Physics of Renewable Energy Systems
Professor Amreesh Chandra
Department of Physics
Indian Institute of Technology, Kharagpur
Lecture 33
Electrochemical Techniques for Supercapacitors and Batteries

Welcome again, to the course on physics of renewable energy systems. Today, we will start with a new module, which is going to deal with the characterization of super capacitors and batteries. And then we will talk to you about choice of materials, how you will choose materials? And then how do you fabricate a device, that will be discussed in the second lecture of this week. And in the final two lectures of this week, we will be talking to you about the real world application of a device.

Which means, that you may fabricate and characterize a device in a laboratory, but when you take that device to a real world application, where you may see changing temperature conditions, variation in electric or magnetic field or you can see change in pressure or you can encounter vibrations which are induced by external factors, then how does your device actually performs. So, these two aspects would be discussed in the final two lectures of this week.

And you will see that as you take a device from lab to market, there are additional factors which come into picture. And once you have optimized those parameters, then only the device can be integrated in applications, be it be autumn motive applications or be it be integration with mobile technologies. So, today let us start with our first topic, that is what are the two important characterization tools which are used to characterize the performance of super capacitors and batteries.

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CONCEPTS COVERED

☐ Cyclic Voltammetric Profile

☐ Charge-Discharge Profile

☐ Electrochemical Instrument

So, the concepts which would be covered in today's lecture are we will talk to you about the technique which is called as cyclic voltammetry. And following that, we will also be talking to you about the charge-discharge technique. How do you actually analyze the cyclic voltammetric profiles or the charge discharge profiles, to extract information about the device.

These two measurements can be performed using a potentiostat or a galvanostat or any electrochemical instrument, which can collect the relevant parameters, that are going to be used to plot these cyclic voltammetric profiles or the charge discharge profiles.

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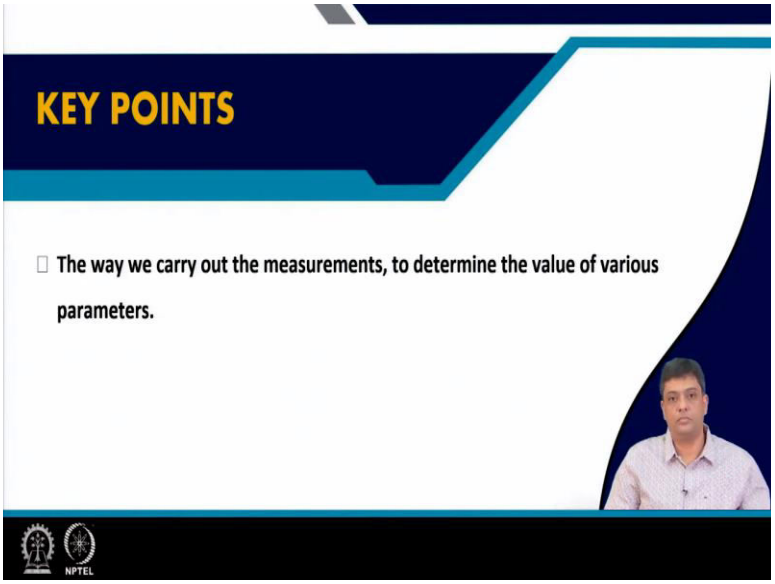

KEY POINTS

☐ The way we carry out the measurements, to determine the value of various parameters.

It is important to understand the way you actually carry out the measurements. Because, if you do not take precautions and follow the set protocols, then the results which you may get may be inconsistent. And you may not be able to extract the correct information about a device. And then its applicant, applicability is seriously hampered. So, this will also be discussed in detail.

And by the time you have understood the concept, which are going to be presented in today's lecture, you will be able to understand clearly the way we perform the measurements to determine the value of various parameters which are relevant to electrochemical devices, which have been discussed. Namely, the lithium ion batteries and supercapacitors.

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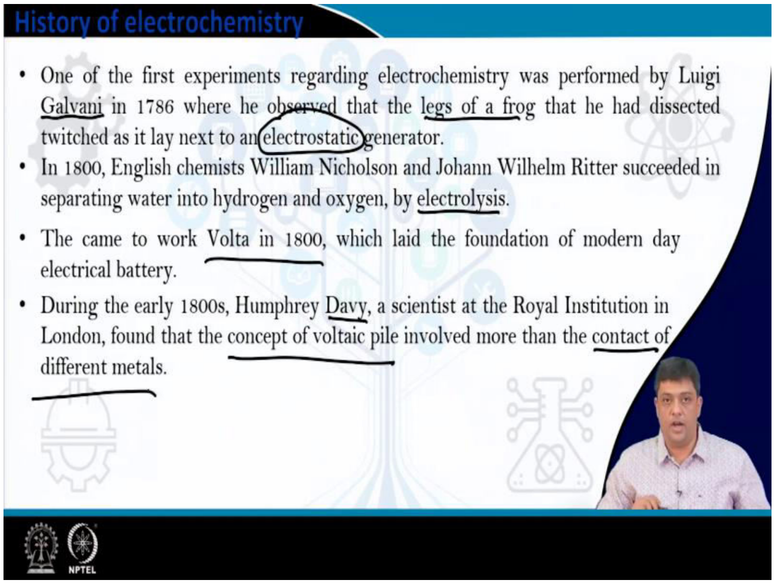

History of electrochemistry

- One of the first experiments regarding electrochemistry was performed by Luigi Galvani in 1786 where he observed that the legs of a frog that he had dissected twitched as it lay next to an electrostatic generator.
- In 1800, English chemists William Nicholson and Johann Wilhelm Ritter succeeded in separating water into hydrogen and oxygen, by electrolysis.
- The came to work Volta in 1800, which laid the foundation of modern day electrical battery.
- During the early 1800s, Humphrey Davy, a scientist at the Royal Institution in London, found that the concept of voltaic pile involved more than the contact of different metals.

As we have been moving in all the modules, before we actually start a particular concept or the discussion on a particular concept, we are trying to understand as to how it has developed over a period of time. This gives us the background to understand that any technology, any concept is not necessarily new. And it takes a significant amount of time for any knowledge to become useful to mankind.

If you look into electrochemistry, then it also is a phenomena which was observed way back in 1700s. When Galvani observed that the legs of a frog that he had dissected was twitching when they were lying next to an electrostatic generator. So, why there was twitching in the legs of a frog, when it was very near to an electrostatic generator? Please remember. To, so, then people started believing yes, that you can have any interaction between charges.

Then in early 1800s, Nicholson and Ritter were able to show that water can be broken down into hydrogen and oxygen by electrolysis. So, you have the electrodes, you pass current and then you can get hydrogen and oxygen evolution. And then also we have seen in the previous modules, the work of Volta in early 1800s, which laid down the foundation for the modern, modern day electrical batteries.

Similarly, after the work of Volta, Davy came in and then found that the concept of a voltaic pile involved more than the contact of different metals. That means, the whole concept was much more involved, you had initial features coming into picture which needed to be understood before the operation of a voltaic pile could be explained clearly.

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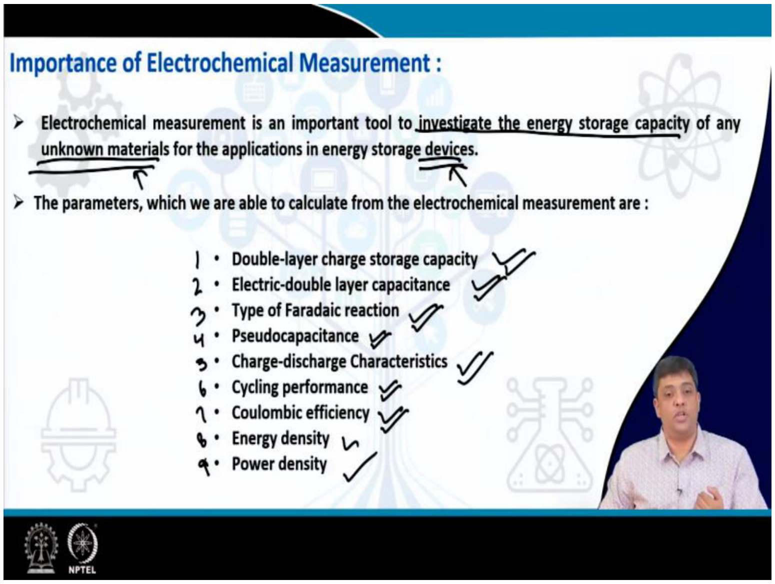

Importance of Electrochemical Measurement :

- Electrochemical measurement is an important tool to investigate the energy storage capacity of any unknown materials for the applications in energy storage devices.
- The parameters, which we are able to calculate from the electrochemical measurement are :
  1. Double-layer charge storage capacity
  2. Electric-double layer capacitance
  3. Type of Faradaic reaction
  4. Pseudocapacitance
  5. Charge-discharge Characteristics
  6. Cycling performance
  7. Coulombic efficiency
  8. Energy density
  9. Power density

And now, we are talking about 2021. So, you see that, still the concepts are very relevant. And by analyzing the data which you get from electrochemical measurements, new understandings are being developed about devices, devices like batteries, supercapacitors, or any kind of hybrid systems. So, still you are adding to the knowledge, which was first proposed more than a couple of 100 years back.

And the measurements which we are using and are going to discuss in today's lecture would be to investigate the energy storage capacity of a device or unknown materials. So, either the capacity of the material or the complete device as per saying. And by analyzing the data which you obtain from electrochemical measurements, let me just list a few of the parameters which you can determine.

I said a few, there are many more features which can be extracted by analyzing the data even further. To start, the parameters which are important to us and the information about these can be extracted using the electrochemical measurements, which we are going to discuss today are the charge storage capacity in double layer capacitors, the electric double layer capacitance. We had seen in the previous module that you have EDLC and pseudo capacitance.

One involved non faraday type reactions, whereas the latter was associated with a faraday type reaction where you were observing both oxidation and reduction processes. So, by analyzing the data of electrochemical measurements, you can even get information about the type of faradic rate reactions which are taking place. And once you obtain that, you can then calculate the magnitude of pseudo capacitance.

If you look into a capacitor the, the major parameter which defines the usability of a capacitor is, is its charge discharge characteristics. This can also be determined by the electrochemical measurements. Now, we had said that the capacitors which we are talking about or even batteries which we had discussed, they have to have a reasonably high cycling stability. That means, for batteries typically we are talking about 1000 plus cycles.

And for capacitors or super capacitors you are looking at 100,000 or plus cycles. So, how do you analyze it? Again the same measurements can be used to determine the cyclic performance of these devices. Coulombic efficiencies it means, the ratio of the energy which can be extracted with respect to the energy which was actually sent in to be stored. And the usable energy is what? The energy which is being delivered by the capacitors, not what are being accepted by the capacitors.

So, you can find out the coulombic efficiencies and finally, if you have the values of c that is pseudo capacitance or EDLCs then you can talk about the energy densities and power densities. Energy density, half CV square power densities, you are talking about the ratio E by t. So, just by couple of measurements, let us see how many parameters you can extract one, two, three, four, five, six, seven, eight and nine, and these are just the preliminary analysis of the data. So, if you spend even more time, many more detailed information can be extracted.

