Electrochemical Energy Storage
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Module - 02
Definitions and measuring methods
Lecture - 08
Measurements: Cyclic Voltammetry, Nominal Voltage, Capacity, Rate Performance, Cycleability, GITT and PITT Measurements

Welcome to my course Electrochemical Energy Storage and this is module number 2, where we are discussing Definitions and measuring methods. And this is lecture number 8, where we will talk about certain important Measurements pertinent to the electrochemical energy storage battery in terms of Cyclic Voltammetry, Nominal Voltage concept, Capacity, Rate Performance, Cycleability and the several electrochemical titration measurement technique.

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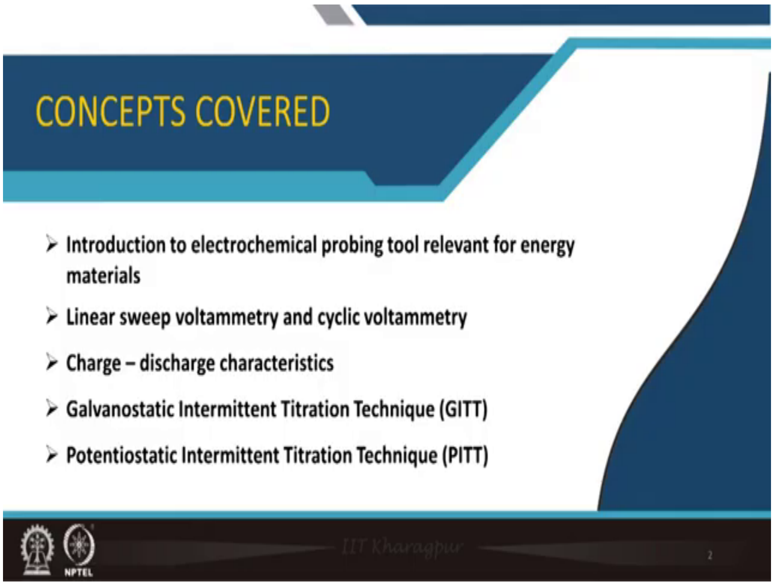

CONCEPTS COVERED

- 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)

So, first we will introduce the electrochemical probing tool, which is relevant for energy materials; then we will introduce the concept of linear sweep voltammetry and cyclic voltammetry. Then we will talk about the charge discharge characteristics measurement and finally, Galvanostatic Intermittent Titration Technique and Potentiostatic Intermittent Titration Technique they are abbreviated respectively as GITT, GITT and PITT, PITT this will be introduced.

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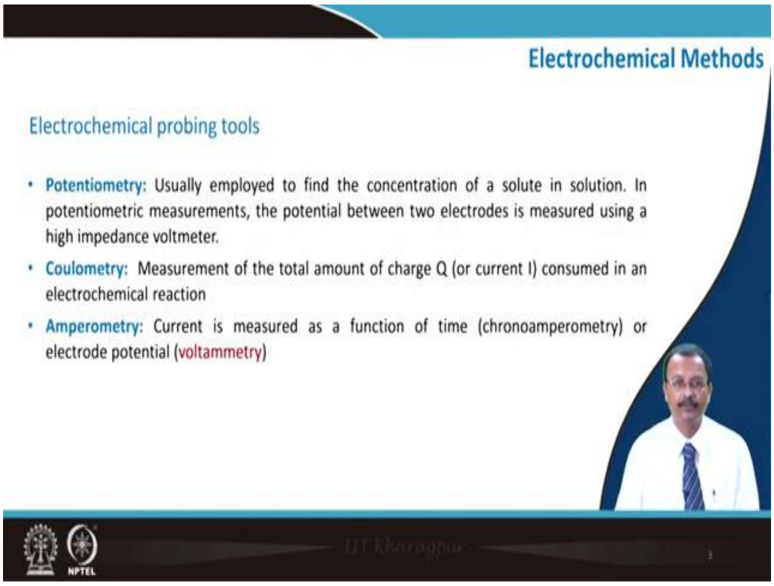

Electrochemical Methods

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)

So, in one of my earlier lectures, already we talked about electrochemical probing tools; we talked about potentiometry and that potentiometry is usually employed to find the concentration for example, of a solute in a solution. And this type of measurement, the potential between two electrode is measured with a high impedance voltmeter. Then coulometry that is the measurement of the total amount of charge or the current that is consumed in an electrochemical reaction that is measured.

And amperometry, which basically we will be using mostly; current is measured as a function of time we call this is chronoamperometry and it is also measured as a function of electrode potential, when we will call this is voltammetry. So, our measurement is based on this preliminary concept, which already I talked about as a part of my earlier lectures.

