Non - Metallic Materials
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Module - 06
Optical and Electrochemical Properties of Non-Metallic Materials
Lecture - 32
Introduction to electrochemical methods; cyclic voltammetry and other related techniques

Welcome to my course Non-Metallic Materials. And today, we are in module number 6; Optical and Electrochemical Properties of Non-Metallic Materials. And this is lecture number 32, where I will introduce various electrochemical methods including cyclic voltammetry and other related techniques.

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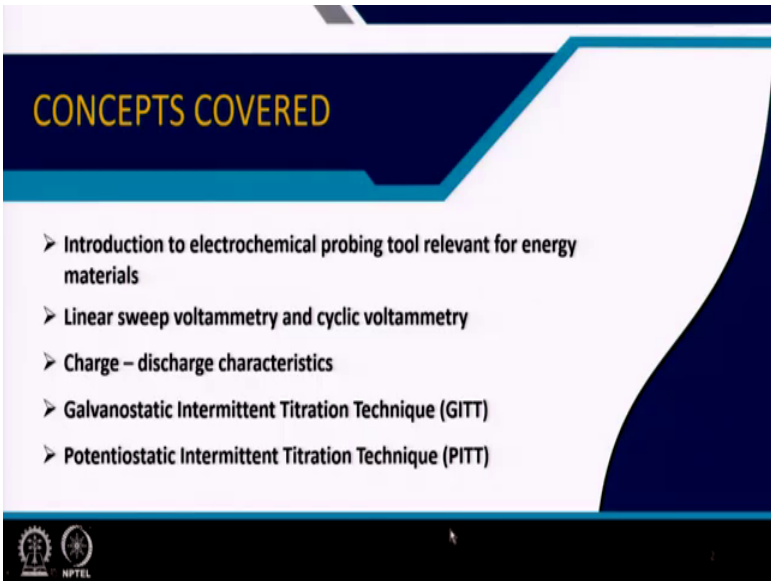

CONCEPTS COVERED

- Introduction to electrochemical probing tool relevant for energy materials
- Linear sweep voltammetry and cyclic voltammetry
- Charge – discharge characteristics
- Galvanostatic Intermittent Titration Technique (GITT)
- Potentiostatic Intermittent Titration Technique (PITT)

And already, you have learnt about basic electrochemistry and in particular rechargeable ion batteries. So, how to characterise those systems. So, I will introduce certain concepts. So, first I will introduce electrochemical various types of probing tools which are relevant for energy materials and this includes linear sweep voltammetry to characterise mainly the electrolyte which are used and also the cyclic voltammetry.

Then, we will talk about charge discharge characteristics and then, in order to measure the diffusion coefficient of the diffusing species. Here, it is either lithium or sodium in place of lithium and sodium ion batteries. We occasionally use Galvanostatic

Intermittent Titration Technique which is abbreviated as GITT. So, that will be introduced and Potentiostatic Intermittent Titration Technique which is abbreviated as PITT; that will also be talked about.

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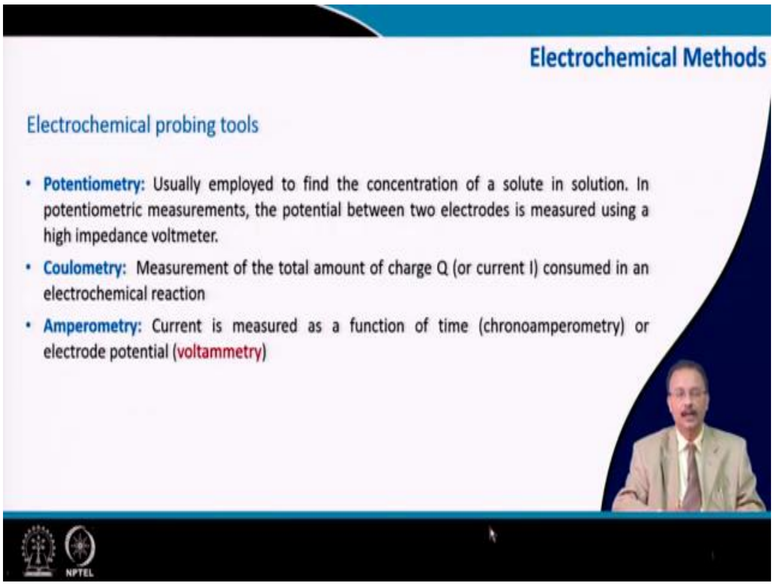

Electrochemical Methods

Electrochemical probing tools

- **Potentiometry:** Usually employed to find the concentration of a solute in solution. In potentiometric measurements, the potential between two electrodes is measured using a high impedance voltmeter.
- **Coulometry:** Measurement of the total amount of charge Q (or current I) consumed in an electrochemical reaction
- **Amperometry:** Current is measured as a function of time (chronoamperometry) or electrode potential (voltammetry)

Now, you know that the term there are various electrochemical probing techniques that is available in order to characterise the rechargeable batteries and electrochemical systems or other types of power source including, fuel cells. And potentiometry; that is usually employed traditionally to find the concentration of a solute in a solution.

So, in this particular technique in this measurements potential between the electrodes that is measured using a high impedance voltmeter.

So, that is one thing and I have already told you about the pH meter functionality and that is one example of the potentiometry. Other than that, we use coulometry also; that is measurement of amount of charge that is consumed in an electrochemical reaction and you know that when charge flows that is nothing but current. So, coulometry is the measurement of charge in the system.

And third one is amperometry here current is measured as a function of time and we termed this as chronoamperometry or sometimes the electrode potential that is also measured. We term this one as voltammetry.

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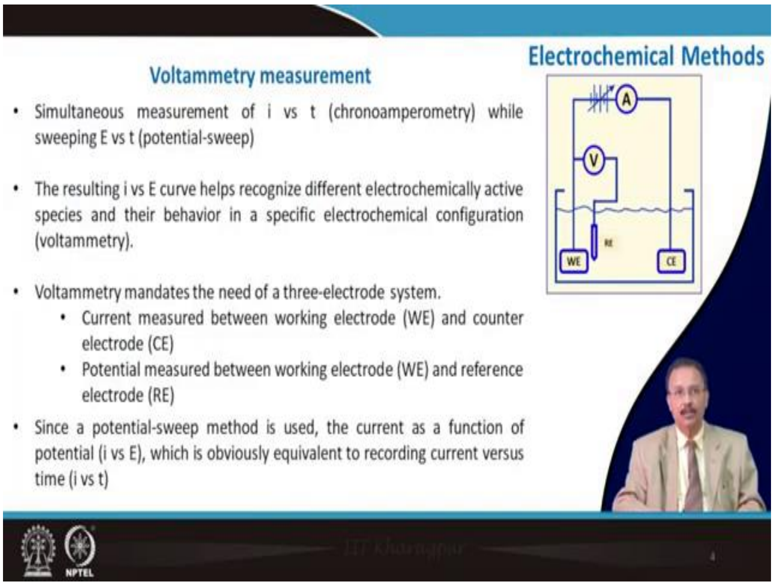

Electrochemical Methods

Voltammetry measurement

- Simultaneous measurement of i vs t (chronoamperometry) while sweeping E vs t (potential-sweep)
- The resulting i vs E curve helps recognize different electrochemically active species and their behavior in a specific electrochemical configuration (voltammetry).
- Voltammetry mandates the need of a three-electrode system.
  - Current measured between working electrode (WE) and counter electrode (CE)
  - Potential measured between working electrode (WE) and reference electrode (RE)
- Since a potential-sweep method is used, the current as a function of potential (i vs E), which is obviously equivalent to recording current versus time (i vs t)

So, mainly we will be focussing on the voltammetry measurements and in voltammetry measurements, it is a simultaneous measurement of current as a function of time which I defined as chronoamperometry and at the same time the voltage that is also sweep across the system. So, E is also applied in different types of wave front that is applied into the system. So, voltage is applied as a function of time. We call it is a potential-sweep.

So, resultant is finally, what we actually get is current verses voltage curve to recognise various electrochemically active species and their behavior in a specific electrochemical configuration. So, that is our voltammetry. And for this voltammetry measurement, it is almost mandatory to use a three-electrode system you can see in this view graph. So, there are three electrode here, the one marked as WE is the working electrode.

This one is a counter electrode and this is a reference electrode. So, the voltage is measured in between working electrode and the reference electrode. So, this is a measured voltage. And the current which is measured from this working electrode and the counter electrode. So, a ammeter is connected to measure the current in the system.