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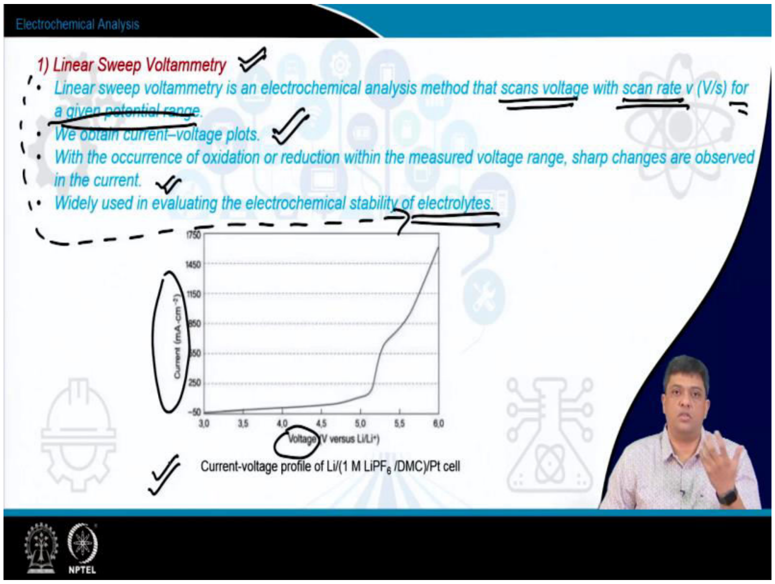

Electrochemical Analysis

1) Linear Sweep Voltammetry

- Linear sweep voltammetry is an electrochemical analysis method that scans voltage with scan rate v (V/s) for a given potential range.
- We obtain current–voltage plots.
- With the occurrence of oxidation or reduction within the measured voltage range, sharp changes are observed in the current.
- Widely used in evaluating the electrochemical stability of electrolytes.

Current-voltage profile of Li/(1 M $LiPF_6$ /DMC)/Pt cell

There are various types of electrochemical analysis, which you can perform. The first one is the linear sweep voltammetry. As the name suggests, it involves the scanning of the voltage with scan rate. So, you, you define at what rate you want to scan the voltage for a given potential range, for a given potential range. And what do you obtain? You obtain the current versus voltage plots.

When you analyze the data, you will see that if there is an occurrence of oxidation or there is a reduction process, which is occurring within the voltage range then you will see some changes in the current. So, you will see change in the current, which will be happening why? Because either electron is becoming available or is being taken out from a material. And this technique is mostly used and widely used for evaluating the electrochemical stability of the electrolytes.

So, linear sweep voltammetry, very useful for determining the stability of the electrolyte. So, this is the current voltage profile of lithium with respect to one molar LIPF6 in DMC. And then the whole is, the whole setup is in the platinum set. So, you get a linear sweep voltammetry.

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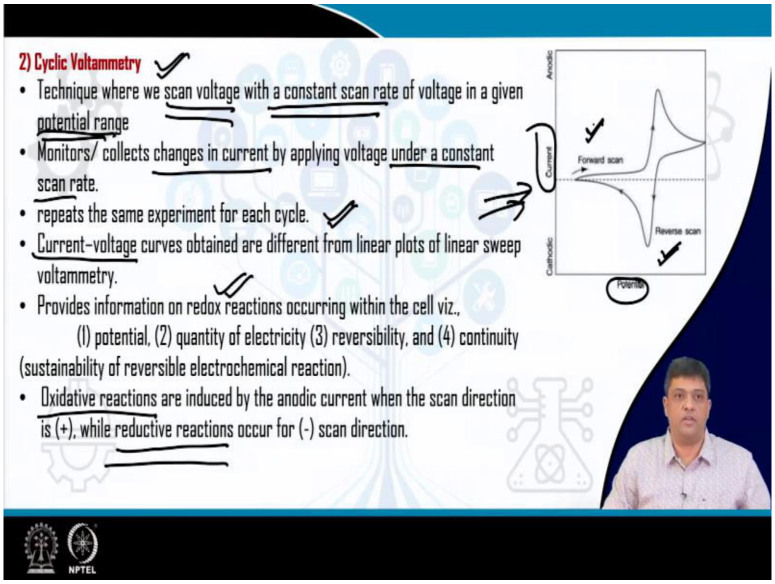

2) Cyclic Voltammetry

- Technique where we scan voltage with a constant scan rate of voltage in a given potential range
- Monitors/ collects changes in current by applying voltage under a constant scan rate.
- repeats the same experiment for each cycle.
- Current-voltage curves obtained are different from linear plots of linear sweep voltammetry.
- Provides information on redox reactions occurring within the cell viz.,
  (1) potential, (2) quantity of electricity (3) reversibility, and (4) continuity (sustainability of reversible electrochemical reaction).
- Oxidative reactions are induced by the anodic current when the scan direction is (+), while reductive reactions occur for (-) scan direction.

The second technique is called the cyclic voltammetric. Cyclic, word if that becomes clear you will understand the process much more easily. Cyclic means, you are repeating a particular cycle, so, cyclic voltammetry. So, if you can now understand what is voltammetry, you will understand that in cyclic voltammetry the process is be repeated many times. This technique involves the scanning of the voltage with a constant scan rate of voltage in a given potential range.

So, you scan voltage with a constant scan rate of voltage, but in a given voltage. What do you monitor? We monitor or collect or observe the changes in the current, which is happening because of this applied voltage under a constant rate. So, you change the voltage at a constant rate and then you see, what is the current you obtain. So, that is voltammetry, change in voltage, observe parameter current and then you repeat the cycle.

So, the whole process is repeated over many sites. So, you had cyclic voltammetry. What do you obtain? You obtain current versus voltage curves, and these curves are clearly looking different from the linear sweep voltammetry. By analyzing such curves, you can get information about the redox reactions taking place within the cell. What type of redox reactions? What is the potential in of the cell? What is the quantity of electricity which you get?

What is the nature of reversibility? When, if you reverse the cycle do you get the same performance? What is then the information about the continuity? Whether the system is able to sustain this cycling performance or not? So, you can get all these information by analyzing these kinds of curve. And the oxidative reactions take place in the positive scan direction, whereas, the reductive reactions occur in the negative scan direction.

So, if you can look these are the current versus potential curves. And when you talk about the reverse direction or the forward direction, then in the forward direction we are looking at the oxidative reactions. Whereas in the reverse direction, you are looking at the reactive reactions.

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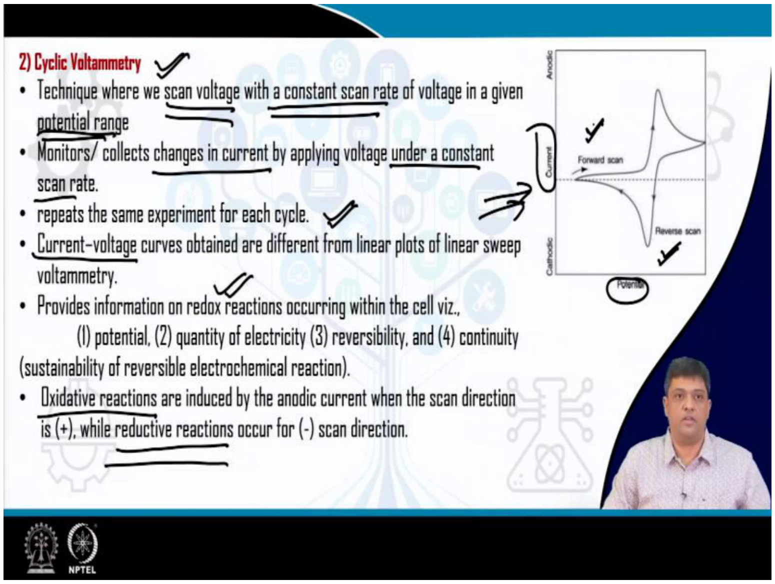

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The third type of measurement is the constant current or the galvanostatic measurements. These measure the characteristics in an electrochemical cell by monitoring the changes in voltage over time, but under a constant current. So, earlier you were scanning over a voltage range, at a constant scan rate of voltage and monitoring current. Here, you are doing the opposite, what you are doing? You are measuring changes in voltage over time, under constant current.

This can give information about the capacity, the reversibility, the resistance and the rate of diffusion. Based on the nature of termination conditions, how do you stop? Or what is the range in which you are going to perform such measurements? You have two types of galvanostatic measurements. Either the cutoff voltage control or the constant capacity cutoff control. The first one that is the cutoff voltage control, derives the quantity of electrical charge under continuous charging and discharging with varying voltage over time.

It thus allows the calculation of coulombic efficiency. And you can determine coulombic efficiencies for each charging and discharging cycle. If I ask you a question at this moment, suppose, you have charging and discharging cycles, where the area under the discharge curve remains the same throughout. Then, what is the columbic efficiency we are talking about? For that condition, where the charge, area under the charging curve is also the same.

So, what is happening? The area under the discharge curve is same throughout for, let us say n number of cycles. And the time taken to charge the devices also remains the same for the n number of cycles. That means, your system does not change its characteristics, over these n cycles. And therefore, your coulombic efficiencies would be very high. But if you go on seeing changes in the charging and the discharging cycles after each cycle, then your coulombic efficiencies would be continuously changing.

Using this cutoff voltage control based galvanostatic measurement, you can also obtain the differential capacity curve, that is differential capacity dQ by dV curve against voltage based on time and voltage values. And if you have obtained these dQ by dV, dV values, then you can accurately measure these specific voltage of electrochemical reactions. In the next case, what you do? You basically control the amount of electric charge and such kind of measurements are mostly used to determine the characteristics of the anode.

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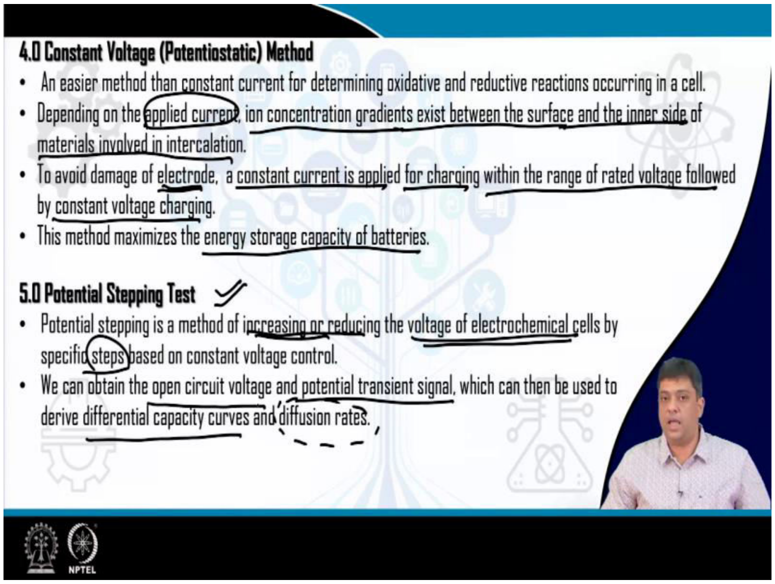

4.0 Constant Voltage (Potentiostatic) Method

- An easier method than constant current for determining oxidative and reductive reactions occurring in a cell.
- Depending on the applied current, ion concentration gradients exist between the surface and the inner side of materials involved in intercalation.
- To avoid damage of electrode, a constant current is applied for charging within the range of rated voltage followed by constant voltage charging.
- This method maximizes the energy storage capacity of batteries.