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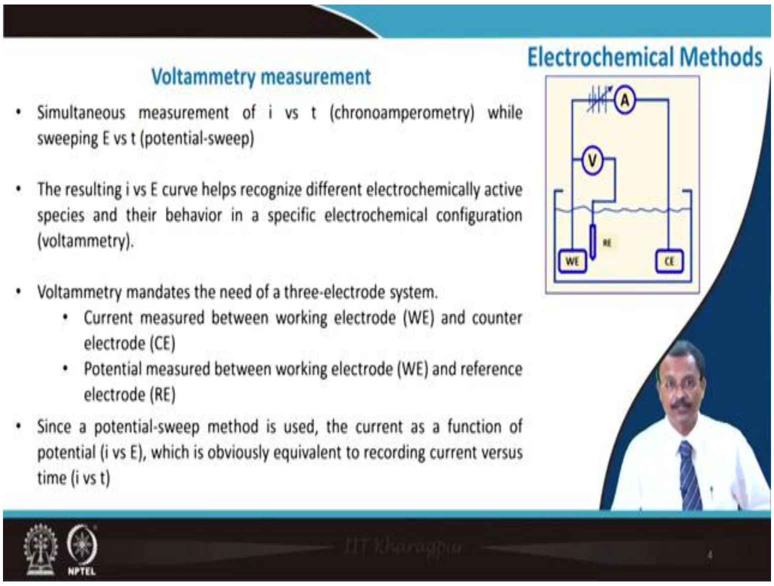

Electrochemical Methods

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, again we will come back to this three electrode system, which I talked about in my earlier lectures. So, in voltammetry measurement, simultaneously we measured i versus t which is chronoamperometry and simultaneously we sweep voltage potential as a function of time.

So, this is potential sweep as well. So, that results i versus E curve and this helps us to recognize different electrochemically active species in their behavior in a specific type of electrochemical configuration and we call this is voltammetry. So, this voltammetry, voltammetry that mandates the need of three electrode and current is basically measured between the working electrode and the counter electrode, and potential is measured between the working electrode and the reference electrode.

So, a potential sweep method since it is being used, the current as a function of potential; that means i versus E is measured and obviously, it is equivalent to recording current versus time, because both are either being measured as a function of time or being applied in case of voltage as a function of time. So, always current versus time also you can get out of this type of measurements

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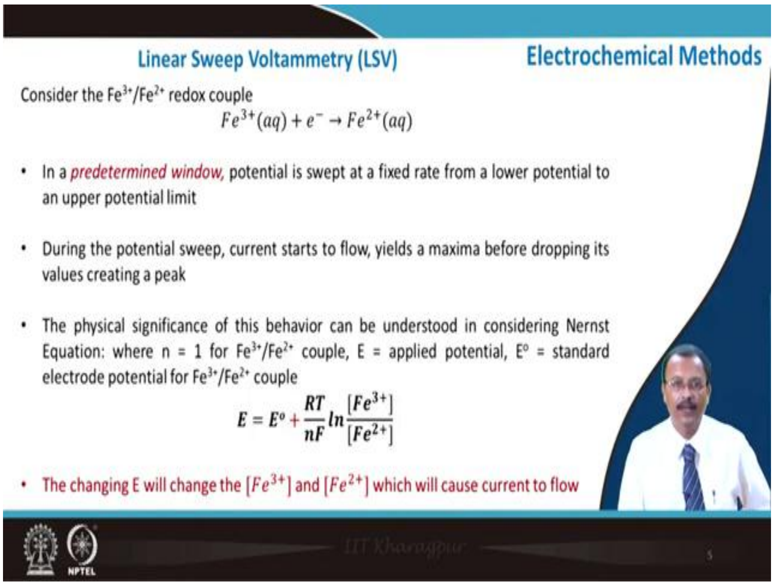

Linear Sweep Voltammetry (LSV) **Electrochemical Methods**

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

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So, first let us introduce the Linear Sweep Voltammetry, which is abbreviated as LSV.

And one redox couple that we are considering in aqueous solution of F e 3 plus; it takes electron to form F e 2 plus, it is getting reduced. So, we will have to take a pre determined window potential and which is a bit arbitrary, you will have to guess depending the reduction potential and then the potential is swept at fixed rate from that lower potential to an upper potential limit.

And during this potential sweep, current starts to flow and that basically yields a maxima and then eventually it drops and that creates a peak, we will show that. The physical significance of this behavior that can be understood by the Nernst equation which already I introduced earlier. Here n is equal to 1 for this particular couple and E is a applied potential and E 0 is the standard electrode potential for this couple.

$$\boldsymbol{E = E^{0} + (RT/F)\frac{[Fe^{3+}]}{[Fe^{2+}]}}$$

And you know that this negative sign is actually positive; because this I have taken in the reverse way, not the product versus reactant. So, that is that is why this is positive. So, the changing of this potential will change this concentration F e 3 plus and F e 2 plus and that actually cause the current to flow.