So, current is measured between working electrode and counter electrode and potential measurement is usually done between working electrode and the reference electrode. So, since in this type of measurement we are applying a potential sweep; the current as a function of potential that is the resultant i as a function of the voltage.

Basically, whatever you are measuring, because you see the time parameter is both with time and voltage. So, basically you are measuring current as a function of time in this kind of system.

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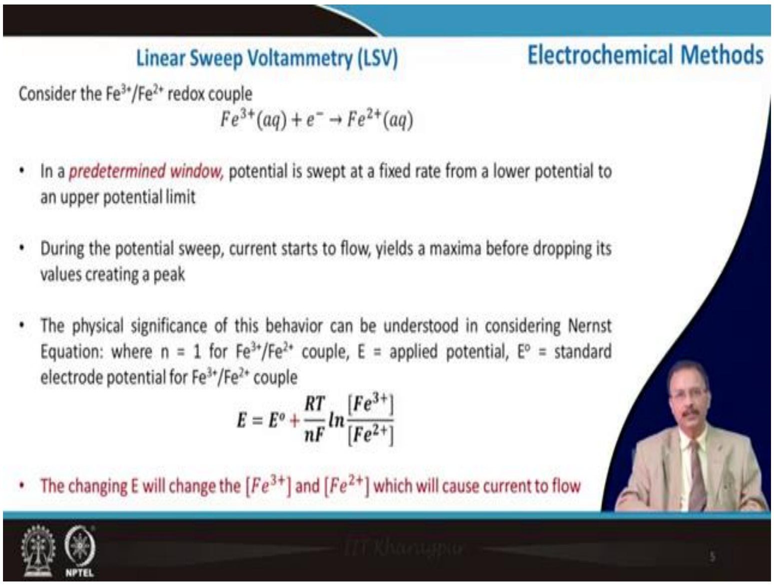

Linear Sweep Voltammetry (LSV)

Electrochemical Methods

Consider the Fe^{3+}/Fe^{2+} redox couple

$$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$$

- In a *predetermined window*, potential is swept at a fixed rate from a lower potential to an upper potential limit
- During the potential sweep, current starts to flow, yields a maxima before dropping its values creating a peak
- The physical significance of this behavior can be understood in considering Nernst Equation: where n = 1 for Fe^{3+}/Fe^{2+} couple, E = applied potential, E^{o} = standard electrode potential for Fe^{3+}/Fe^{2+} couple

$$E = E^{o} + \frac{RT}{nF} ln\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

- The changing E will change the $[Fe^{3+}]$ and $[Fe^{2+}]$ which will cause current to flow

So, linear sweep voltammetry; that is usually we use to know the stability of the electrolyte. So, I will start from a very basic equation where as you can see that the redox couple involved plus 3 iron ferric ion and ferrous ion. So, that is the redox couple and we are considering that we are in a aqueous system. So, this one is getting reduced F e 3 plus is taking an electron to reduce to F e 2 plus in aqueous system.

So, you need to have a predetermined potential window. And in this potential window where you exactly want to measure the system performance, a potential is swept at a fixed rate from a lower potential to a upper potential. And during this potential sweep of course, current will start to flow and usually, it yields a maxima before it dropping out to a certain value.

The physical significance of this kind of behavior that can be understood by considering the Nernst equation which already I have defined. So, this is the Nernst equation the positive sign is coming, because I have just reversed it. It should be product by reactant. So, here it is just reverse. So, this plus term is coming.

So, here n is 1, because we are considering this F e 3 plus F e 2 plus couple and E is the applied potential and E 0 is the standard electrode potential. So, the changing of E. If you now, apply a potential from outside if you change it, then the concentration of this F e 3 plus and F e 2 plus ion will of course, change and which will also cause the current to flow in the system.

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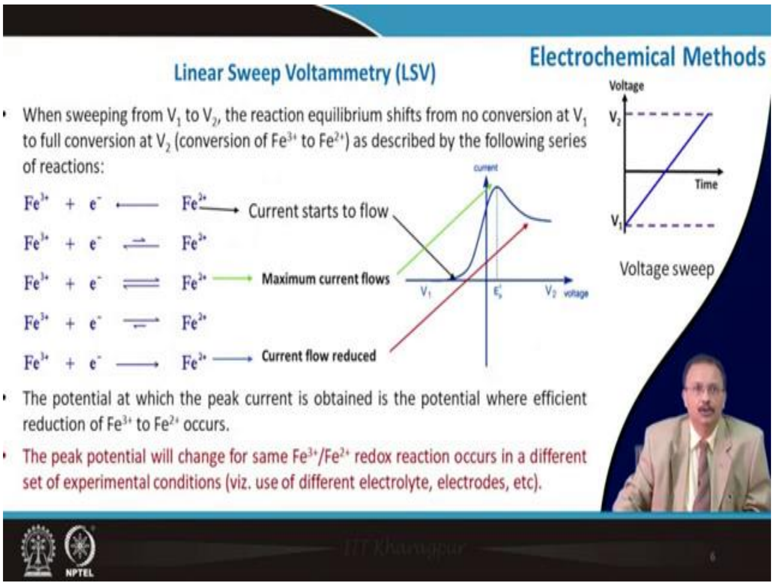

Electrochemical Methods

Linear Sweep Voltammetry (LSV)

- When sweeping from V_1 to V_2, the reaction equilibrium shifts from no conversion at V_1 to full conversion at V_2 (conversion of Fe^{3+} to Fe^{2+}) as described by the following series of reactions:

$Fe^{3+} + e^- \longleftarrow Fe^{2+}$ → Current starts to flow

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ → Maximum current flows

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ → Current flow reduced

- The potential at which the peak current is obtained is the potential where efficient reduction of Fe^{3+} to Fe^{2+} occurs.
- The peak potential will change for same Fe^{3+}/Fe^{2+} redox reaction occurs in a different set of experimental conditions (viz. use of different electrolyte, electrodes, etc).

So, while you sweep from a voltage window from V 1 to V 2. So, constantly you are just going like this. Actually, this is not a straight line kind of fashion it is done. So, always you are giving a step voltage. So, you have a step height and you have a duration of giving this voltage. So, once you sweep it the reaction equilibrium shift from no conversion.

Initially, there is no conversion of this F e 3 plus ion to F e 2 plus ion and then, progressively it will convert. So, it will start something like this. So, I have just divided it in number of steps. So, this is the initial state when the current is almost 0 and then slowly, the reaction start to convert from this side left-hand side to right-hand side and the resultant current you see that it increases and then finally, it ceases, because most of the conversion is over.

So, it just ceases. So, you get a peak and you get peak potential; the potential at which the peak current is obtained that is the potential where efficient reduction of F e 3 plus to

F e 2 plus occurs. And this peak potential will also change. Even if the same kind of redox is available ah, but if different set of experimental condition if you do.

For example, you change different electrolyte, you can chase the electrode materials which are involved, then you will see that this peak potential the potential correspond to the maximum current that will be shifted.

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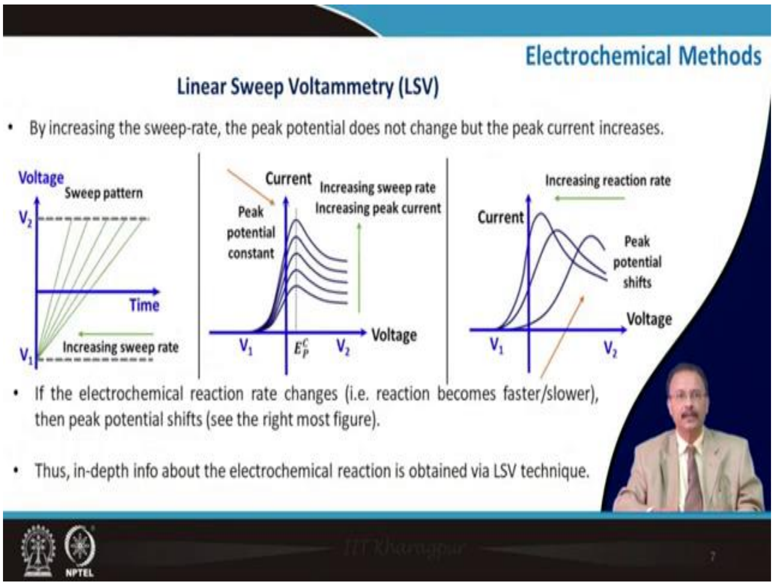

Electrochemical Methods

Linear Sweep Voltammetry (LSV)

- By increasing the sweep-rate, the peak potential does not change but the peak current increases.