5.0 Potential Stepping Test

- Potential stepping is a method of increasing or reducing the voltage of electrochemical cells by specific steps based on constant voltage control.
- We can obtain the open circuit voltage and potential transient signal, which can then be used to derive differential capacity curves and diffusion rates.

The next one is your potential static method, that is the constant voltage. This is much easier than the constant current, kind of measurements for determining the oxidative or the reductive reactions. Which are happening in the electrochemical cell or the device which we have discussed. I am depending upon the applied current. So, earlier it was the applied voltage now, it is the applied current.

There is an ion concentration gradient, which will appear, appear where? Between the surface and the inner side of the materials, involved in intercalation. So, probably aconcentration gradient exists between the surface and the inner side of the material involved in intercalation. This sentence is indicating to you towards the formation of some kind of layers. But if you go on increasing the voltage, then you may end up damaging the material itself.

So, to avoid the electrode materials damage, what do you do? You have a constant current which is applied for charging, but within a range of rated voltage. So, I know up to what voltage range my material will be stable, and that is the range in which this measurement is performed. And then you can perform these measurements by constant voltage charging, but within the range of rated voltage.

And this method, gives you detailed information about the energy storage capacities of batteries or hybrid devices. And the final technique, which is relevant to us at this moment is the potential stepping test. This method is what? It is a method of increasing or reducing the voltage of electrochemical cell by specific steps. So, now, we will tell the device that you have to move from one voltage to the next, at a given fixed step rate.

So, so, the steps are fixed. And we can obtain information about the open circuit voltage, the potential transient signals, which can then be used to derive the differential capacity curves and the diffusion rates. So, you see, that there are various techniques or various combinations of changing the current or the voltage. And by analyzing them you can get the data about the electro chemical set. So, but the three things we are looking at are either changing current, changing voltage for a fixed time or for different time periods.

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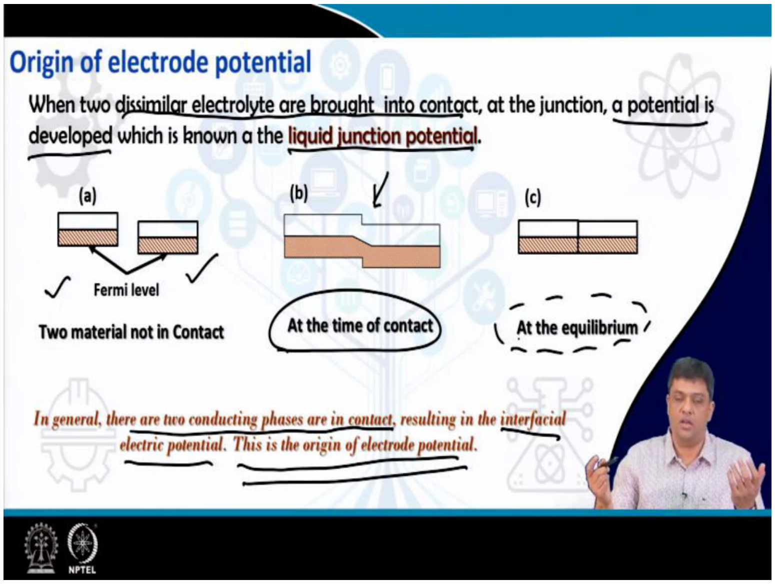

Origin of electrode potential

When two dissimilar electrolyte are brought into contact, at the junction, a potential is developed which is known a the liquid junction potential.

In general, there are two conducting phases are in contact, resulting in the interfacial electric potential. This is the origin of electrode potential.

Let us start with the concept, we are trying to understand the electrode potential. But what is the origin of electrode potential? So, let us consider two dissimilar electrolytes, which are brought into contact. So, you have one electrolyte coming in contact with the other. What happens at the junction? At the junction of potential is developed which is known as the liquid junction potential. And this concept is further extended.

In general if you consider two conducting phases, which are brought into contact then you have an interfacial electric potential, which ensures that there is wave function matching on both sides of the junction. And this drives the origin of electrode potential. So, at the time of contact, there is change at the interface, but once you let the system reach, the equilibrium condition, you will find that the potential on both the sides of the interface would be similar.

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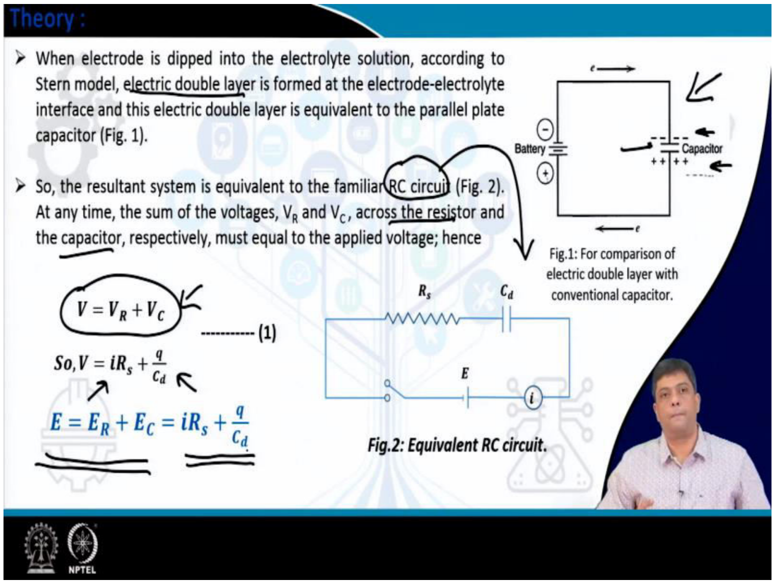

Theory :

- When electrode is dipped into the electrolyte solution, according to Stern model, electric double layer is formed at the electrode-electrolyte interface and this electric double layer is equivalent to the parallel plate capacitor (Fig. 1).
- So, the resultant system is equivalent to the familiar RC circuit (Fig. 2). At any time, the sum of the voltages, V_R and V_C, across the resistor and the capacitor, respectively, must equal to the applied voltage; hence

$$\boxed{V = V_R + V_C} \quad \text{-----------} (1)$$

$$So, V = iR_s + \frac{q}{C_d}$$

$$E = E_R + E_C = iR_s + \frac{q}{C_d}$$

Fig.1: For comparison of electric double layer with conventional capacitor.

Fig.2: Equivalent RC circuit.

If you want to analyze the theory associated with it further, then let us look into the case, where the electrode is dipped in an electrical light solution. Now, we had discussed about the Helmholtz model, the Gouy-Chapman model and the stern model in the previous module. And we had shown that stern model is able to describe the formation of double layer in the best possible way by combining the propositions of the Helmholtz model and the Gouy-Chapman model.

So, let us consider an electrode which is dipped in - the electrolyte. And the stern model which describes the formation of an electric double layer at the electrode electrolyte interface is considered and you can get the typical picture, which is given in figure number one of this slide. If you look into this picture this looks very similar to a conventional capacitor but you have the formation of the layers that is the double layers at the interface of the solid and the electrolyte or the electrode electrolyte interface.

So, this system can be model using us RC circuit. And if I consider this then what am i considering I am considering the voltage drop that is VR and VC across the resistor and the capacitor. So, you have the resistive drop and the capacitive drop and the total voltage which you get is the sum of these two voltages V is equal to the value of VR plus the value of VC. This can be written as iRs plus q by Cd. And if I define the voltage window then E is equal to ER by EC that is equal to i Rs plus q by Cd. So, E is defining your voltage window.

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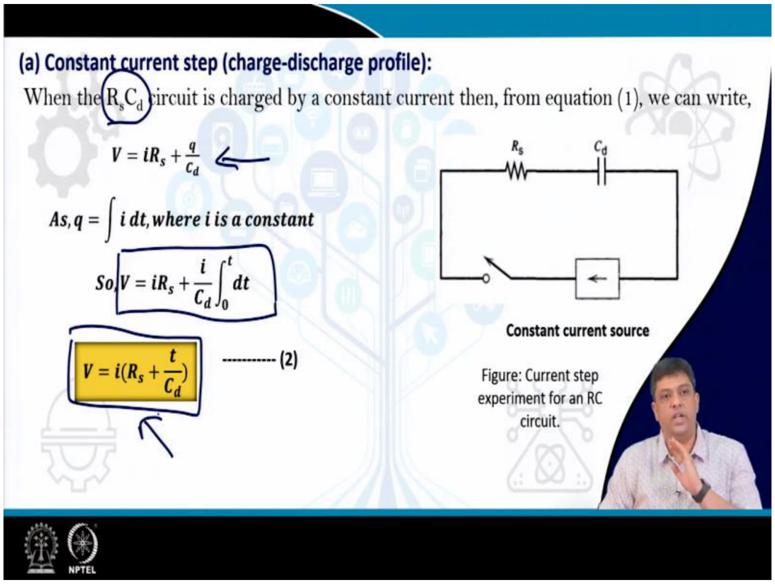

(a) Constant current step (charge-discharge profile):

When the R_sC_d circuit is charged by a constant current then, from equation (1), we can write,

$$V = iR_s + \frac{q}{C_d}$$

As, $q = \int i\,dt$, where i is a constant

So, $V = iR_s + \frac{i}{C_d}\int_0^t dt$

$$\boxed{V = i(R_s + \frac{t}{C_d})} \text{ ---------- (2)}$$

Figure: Current step experiment for an RC circuit.

If we consider the constant current step that is the charge discharge profile what will happen you will find that this circuit which is given by the component Rs and Cd, then Rs Cd is what is the time constant. This is charged by a constant current. We have seen this equation V is equal to iRs plus q by Cd. We know q is equal to integration of i dt where i is a constant in this case. So, I can write V is equal to i into Rs plus i by Cd 0 to t dt. Hence, what do we get? We get V is equal to i bracket Rs plus t by Cd bracket closed. So, we can find out what is the voltage that would be obtained.

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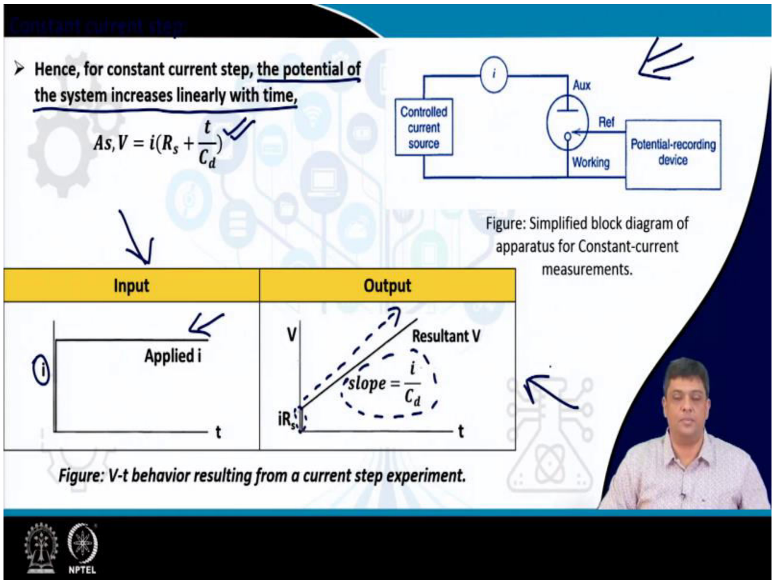

Constant current step:

- Hence, for constant current step, the potential of the system increases linearly with time,

$$As, V = i(R_s + \frac{t}{C_d})$$

Figure: Simplified block diagram of apparatus for Constant-current measurements.