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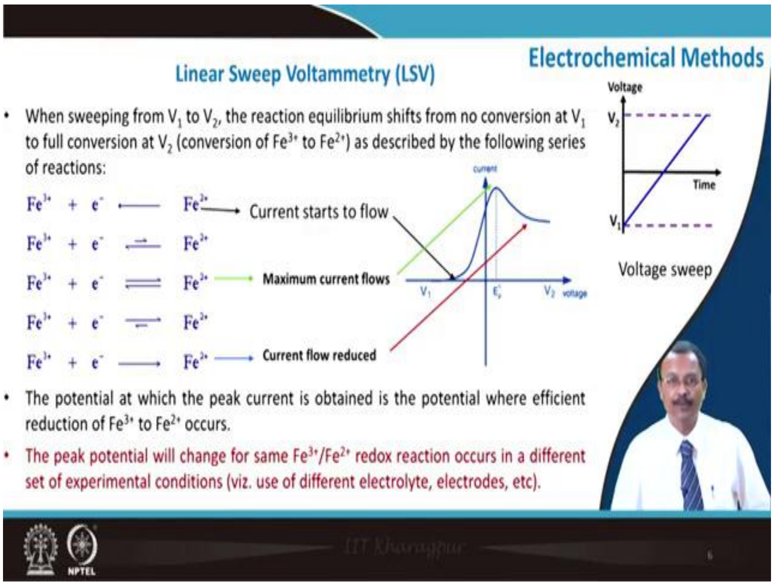

Electrochemical Methods

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, if you see this kind of behavior and try to understand it. So, we are sweeping it from V 1 to V 2 at a constant rate. So, this is basically a straight line. And the reaction equilibrium, they shifts from no conversion, initially there will not be any conversion reaction at a say V 1 here, at this region; it is the current will start to flow when this reaction will eventually take place.

So, actually this will yield you a peak here; the potential where this peak current is obtained is this potential where efficiently reduction is going place going to take place F e 3 plus to F e 2 plus is occurring. And the peak potential will change for the same redox reaction in a different set of experimental condition.

That means, if I change the electrolyte or if I change the electrode; then this peak potential is slightly it will shift its position. Now, you can increase the sweep rate, if you increase the sweep rate, the peak potential cannot change; increase sweep rate in this direction will only increase the peak current, but this position will not change. So, the peak current will only increase in this voltage window of V 1 and V 2.

The electrochemical reaction rate change, the reaction becomes faster or slower; if that is the case, then the peak potential shifts. So, here you can see that if the reaction rate change in this direction; then eventually when it is slowing down, then this potential change. So, in depth info about the electrochemical reaction can be obtained via this linear sweep voltammetry technique.

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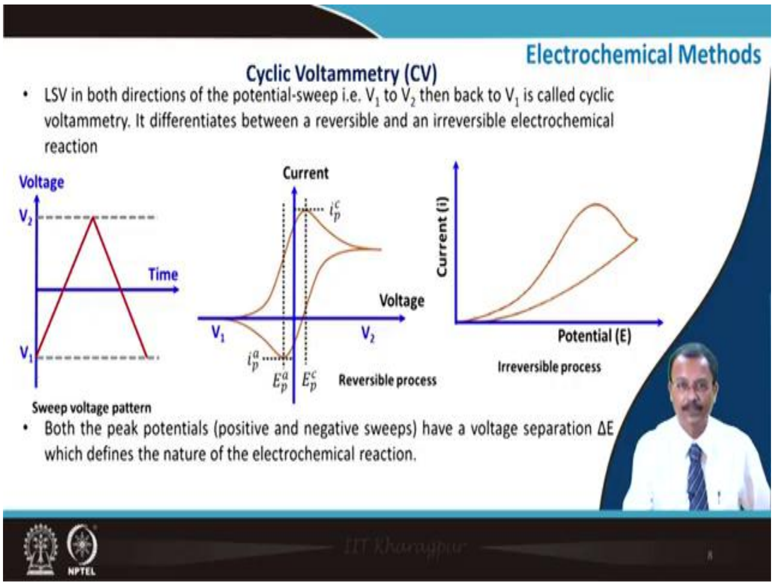

Electrochemical Methods

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.