- If the electrochemical reaction rate changes (i.e. reaction becomes faster/slower), then peak potential shifts (see the right most figure).
- Thus, in-depth info about the electrochemical reaction is obtained via LSV technique.

So, you can increase the sweep-rate. So, this is an example that the sweep rate is increased in this direction. So, it is progressively increased then, this current will progressively increase. You see the increase in the sweep rate increases the peak current, but the position remains same right the position is all remaining same.

Now, it is also possible if the electrochemical reaction rate changes; that is the reaction becomes faster or slower then, peak potential also shifts. So, this is an example of the shifting of the peak position. So, in depth info about the electrochemical reaction is obtained by this kind of linear sweep voltammetry. Mainly, what is the position of this peak, how much current that is generating and how it is changing with the sweep rate. So, this gives lot of information.

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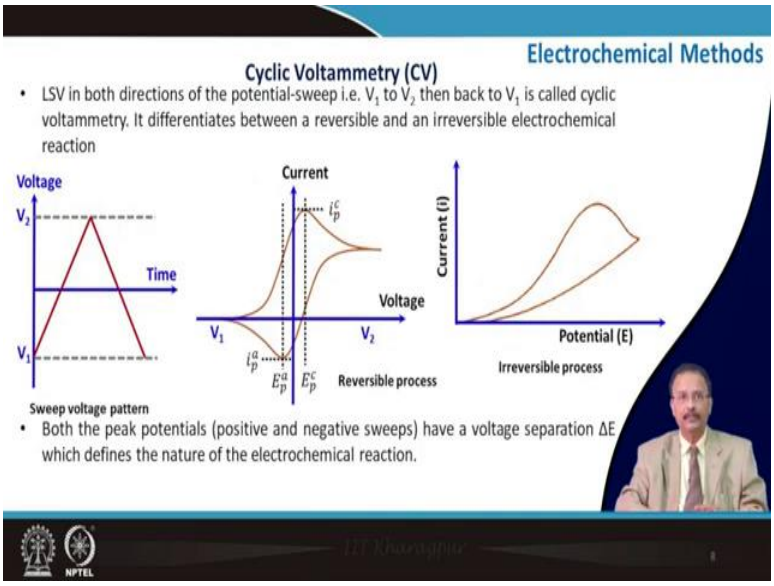

Electrochemical Methods

Cyclic Voltammetry (CV)

- LSV in both directions of the potential-sweep i.e. V_1 to V_2 then back to V_1 is called cyclic voltammetry. It differentiates between a reversible and an irreversible electrochemical reaction

Sweep voltage pattern

Reversible process

Irreversible process

- Both the peak potentials (positive and negative sweeps) have a voltage separation ΔE which defines the nature of the electrochemical reaction.

Now, if I do this LSV in both the direction it is not a linear sweep going from one direction, but it is going from one lower potential window to high one and, then again, it comes back to its original position something of like this the voltage sweep pattern if you get. Then, you will get two such peak.

You can see the current increases and then, there is a peak. So, this is your peak current in the positive and this is the oxidation part and the this one is the negative part. So, you will get two such peak, if the system is reversible if the reduction and oxidation takes place in both the direction, then it is a reversible reaction. So, it can readily be identified by a voltammetry we term this as a cyclic voltammetry.

So, it is something similar to LSV in one side two LSV simultaneously, is giving you cyclic voltammetry and you get one peak corresponding to the oxidation reaction and another peak is corresponding to the reduction reaction and usually, they are slightly shifted to each other. So, there is a separation and which defines in fact, the nature of the electrochemical reaction, but in certain cases you will see only one type of reaction takes place.

So, in oxidation you can see the oxidation side you have a peak correspond to maximum i and in case of the reduction thing you are missing that. So, that is that reaction you will term that is irreversible process. So, for the rechargeable battery always we need a reversible process.

So, simultaneously it is discharged and charged and you can use the battery for many time, but in many of the reaction this is not reversible. So, then you will be missing. For example, in this case the cathodic peak that is missed.

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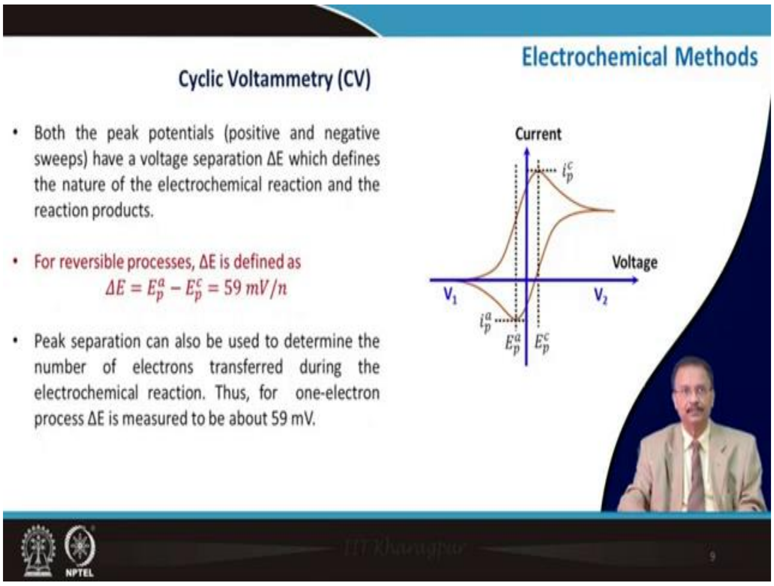

Electrochemical Methods

Cyclic Voltammetry (CV)

- Both the peak potentials (positive and negative sweeps) have a voltage separation ΔE which defines the nature of the electrochemical reaction and the reaction products.
- For reversible processes, ΔE is defined as
  $$\Delta E = E_p^a - E_p^c = 59\ mV/n$$
- Peak separation can also be used to determine the number of electrons transferred during the electrochemical reaction. Thus, for one-electron process ΔE is measured to be about 59 mV.

So, both the peak potential, whether it is positive and negative have a voltage separation that I have already mentioned. So, daily which defines the nature of the electrochemical reaction and the reaction product of course. For reversible process based on the Nernst equation, which already I think in one of my lectures I also derived that, that if this separation of this voltage that you can calculate from the Nernst equation, it will come about 59 milli volt per n and n is the number of electron involved.

So, this peak separation can also be determine the number of electron that is being transferred during this electrochemical reaction. If you consider only one electron is involved like the process that I told you F e 3 plus F e 2 plus this process only one electron is involved. So, experimentally you can find that the separation value is about 59 milli volt.

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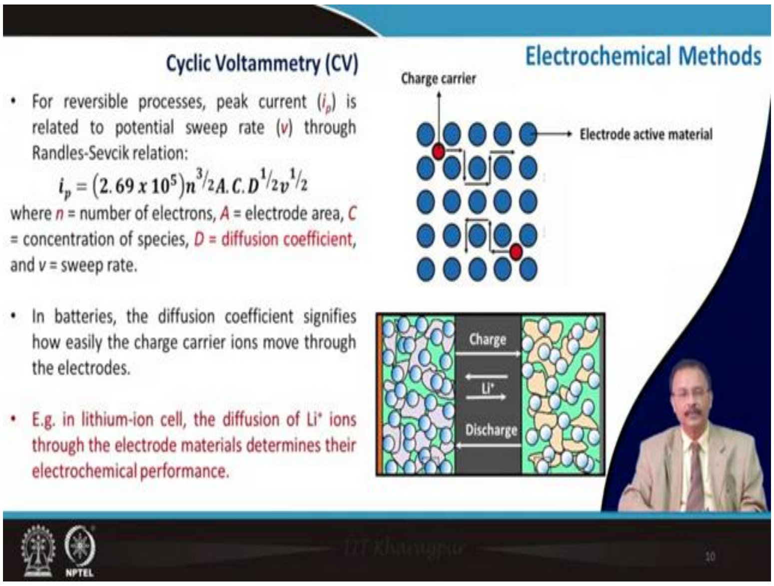

Electrochemical Methods

Cyclic Voltammetry (CV)

- For reversible processes, peak current (i_p) is related to potential sweep rate (v) through Randles-Sevcik relation:

$$i_p = (2.69 x 10^5) n^{3/2} A.C.D^{1/2} v^{1/2}$$

where n = number of electrons, A = electrode area, C = concentration of species, D = diffusion coefficient, and v = sweep rate.