Figure: V-t behavior resulting from a current step experiment.

So, for this the potential of the system increases linearly with time. So, we are seeing that the potential is increasing linearly with time. And this is the typical setup where you will be measuring the constant current step based changes in potential. So, if you have the input where you have the current which is applied and then it takes a constant value then you will find that beyond this iRs value you have a linear growth in the voltage.

And if you plot this curve you will get the slope which is given by i by Cd. So, from this curve if I asked you can you derive the value of Cd if I know what is i. So, if I Know what is the maximum current I am going to apply or what is the current which is fixed after there is an increase from 0 and then I have fixed the step at the value i can I get the value of Cd if the experimental data is there? I think you are very clear about this that you can measure the capacitance value forming in a double layer quite easily.

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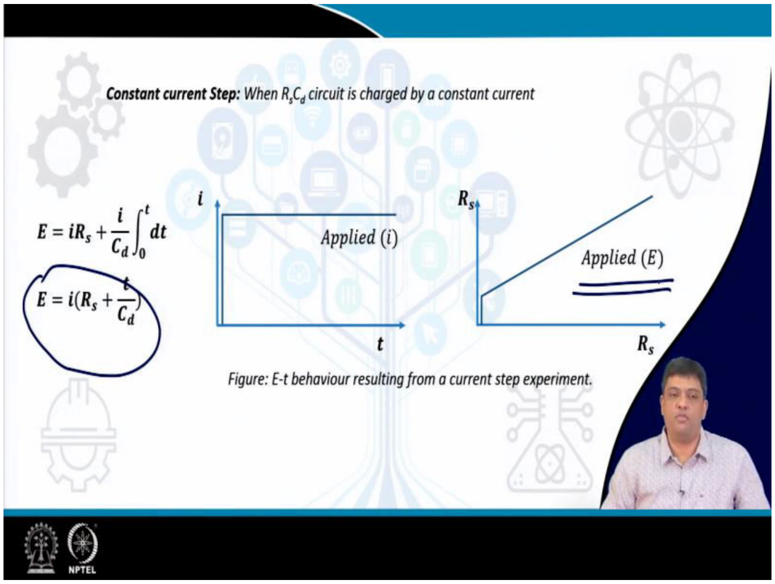

Constant current Step: When R_sC_d circuit is charged by a constant current

$$E = iR_s + \frac{i}{C_d}\int_0^t dt$$

$$E = i(R_s + \frac{t}{C_d})$$

Figure: E-t behaviour resulting from a current step experiment.

And this is what is there. So, if you have in terms of applied voltage then you can explain the same results in terms of E.

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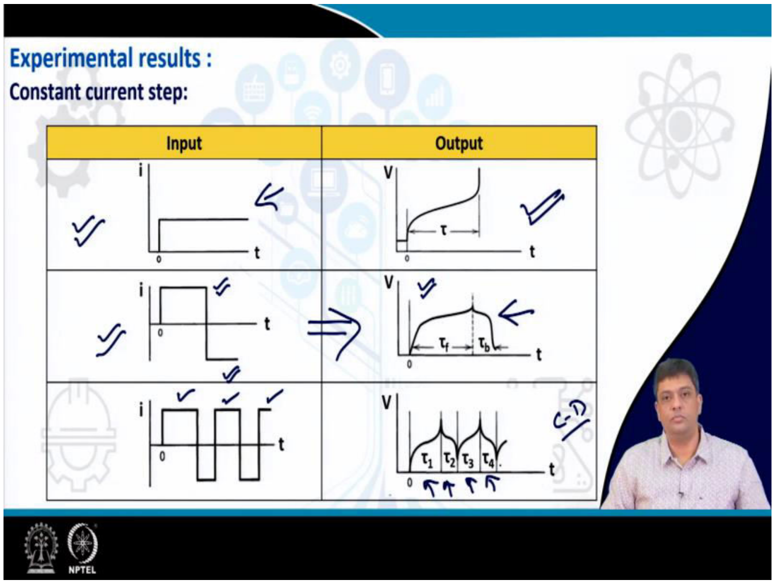

Experimental results :

Constant current step:

So, now you can have various types of combinations, combinations such as input where it is a step function and then the value remains nearly constant. Then what is the kind of output curve we are getting you are getting the output which we have discussed in the earlier case. So, second could be that you take the value to i and then reverse the polarity and then fix it to minus i then what kind of curves you can get is the one where you will have you can call this as the charging cycle and this as the discharging cycle.

So, either in the forward direction or the reverse direction and if you repeat these kinds of cycles if you repeat this kind of variations you will get the CD curves that is charging discharging and then you can measure the values tau 1, tau 2, tau 3, tau 4 if you say tau 1, tau 3, tau 5 are the time taken for the system to reach the voltage V then tau 2, tau 4, tau 6 is the time in which the system goes back to its initial condition.

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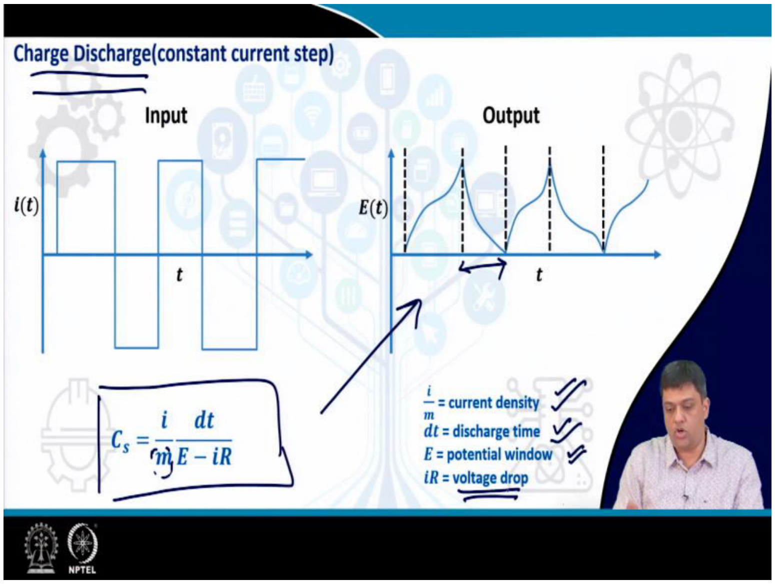
Charge Discharge(constant current step)

$$C_s = \frac{i}{m}\frac{dt}{E - iR}$$

$\frac{i}{m}$ = current density

dt = discharge time

E = potential window

iR = voltage drop

And this is what we are talking about as the charge discharge curves. And the specific capacitance that is divided by mass is therefore, given by i by m dt by E minus iR which is obtained from this curve where i by m is the current density dt is the discharge time. E is the potential window in which you are scanning and iR is the voltage drop.

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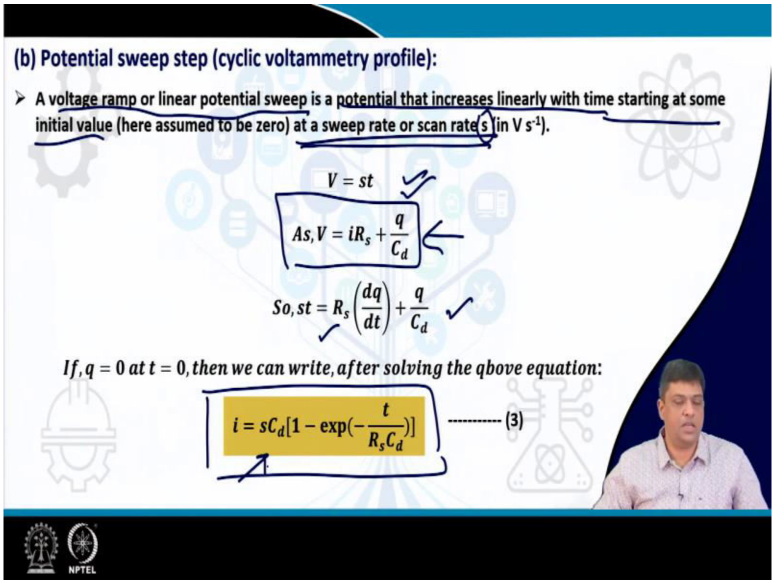
(b) Potential sweep step (cyclic voltammetry profile):

- A voltage ramp or linear potential sweep is a potential that increases linearly with time starting at some initial value (here assumed to be zero) at a sweep rate or scan rate s (in V s^{-1}).

$$V = st$$

$$As, V = iR_s + \frac{q}{C_d}$$

$$So, st = R_s\left(\frac{dq}{dt}\right) + \frac{q}{C_d}$$

If, q = 0 at t = 0, then we can write, after solving the qbove equation:

$$i = sC_d[1 - \exp(-\frac{t}{R_sC_d})] \quad \text{---------- (3)}$$

So, that was your charge discharge measurements, what happens in the cyclic voltammetric measurements? Here you are performing slightly different measurements you are measuring current versus voltage curves and then repeating the old steps. So, you have changes in the current or when you have a voltage ramp or a linear potential sweep that increases with time. But, you can also describe in terms of these linear potential sweeps which are at a fixed sweep rate or voltage ramp which are fixed or different scan rates s.

So, V is equal to s into t from the earlier postulate we had seen V is equal to iRs plus q by Cd. So, st becomes equal to Rs dq by dt plus q by Cd, if charge is 0 at time is equal to 0, then we can write the above equation as i is equal to S into Cd 1 plus exponential minus t by Rs Cd.

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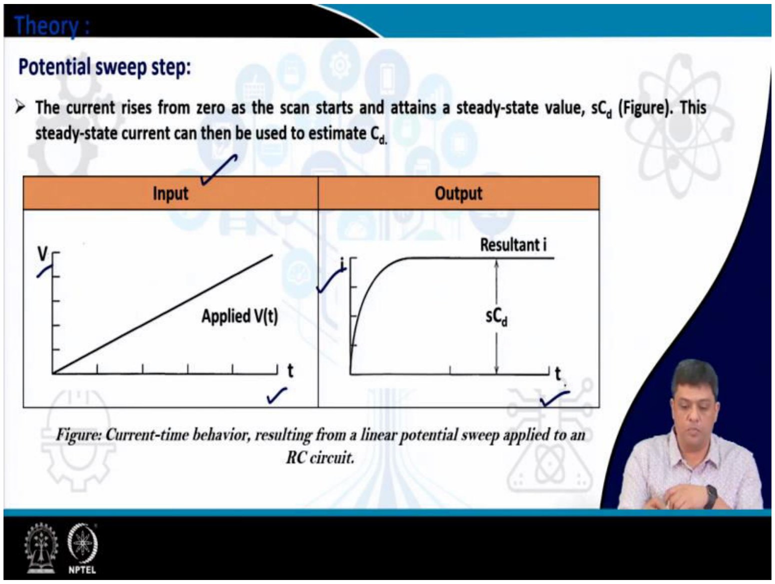

Theory :

Potential sweep step:

- The current rises from zero as the scan starts and attains a steady-state value, sC_d (Figure). This steady-state current can then be used to estimate C_d.

Input	Output

Figure: Current-time behavior, resulting from a linear potential sweep applied to an RC circuit.

Easily you can solve this equation and then you will get the values of Cd. So, if you have a voltage ramp then you get the change in current. So, input and output.

