is given as C_{dl} and Z_F. Solution resistance is present, If it is negligible when you have lot of supporting electrolyte; supporting electrolyte for ex ample can be sodium perchlorate. Then all the potential drop in the working electrode will occur just across the interface. If you look at the potential, I have drawn here; It is going to go from a large voltage to a lower voltage in a very small space. This is to indicate about 1 nanometer or so across the Helmholtz plane. If the conductivity is low, if it is just water with little bit of salt, little bit meaning like millimolar, micromolar of salt, then when you have a reaction that you study, current passes through this interface, current also passes through the electrolyte and significant potential drop will occur across the electrolyte.

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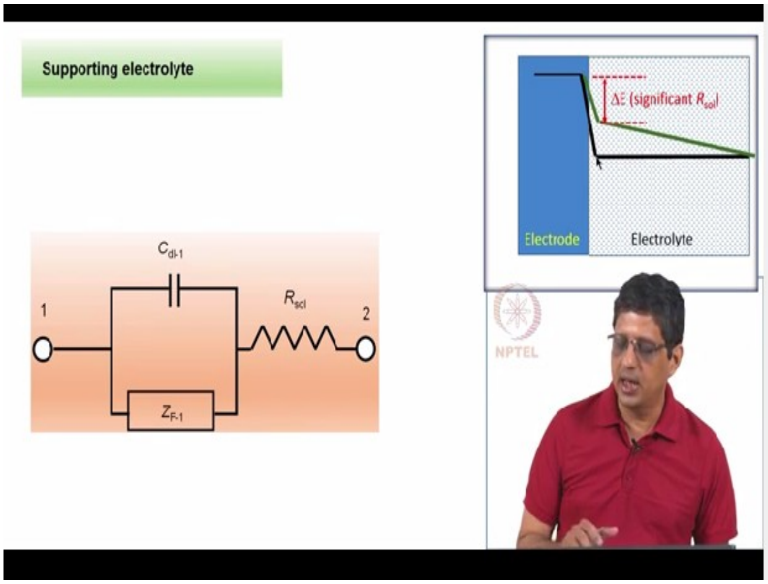

Supporting electrolyte

And whatever we imagine that we are applying this potential, and we are changing the potential, the additional potential is applied across this electrode. We imagine that it is occurring across the electrode but a significant change may occur across the, or between the two electrodes in the system. So this is a description of how the potential will look like if you have high solution resistance. So in order to avoid this, many times we add pretty much inert material, inert material as far as the reaction is concerned but as far as the conductivity is concerned, it increases the conductivity, and basically, it make sure that the electric field is such that all the potential drop occurs only across the interface.