- In batteries, the diffusion coefficient signifies how easily the charge carrier ions move through the electrodes.
- E.g. in lithium-ion cell, the diffusion of Li⁺ ions through the electrode materials determines their electrochemical performance.

Now, the cyclic voltammetry that has its implication in estimating the diffusion coefficient of the diffusing species. So, if you consider a lithium-ion battery. So, lithium-ion diffusion inside the electrode material that you can determine from the cyclic voltametric measurement. So, for reversible process, the peak current is related to the potential sweep rate.

And this particular equation whatever I have written that is known as Randels relation Sevcik sorry I am sorry Sevcik relation and this is the peak current and that is related with the potential scan rate.

So, I can just scan it at 1 milli volt per second or I can scan it at 100 milli volt per second and then, this perform this experiments and we get the peak current and then, you can plot it with this root over of the scan rate and this will be a linear relation and this linear relation can tell you ultimately from the slope what is the diffusion coefficient.

So, n here is the number of electron that is involved, A is the electrode area in consideration, C is the concentration of the species of the mobile species concentration, D is the diffusion coefficient which you want to measure or estimate and v is the sweep rate. In battery it is very important as I have shown that this is your electrode material and actually, this charge carrier is moving through it. So, how fast it goes to consume all the electrode material that is important.

And this is a full cell system where both anode and cathode you can see and lithium is going in case of lithium-ion battery, it is going to both anode and cathode. So, it is quite important that how fast it can go inside the electrode material particularly, when a high power battery is required you want it to go at very fast rate it should not be blocked somewhere.

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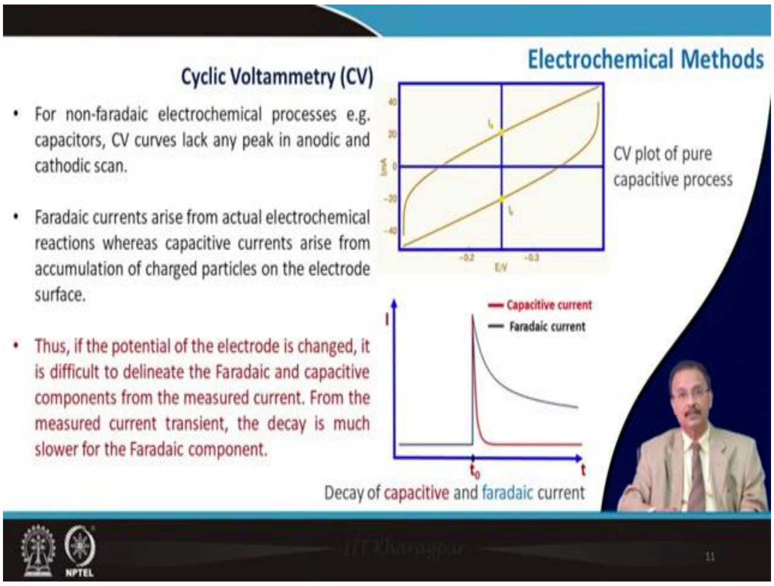

Electrochemical Methods

Cyclic Voltammetry (CV)

- For non-faradaic electrochemical processes e.g. capacitors, CV curves lack any peak in anodic and cathodic scan.
- Faradaic currents arise from actual electrochemical reactions whereas capacitive currents arise from accumulation of charged particles on the electrode surface.
- Thus, if the potential of the electrode is changed, it is difficult to delineate the Faradaic and capacitive components from the measured current. From the measured current transient, the decay is much slower for the Faradaic component.

CV plot of pure capacitive process

Decay of capacitive and faradaic current

So, for those kind of cases, you need to have a precise idea about its diffusion co-efficients. So, this is one way you can measure from cyclic voltammetry by doing the cyclic voltammetry at different voltage sweep rate. There is a possibility for you to measure the diffusion coefficient of this battery.

So, if the process is non-faradaic; that means, no reaction redox reaction is taking place ah. So, then for example, for capacitor like electric double layer capacitor EDLC. This curve will lack this peak, because there is no redox reaction is involved. So, you get some kind of flat rectangular kind of shape both in anodic scan as well as in cathodic scan.

In faradaic currents arise from actual electrochemical reactions and capacitative current they arises from accumulation of the charge particle near the electrode surface. Now, if the electrode potential of the electrode is changed then it is difficult for you to delineate this faradaic process and the capacitative component from the measured current, because the current transient you can see it is something like this.

So, if it is a capacitative current, then it actually falls down very fast in case of a faradaic current, it is having a slower transient. So, it is important for you to identify the what is the process in your electrode material and for many battery material it is of utmost importance.

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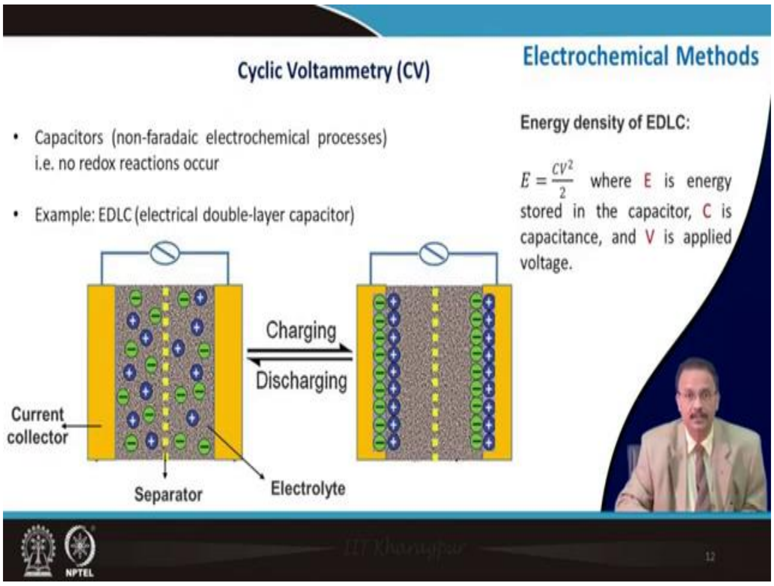

Electrochemical Methods

Cyclic Voltammetry (CV)

- Capacitors (non-faradaic electrochemical processes) i.e. no redox reactions occur
- Example: EDLC (electrical double-layer capacitor)

Energy density of EDLC:

$E = \frac{CV^2}{2}$ where E is energy stored in the capacitor, C is capacitance, and V is applied voltage.

So, if it is a pure capacitative process, then what happens the charge carrier they are basically, strongly adhered to the electrode material and then, they are coming out from the electrode material and that is happen in both so called positive and negative electrode. And total capacitance is basically, two capacitors are connected in series. So, you can calculate the total capacitance or capacity of the capacitor material. And the energy density is calculated by the well-known equation half CV square.

So, energy is E and your C is the capacitance and V is the applied voltage. And actual in this figure, I have only shown the stern layer. So, in the electrode material only the strongly adhered ions are there, but actually it is a diffused double layer formation. So, away from this electrode, you have other charges are also involved so that diffuses out.

So, that is a typical electric double layer theory. And in this system, if you do a cyclic voltammetry as I said that you will get a rectangular kind of feature.

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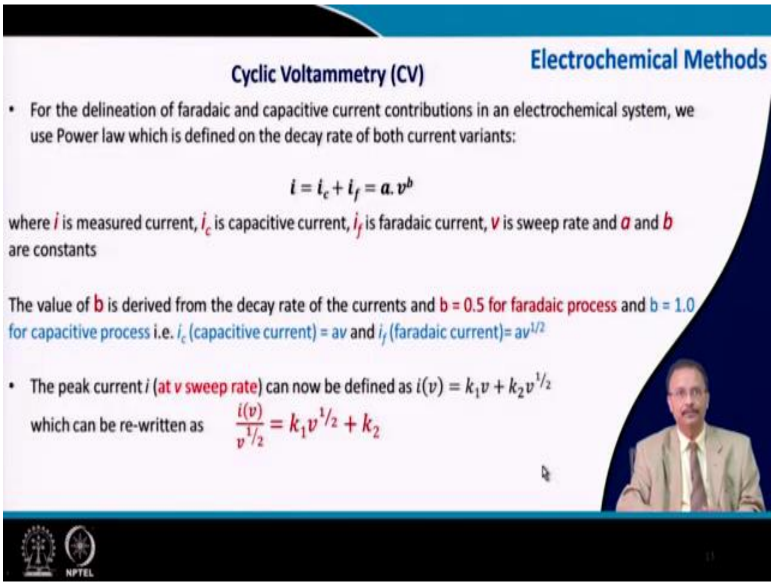

Electrochemical Methods

Cyclic Voltammetry (CV)

- For the delineation of faradaic and capacitive current contributions in an electrochemical system, we use Power law which is defined on the decay rate of both current variants:

$$i = i_c + i_f = a.v^b$$

where i is measured current, i_c is capacitive current, i_f is faradaic current, v is sweep rate and a and b are constants

The value of b is derived from the decay rate of the currents and b = 0.5 for faradaic process and b = 1.0 for capacitive process i.e. i_c (capacitive current) = av and i_f (faradaic current)= a$v^{1/2}$

- The peak current i (at v sweep rate) can now be defined as $i(v) = k_1 v + k_2 v^{1/2}$

  which can be re-written as $\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2$

Now, if in a system you have both the components included, then you it is possible for you to delineate it. So, the total current that will have a component of capacitative current and a faradaic current and that is related to some constant and your scan rate to the power another exponent. So, this a and b they are constant and i f is your faradaic current and i c is your capacitative current.