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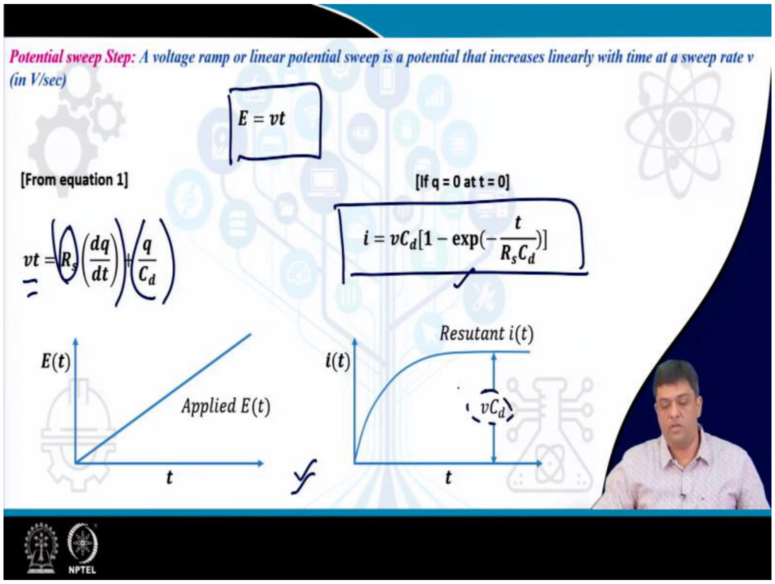

Potential sweep Step: *A voltage ramp or linear potential sweep is a potential that increases linearly with time at a sweep rate v (in V/sec)*

$$\boxed{E = vt}$$

[From equation 1]

$$vt = R_s\left(\frac{dq}{dt}\right) + \left(\frac{q}{C_d}\right)$$

[If q = 0 at t = 0]

$$\boxed{i = vC_d[1 - \exp(-\frac{t}{R_sC_d})]}$$

If you then talk about let us say the potential sweep step, then what are we doing? We are talking in terms of E is equal to vt. We have already seen how do we write at t is equal to 0, q is equal to C0. So, vt is equal to Rs into dq by dt plus q by Cd. Hence, we get the condition i is equal to V Cd plus 1 minus exponential of minus t by Rs Cd. And this is the same curve which we discussed earlier. So, this is the value of V into Cd.

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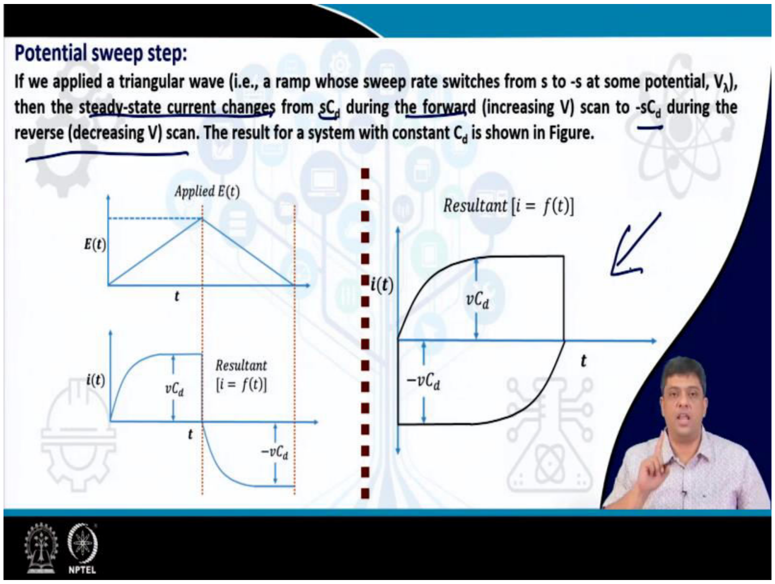

Potential sweep step:

If we applied a triangular wave (i.e., a ramp whose sweep rate switches from s to -s at some potential, V_λ), then the steady-state current changes from sC_d during the forward (increasing V) scan to $-sC_d$ during the reverse (decreasing V) scan. The result for a system with constant C_d is shown in Figure.

So, what will you do? You have basically the if you are plotting a triangular wave or a ramp then the steady current changes from Sd during the forward bias 2 minus sCd during the decreasing voltage scan and you get a similar condition, but now what you are doing increasing the voltage ramp and then going back. So, similar to the condition two charges charge but here you are scanning voltage and current.

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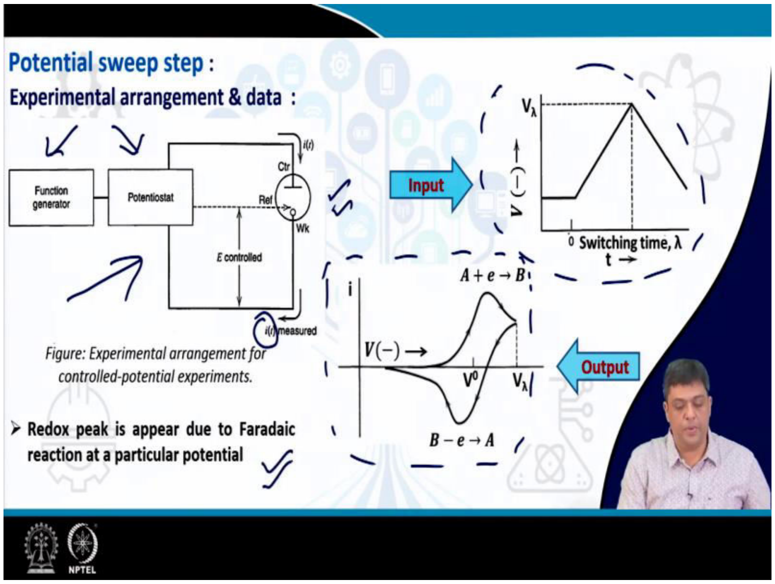

Potential sweep step :

Experimental arrangement & data :

Figure: Experimental arrangement for controlled-potential experiments.

- Redox peak is appear due to Faradaic reaction at a particular potential

So, what do you get from an experimental setup which will obviously involve a function generator suppose you are you have to give a triangular sweep then you have to have a triangular wave then a potential stat and what you will obtain is the measure current. So, input and what you get is the output, you get the voltage iv curves. The redox peaks appear due to the Faradaic reactions at a particular potential.

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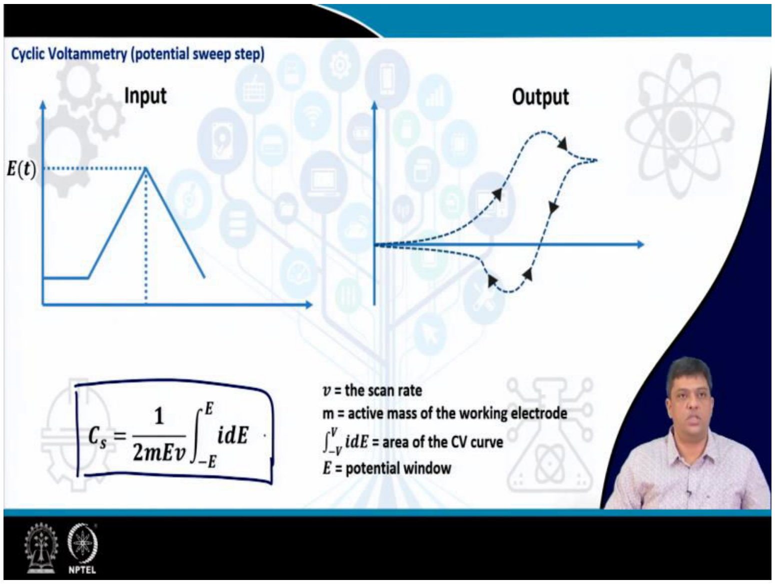

Cyclic Voltammetry (potential sweep step)

$$\boxed{C_s = \frac{1}{2mEv}\int_{-E}^{E} idE}$$

v = the scan rate

m = active mass of the working electrode

$\int_{-V}^{V} idE$ = area of the CV curve

E = potential window

So, this is what you obtain and if you want to get the specific capacitors you can again derive the formula which is given here and will also be discussed with later.

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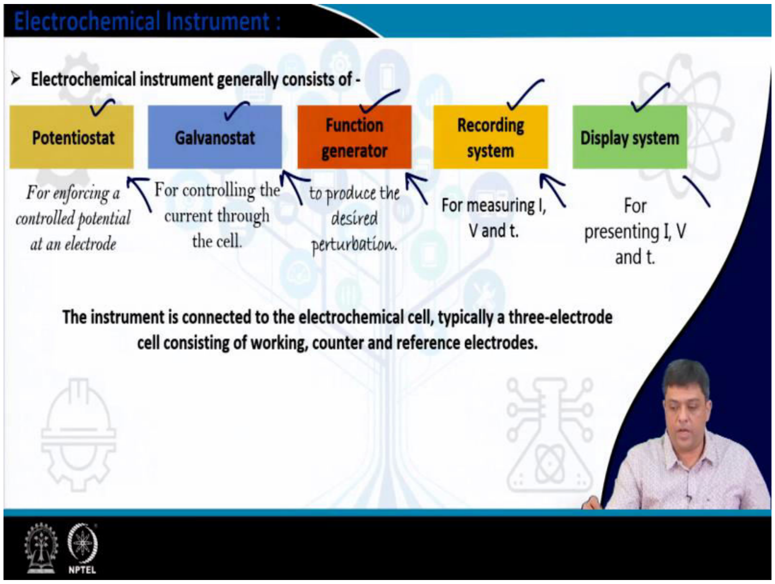

Electrochemical Instrument :

- Electrochemical instrument generally consists of -

Potentiostat	Galvanostat	Function generator	Recording system	Display system
For enforcing a controlled potential at an electrode	For controlling the current through the cell.	to produce the desired perturbation.	For measuring I, V and t.	For presenting I, V and t.

The instrument is connected to the electrochemical cell, typically a three-electrode cell consisting of working, counter and reference electrodes.

So, how would an electrochemical instrument look like it generally involves a Potentiostat a Galvanostat a function generator a system which will collect the data, so, a data collection unit and then if you want to monitor online then it is the display unit. I hope you have understood the purpose of each one of them by now.

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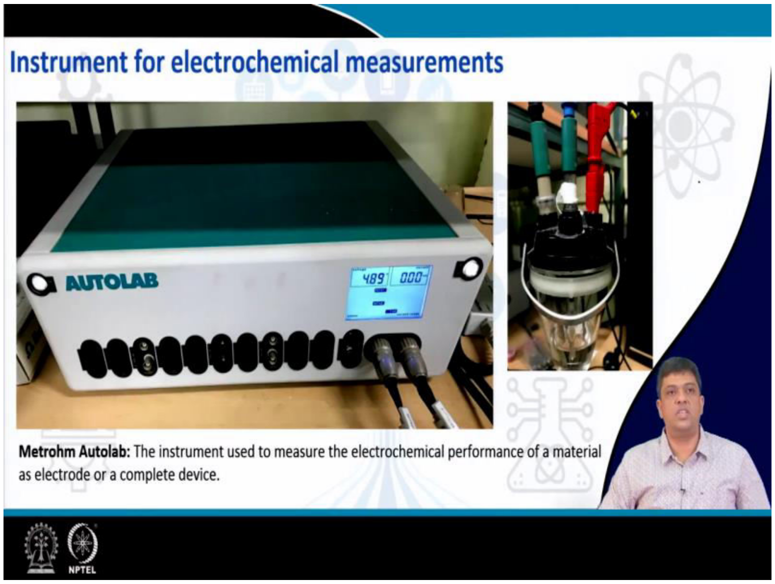

Instrument for electrochemical measurements

Metrohm Autolab: The instrument used to measure the electrochemical performance of a material as electrode or a complete device.

So, this is a typical Metrohm Autolab based system this is a two channel device where you can carry out the measurements and on the right hand side of this curve, you see a three electrode assembly.

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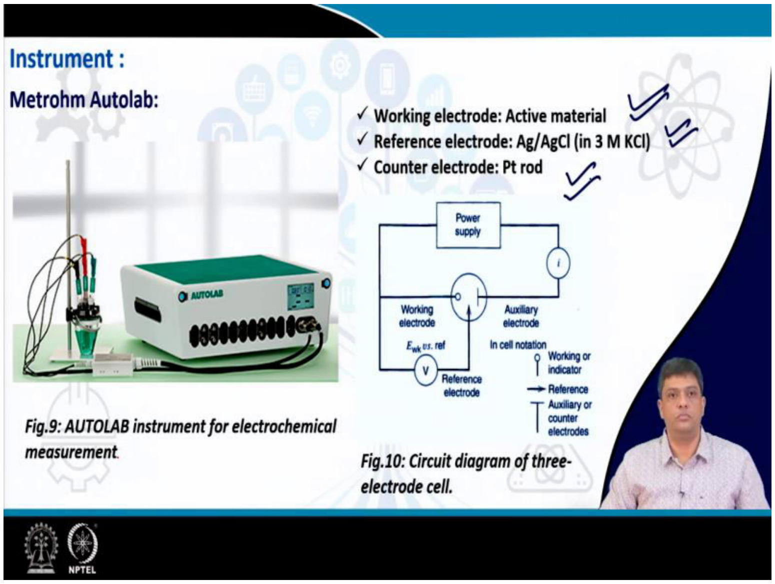

Instrument :

Metrohm Autolab:

- ✓ Working electrode: Active material
- ✓ Reference electrode: Ag/AgCl (in 3 M KCl)
- ✓ Counter electrode: Pt rod

Fig.9: AUTOLAB instrument for electrochemical measurement

Fig.10: Circuit diagram of three-electrode cell.

So, what does this instrument do, it can collect the changes in the current as a function of changing voltage or changes in voltage as a function of changing time, but for a fixed current, so, various combinations can be given and that instrument then collects the relevant information. Generally, for a three electrode system when I am talking about the characterization of the material itself, then you have a working electrode that involves your active material. You have a reference electrode and a counter electrode. These are the three things which are involved.

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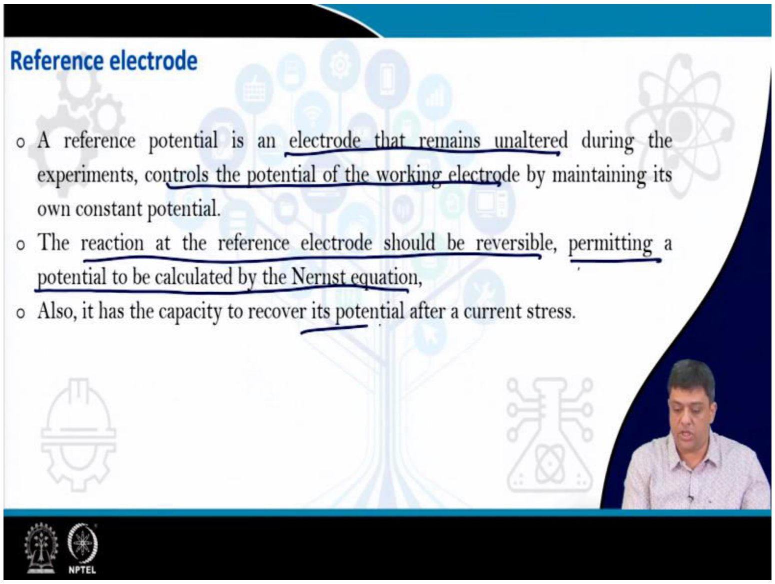

Reference electrode

- A reference potential is an electrode that remains unaltered during the experiments, controls the potential of the working electrode by maintaining its own constant potential.
- The reaction at the reference electrode should be reversible, permitting a potential to be calculated by the Nernst equation,
- Also, it has the capacity to recover its potential after a current stress.

What is a reference electrode? Working electrode, I guess you already understood it involves the active material, which will be taking part in the redox activity. The reference electrode is an electrode that remains unaltered during the experiment. It thus controls the potential of the working electrode by maintaining its own constant potential. The reaction at the reference electrodes is reversible which permits a potential calculation using the Nernst equation. And because you are applying current at the reference electrode has the capacity to recover its potential after the current stress.

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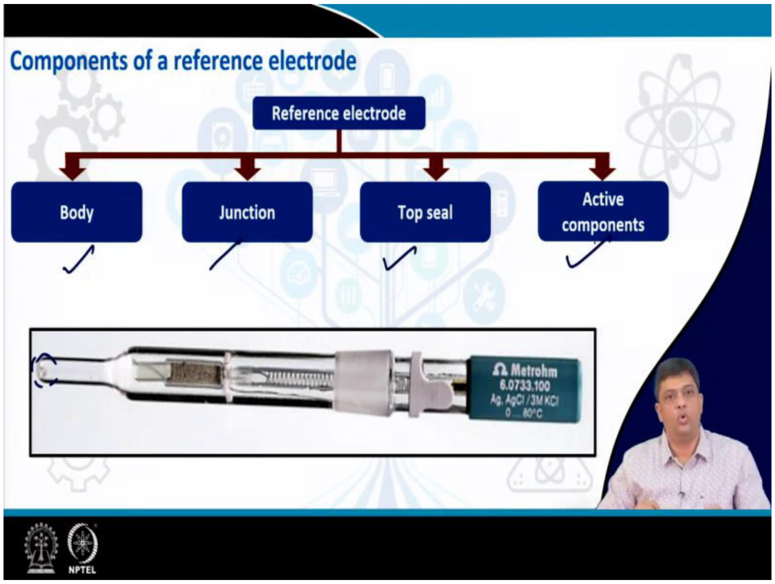

Components of a reference electrode

Reference electrode

Body

Junction

Top seal

Active components

A typical reference electrode looks like this it has the body the junction, the top seal and the active components.

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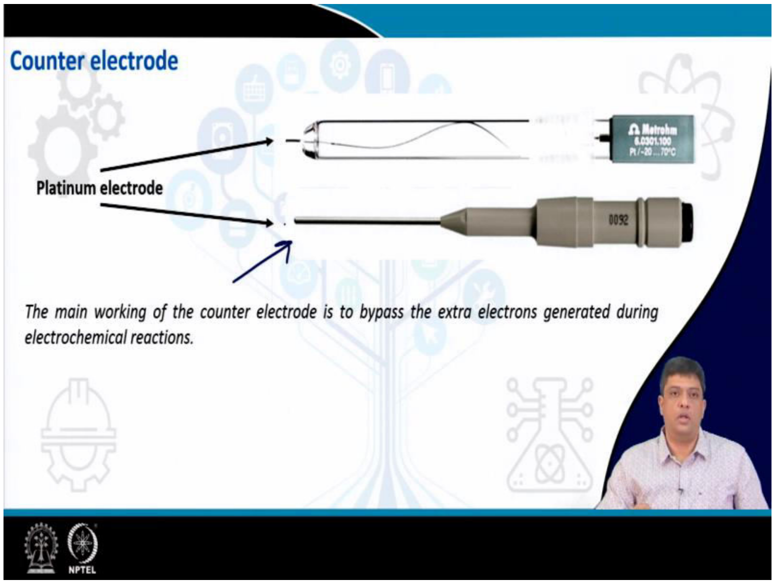

Counter electrode

Platinum electrode

The main working of the counter electrode is to bypass the extra electrons generated during electrochemical reactions.

Next is the counter electrode which basically bypasses the extra electrons which can be generated during the electrochemical reaction and this is based on platinum in this example, which is shown here.

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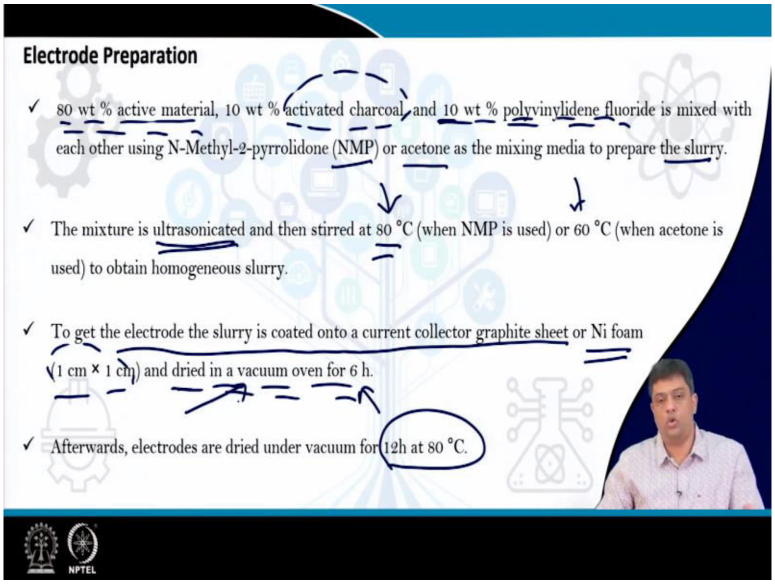

Electrode Preparation

- ✓ 80 wt % active material, 10 wt % activated charcoal and 10 wt % polyvinylidene fluoride is mixed with each other using N-Methyl-2-pyrrolidone (NMP) or acetone as the mixing media to prepare the slurry.
- ✓ The mixture is ultrasonicated and then stirred at 80 °C (when NMP is used) or 60 °C (when acetone is used) to obtain homogeneous slurry.
- ✓ To get the electrode the slurry is coated onto a current collector graphite sheet or Ni foam (1 cm × 1 cm) and dried in a vacuum oven for 6 h.
- ✓ Afterwards, electrodes are dried under vacuum for 12h at 80 °C.

How do you prepare the electrode based on working material or the activity? So, you take let us say 80 percent of the active material then you disperse them in a pvdf solution. What is pvdf? It is a polymer why you need a polymer so, that you can get a fill out of these materials that can be in a powdered form. So, you want to get into a film and then you get an electrode film. But, once you have polymer, then you are actually introducing some insulating character. To counter that you introduce activated carbon or activated charcoal.

These are mixed in a mixing media. We NMP or acetone. So, mostly volatile organic components are used here and then you turn them and make a slurry out of it. To ensure homogeneous distribution you ultrasonicate these mixture and then keep them stirring on a magnetic stirrer depending upon the mixing media which you have used you can choose the temperature for acetone it is generally 60 degrees and for NMP it is around 80 degrees.

And you let these slurry left on this stirrer for let us say eight hours ten hours twelve hours which the time has to be optimized so, that you get a homogeneous slurry. Homogeneous means you have uniform distribution of the particles throughout the film or the slurry as of now. To obtain the electrode what do you do this slurry is coated on a current collector which can be made of graphite sheet or some people mostly use nickel foam cut them into the desired size and then to remove the volatile organic components or these mixing media's you then dry them in vacuum over for an optimized time.