So, based on the value of b which is derived from the decay rate of the currents. So, if that thing is around 0.5, then we call it is a faradaic process. So, battery is a complete faradaic process. So, b is very close to 0.5 and for a capacitative process, it is 1. So, the peak current and at the sweep rate you can just define like this.

So, you have two components and one component; this is actually a linear variation. Another component is varies with half of the scan rate. And then, you divide two side by this scan rate by half and get this relation and this relation is eventually re written by something like this kind of relation.

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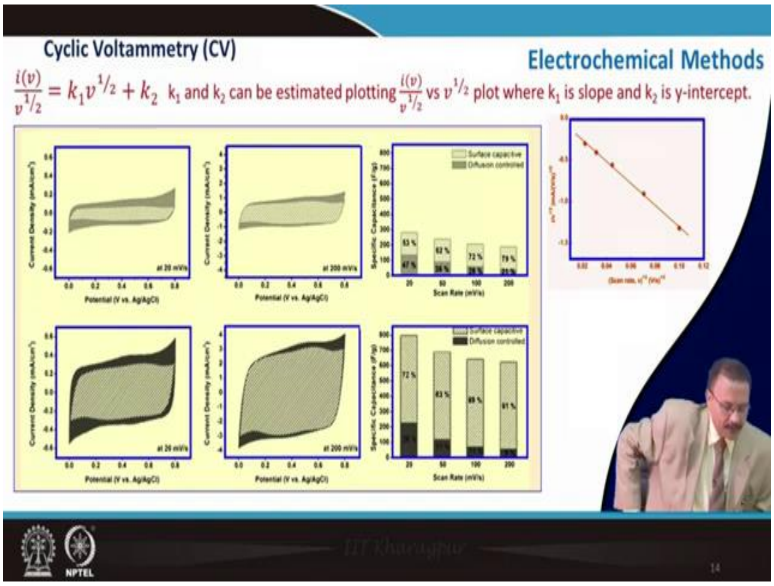

Cyclic Voltammetry (CV)

Electrochemical Methods

$\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2$ k_1 and k_2 can be estimated plotting $\frac{i(v)}{v^{1/2}}$ vs $v^{1/2}$ plot where k_1 is slope and k_2 is y-intercept.

Now, if you have the situation if you know this particular equation and these two things can be estimated from the plot of the y versus x here, x is v to the power half and the slope will give you the k 1 value and k 2 value, you will get from the intercept. So, this is actually done from an experiment experimental cyclic voltammogram.

And as expected, you can see that if I plot this i by v to the power half versus root over of v to the power half; this indeed gives you a straight line and it is done in cathodic sweep that is why this slope is negative. And eventually, you can delineate what is the capacitative component and what is the faradaic component, because you have the total plot CV plot is there.

And by knowing this two component, you can point by point do that what is its faradaic component and what it its capacitative component. And you can very well determine that in a composite battery, what is the capacitative part. You know that if you want to charge the battery at a very fast rate, then you want it to be capacitative type, but if you want to discharge in a long time, then you want it to be in battery type.

So, a hybrid battery is coming up nowadays which is beyond the scope of this particular course. For those kind of battery, hybrid electrode this analysis is very very important.

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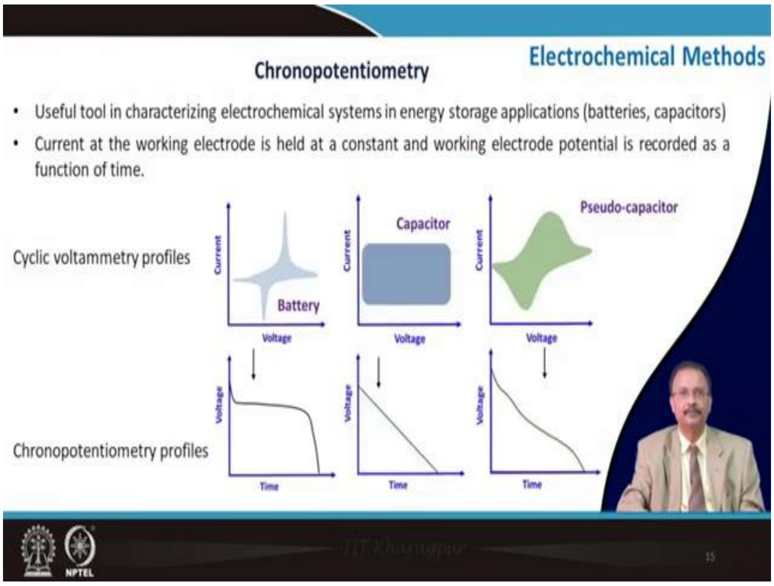

Electrochemical Methods

Chronopotentiometry

- Useful tool in characterizing electrochemical systems in energy storage applications (batteries, capacitors)
- Current at the working electrode is held at a constant and working electrode potential is recorded as a function of time.

Cyclic voltammetry profiles

Chronopotentiometry profiles

Then another measurement that is very routinely done, we call it is a chronopotentiometry. So, current remains constant and then as you can see, in case of the battery you have a discharge profile something like this. In case of capacitative, it is a sloping profile and if you have a pseudo capacitor, it has both faradaic component as well as the component from the capacitor, then it is a mixture between these two.

So, this kind of charge and discharge thing for your example this is shown for only in the battery part is shown here, and the charge discharge part is in the shown in the bottom panel of this. So, cyclic voltammetry is in the top panel and the chronopotentiometry kind of profile is shown in the bottom.

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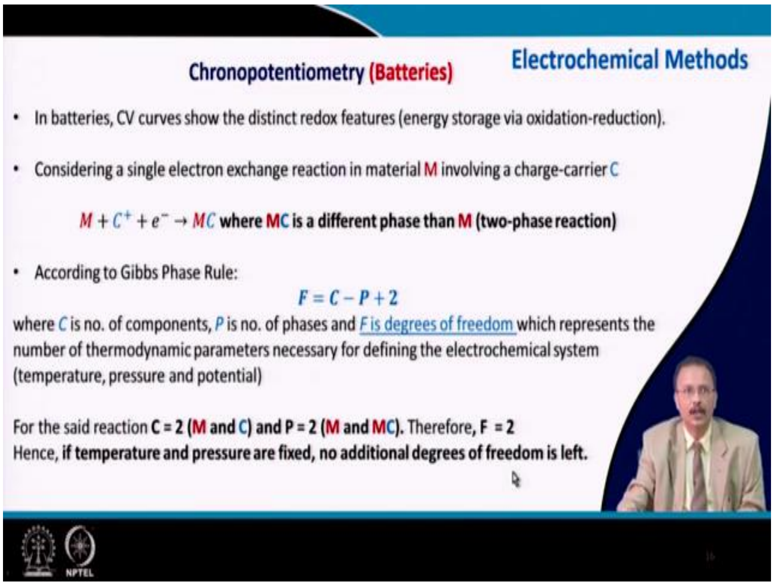

Electrochemical Methods

Chronopotentiometry (Batteries)

- In batteries, CV curves show the distinct redox features (energy storage via oxidation-reduction).
- Considering a single electron exchange reaction in material M involving a charge-carrier C

$M + C^+ + e^- \rightarrow MC$ **where MC is a different phase than M (two-phase reaction)**

- According to Gibbs Phase Rule:

$$F = C - P + 2$$

where C is no. of components, P is no. of phases and F is degrees of freedom which represents the number of thermodynamic parameters necessary for defining the electrochemical system (temperature, pressure and potential)

For the said reaction **C = 2 (M and C) and P = 2 (M and MC).** Therefore, **F = 2**
Hence, **if temperature and pressure are fixed, no additional degrees of freedom is left.**

So, in the battery the CV curve shows the distinct redox feature. So, energy storage versus via oxidation and reduction that usually is done in in the battery material. So, if you consider this reaction a single electron exchange reaction you see that this M and this is the charge carrier.