Once they are dry the films are again dried further at higher temperatures. So, you do not straightaway start hitting the films because if you hit the film and also you are taking air out of the films at a very fast rate because your heat you are drying them in a vacuum oven then you can introduce voids or you can introduce cracks in the film. So, you need to either control the rate at which you will extract the air from these ovens or you need to have a twostep process. But different people can propose any other strategy also.

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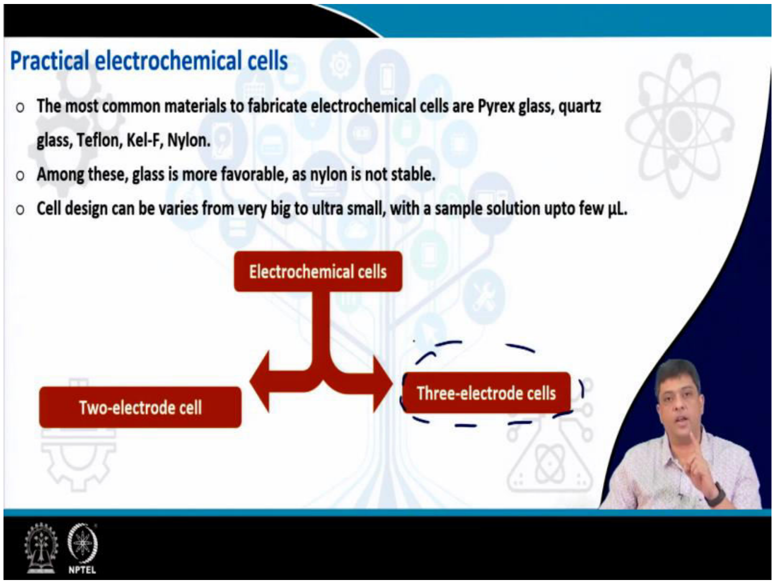

Practical electrochemical cells

- The most common materials to fabricate electrochemical cells are Pyrex glass, quartz glass, Teflon, Kel-F, Nylon.
- Among these, glass is more favorable, as nylon is not stable.
- Cell design can be varies from very big to ultra small, with a sample solution upto few µL.

Electrochemical cells

Two-electrode cell

Three-electrode cells

So, for material characterization, you perform the three electrode measurements and for the determination of the device characteristic you have the full cell or the two electrode system.

(Refer Slide Time: 50:47)

Experimental :

Coin Cell Fabrication :

Slurry Preparation

Active material, binder and conductive agent are mixed together in specific mass ratios.

Magnetic stirrer

Coating

Electrode slurry is coated on current collector by using film coater.

Film Coater

Drying

Drying of electrode in the vacuum oven at 80 °C for 12 h .

Vacuum Oven

Module Cutting

Cutting of round shape electrode for CR2032 coin cell fabrication.

Round shape electrode cutter

Assembly of coin cell inside the Glove Box

Step 1 . Electrolyte preparation

Step 2. Assembly of coin cell.

Step 3. Finally crimping of coin cell.

Glove Box

Crimping Machine

For coin cell fabrication we have already discussed the steps which are involved. So, what you have slurry preparation then coating drying module cutting and finally assembling in a coin cell and if your material is reactive towards air then you have to perform this process in a glove box.

(Refer Slide Time: 51:16)

Experimental :

Pouch Cell Fabrication :

Slurry preparation

Active material, binder and conductive agent are mixed together in specific mass ratios.

Mixing Machine

Coating & drying

By a tape casting procedure the electrode slurry is coated on the current collectors.

Coating Machine

Pressing

The electrodes are compressed with a certain pressure through to massive cylinder.

Roll Press Machine

Module cutting

The electrodes are cut or punched into strips of a desired shape.

Slitting Machine

Stacking

The electrodes are stacked together with the separator.

Electrode Punching Machine

Electrolyte filling

Electrolyte is injected: It is important that the electrolyte fully permeates and fills the pores.

Electrolyte Filling Machine

The other thing which we discussed was the pouch cell this also involves slurry preparation, coating and drying there is an additional step here which comes in that is the pressing of this material. Then you cut into modules stacked over each other if required if you are talking about stack modules and then before you close this pouch cell you have to fill this pouch with an electrolyte.

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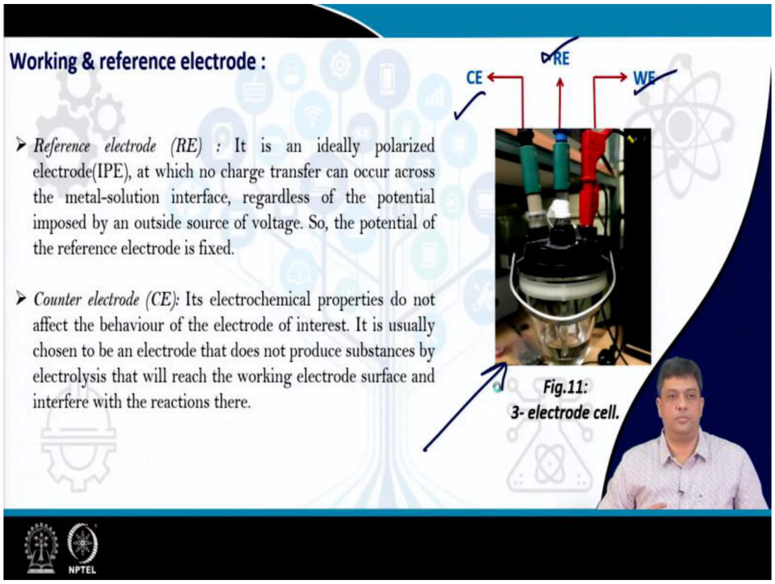

Working & reference electrode :

- *Reference electrode (RE)* : It is an ideally polarized electrode(IPE), at which no charge transfer can occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage. So, the potential of the reference electrode is fixed.
- *Counter electrode (CE)*: Its electrochemical properties do not affect the behaviour of the electrode of interest. It is usually chosen to be an electrode that does not produce substances by electrolysis that will reach the working electrode surface and interfere with the reactions there.

Fig.11: 3- electrode cell.

As I mentioned, you have the reference electrode, the working electrode and the counter electrode and this is a typical three electrode measurement set.

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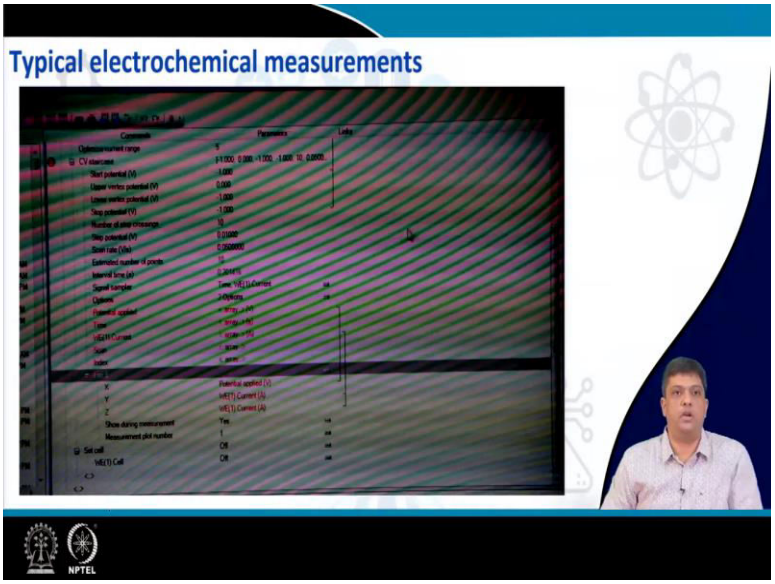
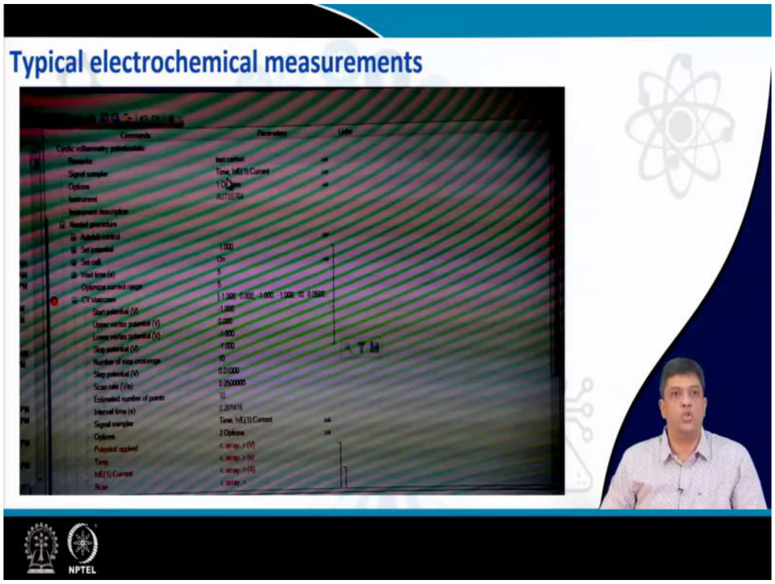
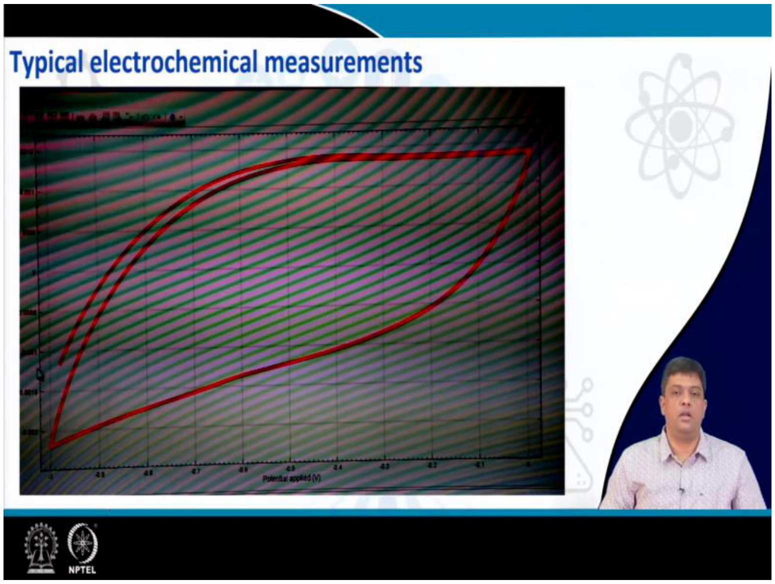


Typical electrochemical measurements

Commands	Parameters	Links
Optimize current range	5	
CV staircase	[-1.000, 0.000, -1.000, -1.000, 10, 0.0500...	
Start potential (V)	-1.000	
Upper vertex potential (V)	0.000	
Lower vertex potential (V)	-1.000	
Stop potential (V)	-1.000	
Number of stop crossings	10	
Step potential (V)	[illegible]	
Scan rate (V/s)	0.0500000	
Estimated number of points	[illegible]	
Interval time (s)	[illegible]	
Signal sampler	Time, WE(1).Current	
Options	2 Options	
Potential applied	<array> (V)	
Time	<array> (s)	
WE(1).Current	<array> (A)	
Scan	<array>	
Index	<array>	
X	Potential applied (V)	
Y	WE(1).Current (A)	
Z	WE(1).Current (A)	
Show during measurement	Yes	
Measurement plot number	1	
Set cell	Off	
WE(1).Cell	Off	



Typical electrochemical measurements



Typical electrochemical measurements

So, let us see how you perform this measurement and if you see this is a typical measurement window. So, you define the range the sample holder, the voltage window in which you are going to perform the measurements and then you either define the scan rate or the current densities at which you want to perform the measurements. So this is the typical CV curve which you obtain for a sample using the three electrode cell.

So, we are characterizing the material and we are performing the CV measurement. So, you can clearly see the blue spot in the front is indicating the point where you are measuring the data. So, after the first cycle the system is reproducing the data once you have ensured that an equilibrium has been reached after the first cycle. So, whatever losses had to occur after the first cycle have occurred and then the system is performing the cycling as desired.

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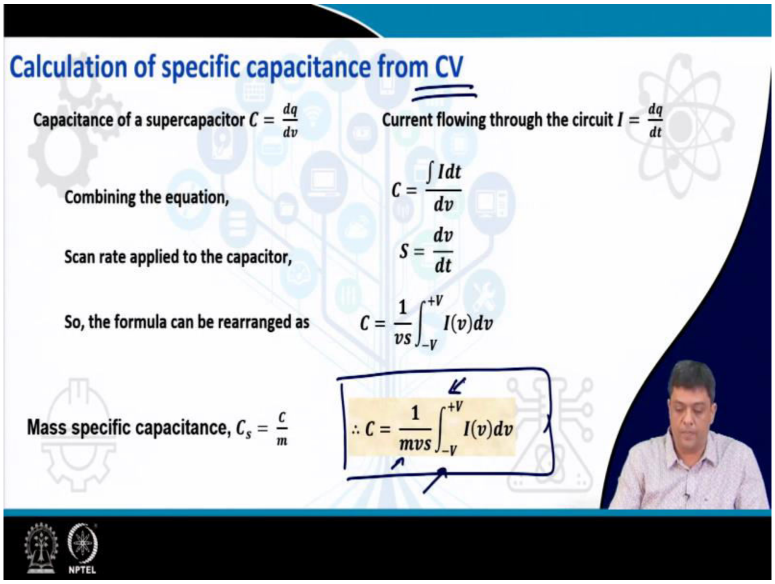

Calculation of specific capacitance from CV

Capacitance of a supercapacitor $C = \frac{dq}{dv}$

Current flowing through the circuit $I = \frac{dq}{dt}$

Combining the equation, $C = \frac{\int I dt}{dv}$

Scan rate applied to the capacitor, $S = \frac{dv}{dt}$

So, the formula can be rearranged as $C = \frac{1}{vs}\int_{-V}^{+V} I(v)dv$

Mass specific capacitance, $C_s = \frac{C}{m}$

$$\boxed{\therefore C = \frac{1}{mvs}\int_{-V}^{+V} I(v)dv}$$

So, you can measure the data of specific capacitance using this formula which comes out as 1 by m where m is the mass v, 1 by mvs integration from minus v to plus v, i V dv.

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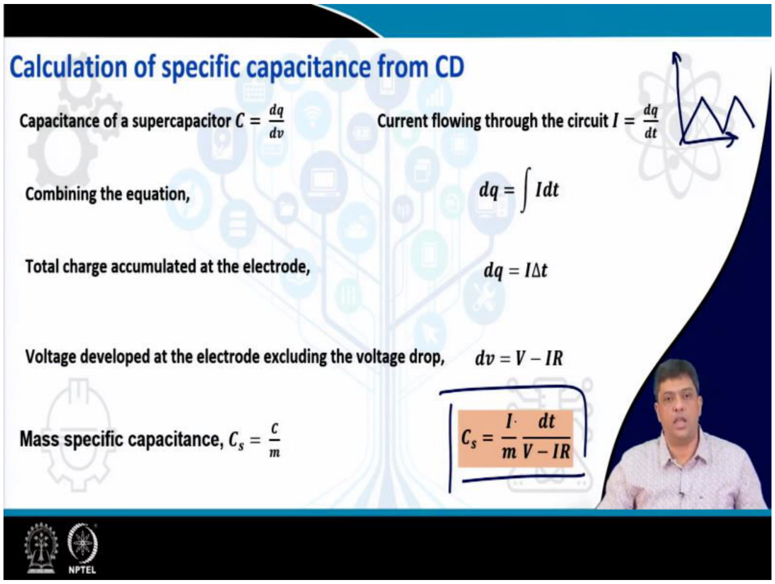

Calculation of specific capacitance from CD

Capacitance of a supercapacitor $C = \frac{dq}{dv}$

Current flowing through the circuit $I = \frac{dq}{dt}$

Combining the equation, $dq = \int I dt$

Total charge accumulated at the electrode, $dq = I\Delta t$

Voltage developed at the electrode excluding the voltage drop, $dv = V - IR$

Mass specific capacitance, $C_s = \frac{C}{m}$

$$\boxed{C_s = \frac{I}{m}\frac{dt}{V - IR}}$$

If you perform the same measurements where you are analyzing the charge discharge cycle then using that you can also get the values of specific capacitors as I by m dt by V minus IR, where IR is your IR drop.

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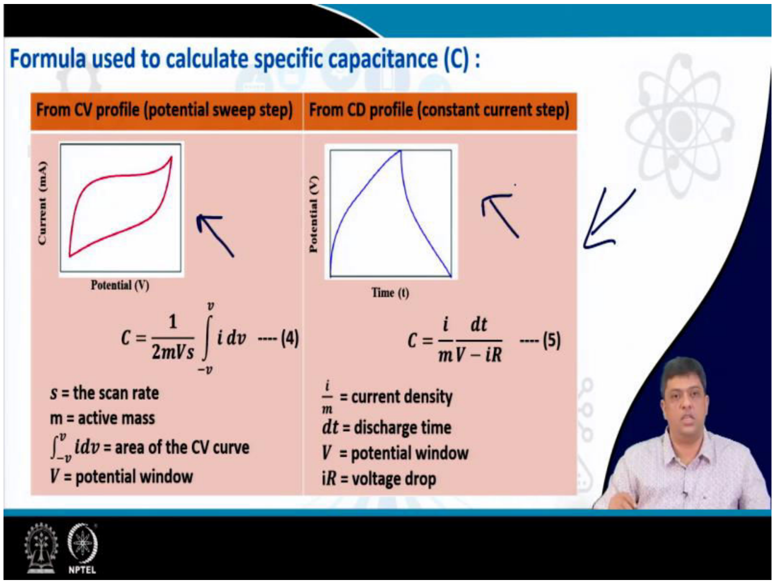

Formula used to calculate specific capacitance (C) :

From CV profile (potential sweep step)	From CD profile (constant current step)
$$C = \frac{1}{2mVs}\int_{-v}^{v} i\,dv \quad \text{---- (4)}$$	$$C = \frac{i}{m}\frac{dt}{V - iR} \quad \text{---- (5)}$$
s = the scan rate m = active mass $\int_{-v}^{v} idv$ = area of the CV curve V = potential window	$\frac{i}{m}$ = current density dt = discharge time V = potential window iR = voltage drop

This slide actually gives you the two formulas and would act as a very good reference point to understand how you calculate the specific capacitance using the CV or the CD measurements.

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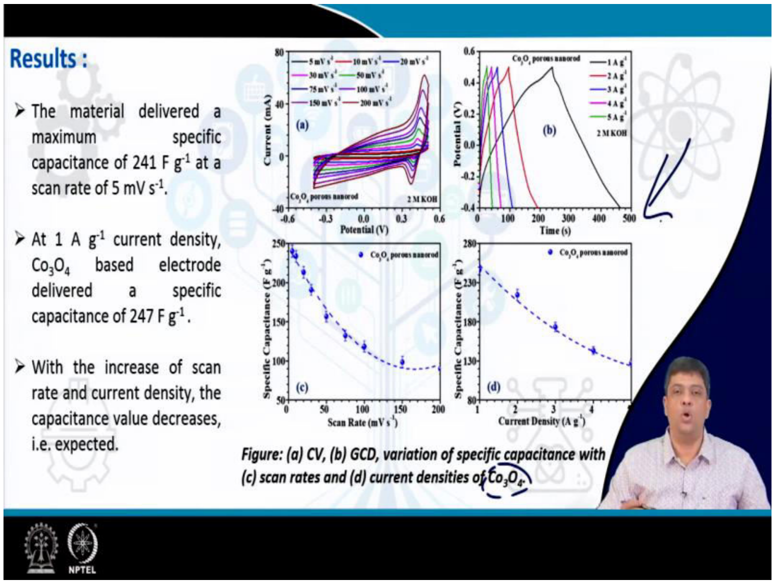

Results :

- The material delivered a maximum specific capacitance of 241 F g^{-1} at a scan rate of 5 mV s^{-1}.
- At 1 A g^{-1} current density, Co_3O_4 based electrode delivered a specific capacitance of 247 F g^{-1}.
- With the increase of scan rate and current density, the capacitance value decreases, i.e. expected.

Figure: (a) CV, (b) GCD, variation of specific capacitance with (c) scan rates and (d) current densities of Co_3O_4.

For material Let it be cobalt oxide, this is a typical CV CD curves. And in the next lecture, you will see that we will describe each and every step about cobalt oxide fabrication and then how do we obtain these curves. This is just to show how a real data looks like.

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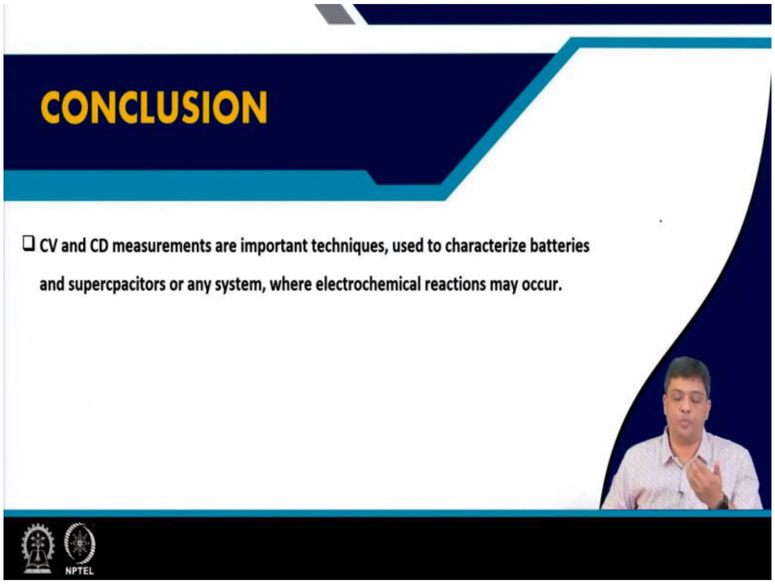

CONCLUSION

❑ CV and CD measurements are important techniques, used to characterize batteries and supercpacitors or any system, where electrochemical reactions may occur.

So, I hope in today's lecture, we have explained two techniques that is cyclic voltammetry and charge discharge measurement techniques which will give you the value of specific capacitance in super capacitors or capacity in batteries. These two techniques are extremely important and you must understand them very clearly if you wish to work in the area of electrochemical energy storage devices.

(Refer Slide Time: 56:10)

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- *Chandra et al. CrystEngComm 22 (9), 1633-1644, 2020*
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These are the major references which were used. And in the next lecture, I will give you detailed process in by which we choose the material and then characterize the same before we start talking about device fabrication or characterization of the device. Thank you very much.