So, for example, this is lithium and this is your anode sorry cathode part. And it is taking the electron from the anode and it is forming a compound which is MC right and then, part of M is also there. You consider lithium cobalt oxide which already I have described. So, in lithium cobalt oxide initially, after charging part of lithium is gone out and went to the negative electrode; that means, the anode and then, during discharge it is coming back.

So, it is coming back and getting inserted in again into the lithium cobalt. So, you have a two-face thing. So, already where the lithium whenever it went out, the part which is remaining and during charging again lithium is coming in and it is taking the electron so neutralise this lithium ion and then again it is intercalating. So, it is a two-face mixture.

So, you can apply the Gibb’s phase rule which already I have described. So, degree of freedom depends on the value of C is the component and P is the phase mixture and these two is coming, because of temperature and pressure the same thing. So, for the said reaction here, number of component is 2 M and C and phase is M is happening and MC

M is going into MC. So, there are phase is 2. So, degree of freedom is only 2. So, if the temperature and pressure are fixed, then no additional degree is left.

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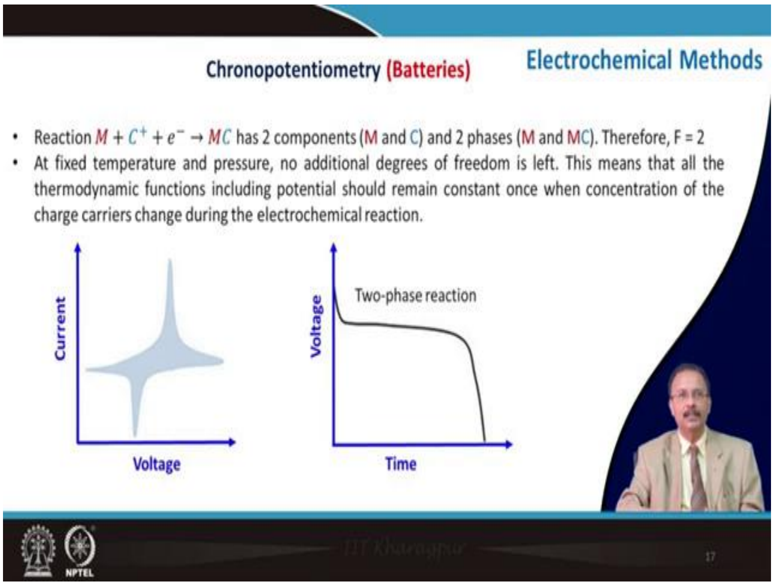

Electrochemical Methods

Chronopotentiometry (Batteries)

- Reaction $M + C^+ + e^- \rightarrow MC$ has 2 components (M and C) and 2 phases (M and MC). Therefore, F = 2
- At fixed temperature and pressure, no additional degrees of freedom is left. This means that all the thermodynamic functions including potential should remain constant once when concentration of the charge carriers change during the electrochemical reaction.

So, what is their implication? You can see here the same reaction I have written here. So, in CV, you see a oxidative curve and a reduction curve and it is a discharge profile. So, we are concentrating on the this part this reduction part. And in constant temperature and pressure if you do, then you cannot change anything else. So, voltage will remain constant. So, that is why you get a plateau out of this kind of system.

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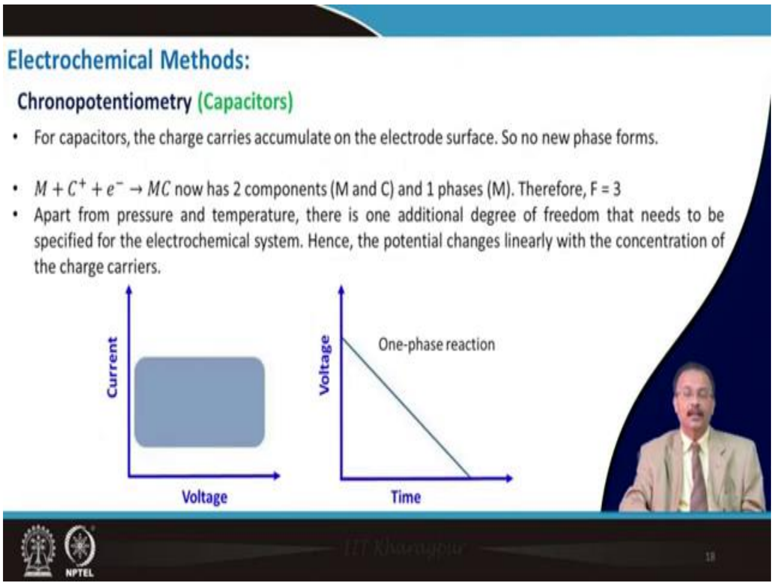

Electrochemical Methods:

Chronopotentiometry (Capacitors)

- For capacitors, the charge carries accumulate on the electrode surface. So no new phase forms.
- $M + C^+ + e^- \rightarrow MC$ now has 2 components (M and C) and 1 phases (M). Therefore, F = 3
- Apart from pressure and temperature, there is one additional degree of freedom that needs to be specified for the electrochemical system. Hence, the potential changes linearly with the concentration of the charge carriers.

In case of capacitor, what is happening? M and C; it is directly getting adhered. So, now, it has two component M and C, but phase is 1 therefore, degree of freedom is 3. So, apart from pressure and temperature, there is one additional thing that you will be able to change and what is that additional thing you can change the voltage and therefore, the voltage does not form a plateau, it is always a sloping nature.

And the hybrid thing, where both capacitative and your battery component is there always you have a mixed kind of effect. So, that has been shown here.

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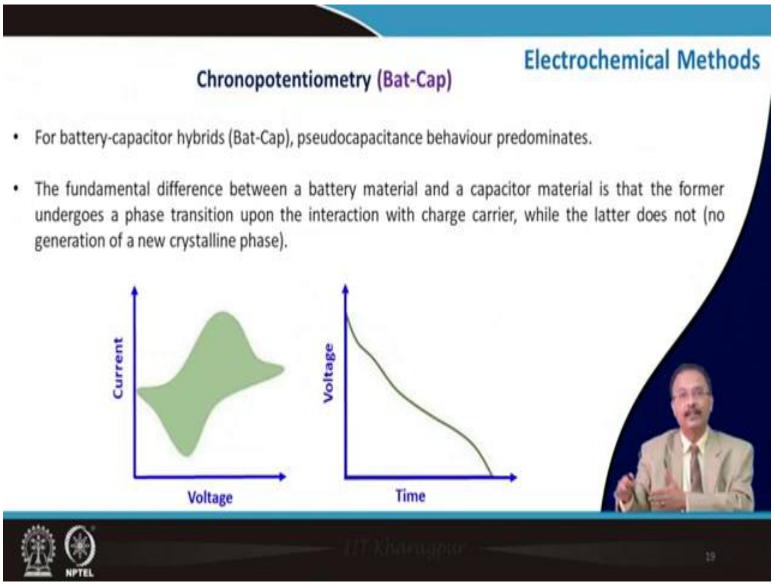

Electrochemical Methods

Chronopotentiometry (Bat-Cap)

- For battery-capacitor hybrids (Bat-Cap), pseudocapacitance behaviour predominates.
- The fundamental difference between a battery material and a capacitor material is that the former undergoes a phase transition upon the interaction with charge carrier, while the latter does not (no generation of a new crystalline phase).

So, in case of a battery capacitor hybrid, you have a plateau kind of thing in some region, but mostly it is a sloping profile that you are getting.

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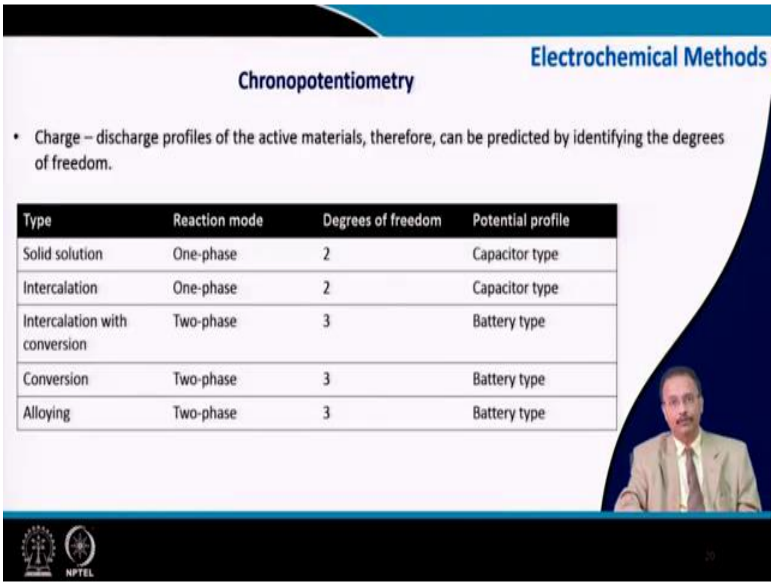

Electrochemical Methods

Chronopotentiometry

- Charge – discharge profiles of the active materials, therefore, can be predicted by identifying the degrees of freedom.

Type	Reaction mode	Degrees of freedom	Potential profile
Solid solution	One-phase	2	Capacitor type
Intercalation	One-phase	2	Capacitor type
Intercalation with conversion	Two-phase	3	Battery type
Conversion	Two-phase	3	Battery type
Alloying	Two-phase	3	Battery type

Now, I have not taught all types of battery material. I have only talked about the intercalating material and ideal C type capacitor material. So, there are other types of battery as well.

We call it is a alloy type battery or conversion type battery. In all the cases, you can always estimate the degree of freedom and you can define that what will be their tentative voltage profile voltage as a function of time and whether it is a capacitative type or whether it is a battery type that you can identify.

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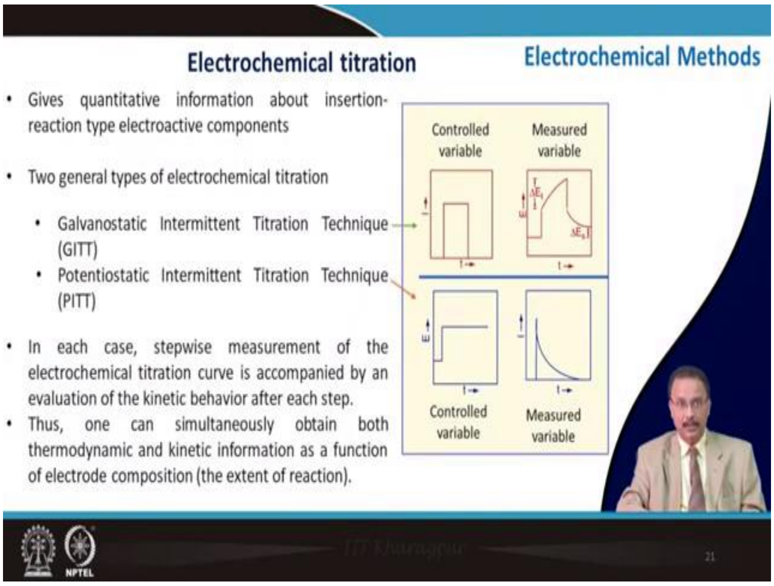

Electrochemical Methods

Electrochemical titration

- Gives quantitative information about insertion-reaction type electroactive components
- Two general types of electrochemical titration
    - Galvanostatic Intermittent Titration Technique (GITT)
    - Potentiostatic Intermittent Titration Technique (PITT)
- In each case, stepwise measurement of the electrochemical titration curve is accompanied by an evaluation of the kinetic behavior after each step.
- Thus, one can simultaneously obtain both thermodynamic and kinetic information as a function of electrode composition (the extent of reaction).

The next two things are Galvanometric Intermittent Titration Technique and Potentiostatic Intermittent Titration Technique. So, in both the cases, stepwise measurement of electrochemical titration curve is accompanied by the evaluation of the kinetic behavior of each stage.

So, in Galvanostatic intermittent thing, you are giving a voltage pulse like this and you are measuring the current value right. In case of a sorry in case of a galvanostatic system, you are applying a current pulse and you are measuring the voltage value just like this. And in case of a potentiostatic system, you are giving a voltage pulse and you are measuring current as a function of time.

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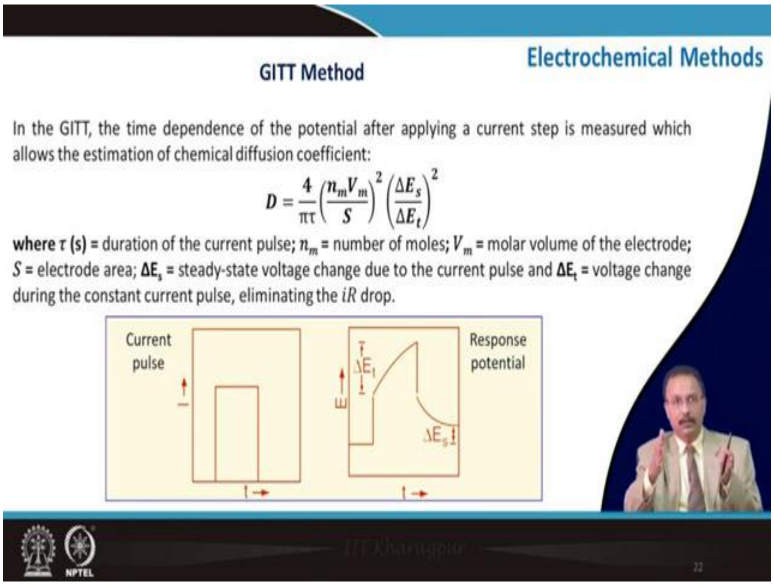

Electrochemical Methods

GITT Method

In the GITT, the time dependence of the potential after applying a current step is measured which allows the estimation of chemical diffusion coefficient:

$$D = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

where τ (s) = duration of the current pulse; n_m = number of moles; V_m = molar volume of the electrode; S = electrode area; **ΔE_s** = steady-state voltage change due to the current pulse and **ΔE_t** = voltage change during the constant current pulse, eliminating the iR drop.

So, now, if you use these two and using this relation again, you can measure the diffusion coefficient and this is a complicated relation, but this relation is valid for most of the battery material. So, what we are doing? We are in a in a particular window chosen window, we are giving a current pulse and this tau s is the duration of the current pulse and number of moles whatever is involved is n m V m is the molar volume and S is the electrode area and this del E is the steady state voltage that change due to the current pulse.

So, that is actually you can get from this particular plot and then, using this relation, you can calculate what is the diffusion coefficient.

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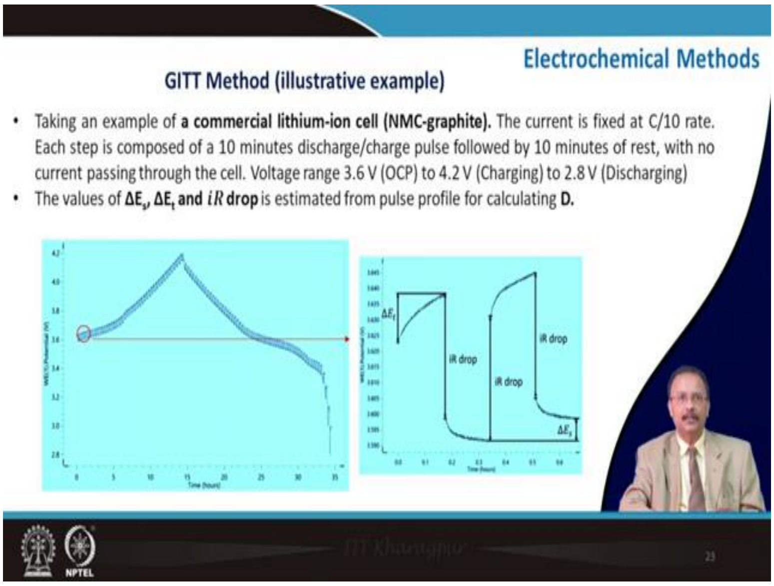

Electrochemical Methods

GITT Method (illustrative example)

- Taking an example of **a commercial lithium-ion cell (NMC-graphite).** The current is fixed at C/10 rate. Each step is composed of a 10 minutes discharge/charge pulse followed by 10 minutes of rest, with no current passing through the cell. Voltage range 3.6 V (OCP) to 4.2 V (Charging) to 2.8 V (Discharging)
- The values of **ΔE_s, ΔE_t and iR drop** is estimated from pulse profile for calculating **D.**

Something similar, that is done in case of GITT method and this is your charge and discharge profile that you are familiar to. And here, in this particular region, we are applying this potential whatever I showed and this is the experimental value whatever you are getting. And this parameters you know electrode area etcetera whatever is required that is shown in this earlier equation and you can calculate the diffusion coefficient as well.

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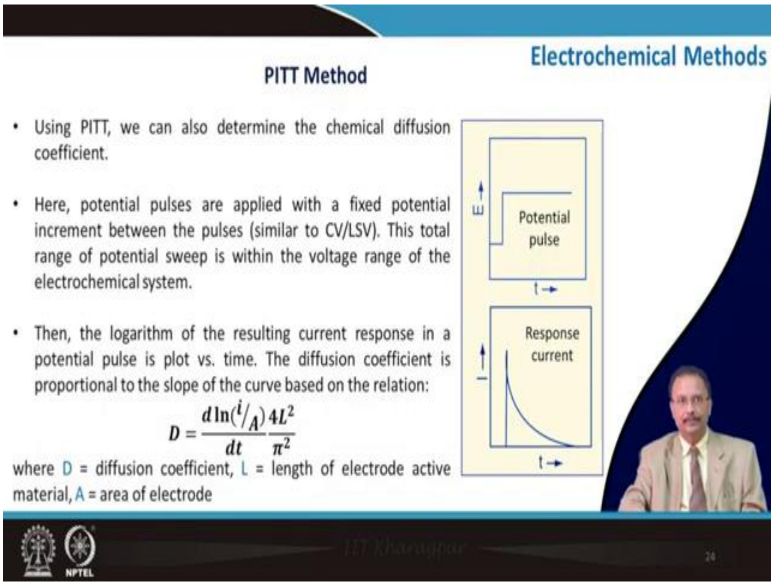

Electrochemical Methods

PITT Method

- Using PITT, we can also determine the chemical diffusion coefficient.
- Here, potential pulses are applied with a fixed potential increment between the pulses (similar to CV/LSV). This total range of potential sweep is within the voltage range of the electrochemical system.
- Then, the logarithm of the resulting current response in a potential pulse is plot vs. time. The diffusion coefficient is proportional to the slope of the curve based on the relation:

$$D = \frac{d\ln(i/A)}{dt}\frac{4L^2}{\pi^2}$$

where D = diffusion coefficient, L = length of electrode active material, A = area of electrode

Using potentiostat, measurement also you can do the similar type of calculation to know the diffusion coefficient. And here, you can see we are applying a potential pulse and we are measuring current as a function of time and the relevant relation to estimate your D is this one D here, is the diffusion coefficient L is the length of the electrode active material and A is the area of the electrode.

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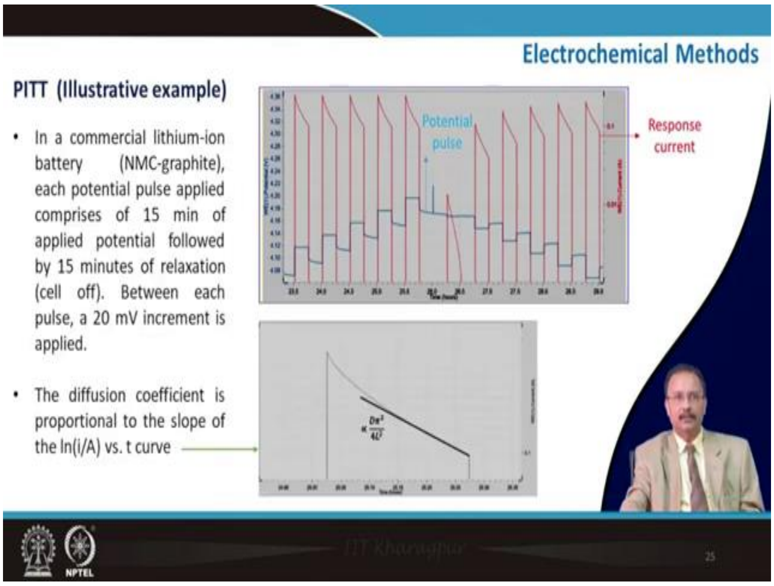

Electrochemical Methods

PITT (Illustrative example)

- In a commercial lithium-ion battery (NMC-graphite), each potential pulse applied comprises of 15 min of applied potential followed by 15 minutes of relaxation (cell off). Between each pulse, a 20 mV increment is applied.
- The diffusion coefficient is proportional to the slope of the ln(i/A) vs. t curve

So, the illustration for this kind of thing is something similar to that. In commercial lithium-ion battery, we have taken NMC as a positive electrode and graphite as a negative electrode and I explained lithium cobalt oxide, while I thought this particular lithium-ion battery. And each potential pulse is applied it comprises 15 minutes of the applied potential followed by 15 minute relaxation time.

And between each pulse, when 20 milli volt increment is applied. So, step by step it is increased. And you are getting the current profile something like this and from the linear part of this curve linear part of this curve, you can measure the diffusion coefficient of the diffusing species in this cases in this case, lithium-ion is the diffusion diffusing species.

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REFERENCES

- **A. J. Bard.** "Electrochemical Methods: Fundamentals and Applications" 2nd Ed. Wiley New York, 2001. **(Reference book)**
- **R. A. Huggins.** "Advanced Batteries: Materials Science Aspects" Springer New York, 2009.
- Metrohm Application Database, Metrohm Switzerland. https://www.metrohm.com/en/applications/
- Gamry Instruments Application Notes, Gamry Instruments USA. https://www.gamry.com/resources/application-notes/

So, this part of the lecture, there is a reference book and very famous book by A.J. Bard. So, that can be used and other than that, this websites can be used for their application notes to better grasp this idea.

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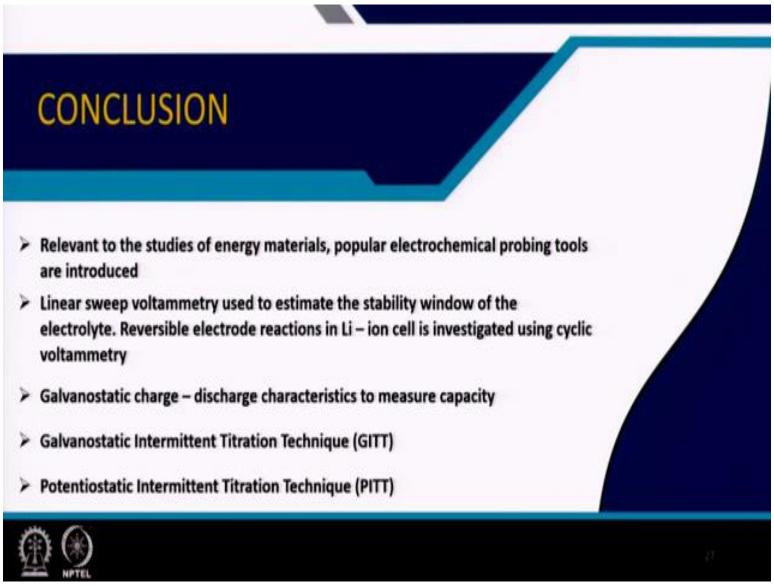

CONCLUSION

- **Relevant to the studies of energy materials, popular electrochemical probing tools are introduced**
- **Linear sweep voltammetry used to estimate the stability window of the electrolyte. Reversible electrode reactions in Li – ion cell is investigated using cyclic voltammetry**
- **Galvanostatic charge – discharge characteristics to measure capacity**
- **Galvanostatic Intermittent Titration Technique (GITT)**
- **Potentiostatic Intermittent Titration Technique (PITT)**

So, relevant studies to the energy materials popular electrochemical probing tools are explained. First, we have talked about linear sweep voltammetry and then, we have talked about cyclic voltammetry then, galvanostatic charge discharge characteristics to measure the capacity of a particular battery which already in the last lecture I have covered a bit. So, how they are characterised we have talked about it.

And to know the diffusion coefficient of the diffusing species other than the cyclic voltammetry in a particular potential range wherever this peaks you are getting the oxidation or reduction peak; it can be applicable to those area as well including the whole potential range either you can apply Galvanostatic Intermittent Titration Technique or Potentiostatic Intermittent Titration Technique to characterise this material.

Thank you so much for your attention.