So, we can apply this linear sweep voltammetry in both the direction of the potential sweep. So, initially from V 1 to V 2 and then back to V 1 and this is then called a cyclic voltammetry. It differentiate between a reversible and irreversible type of electrochemical reaction. So, for example, this is the sweep voltage pattern that we are actually apply across the sample and this is the resultant current as a function of voltage in this voltage window.

So, both peak potential, the positive and negative sweep have a voltage of separation; as you can see that this voltage of separation is usually del E, which is a significant parameter and that defines the nature of this electrochemical reaction. So, if it is a reversible reaction, both oxidation and reduction takes place; then you get this peak current in this direction, in the oxidation direction, you must mention which direction is oxidation and which direction is reduction.

And if it is an irreversible process, then as expected you can have this oxidation current peak; but it will be absent in during the reduction case. So, you can identify whether it is a reversible or irreversible chemical reaction.

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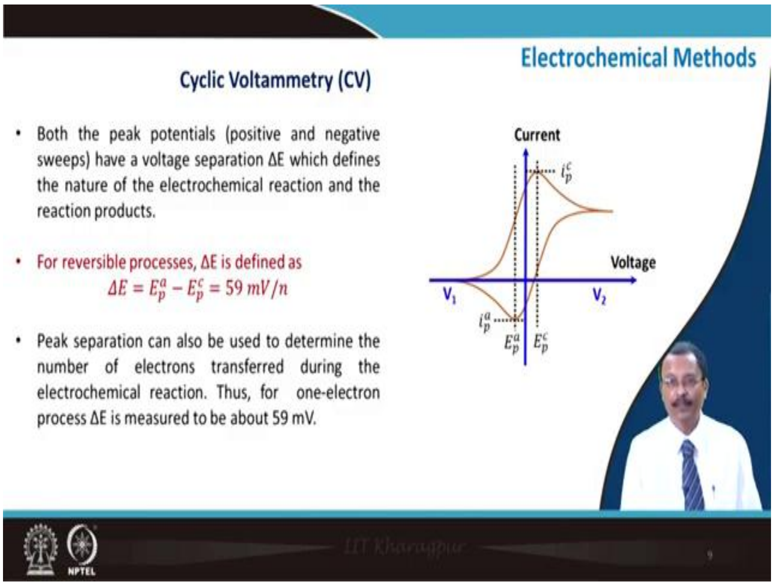

Electrochemical Methods

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, as I mentioned that this positive and negative sweeps have a voltage separation and that defines the nature of the electrochemical reaction and also the reaction product. For reversible process, this del E value that actually depends on this at del p at c is subtracted from this del p at a this one and usually this is 59 milli volt per number of electron.

$$\Delta E = E_p^a - E_p^c = \frac{59mV}{n}$$

So, the per peak separation that can be used to determine the number of electron that is transferred during the electrochemical reaction. So, for one electron process, when the exchange of one electron takes place; then the measured value of this del E is usually 59 milli volt and that you can easily estimate as a part of the assignment problem from the Nernst equation.

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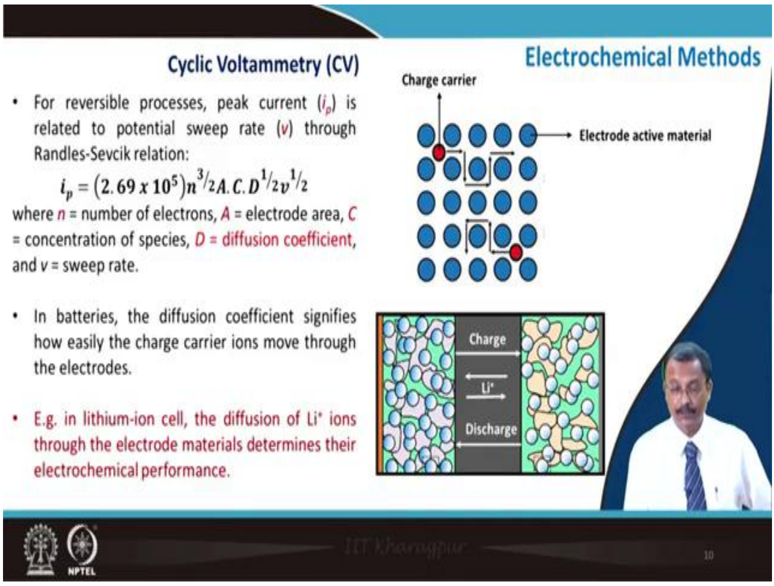

Electrochemical Methods

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.

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So, for the cyclic voltammetry, the reversible process peak, this i p is related to the potential sweep rate, which is defined as nu and this is a through this Randles Sevcik relation, which relates this value of i p with several parameters; that includes the number of electron, then electrode area, the exposed area of the electrode, and then concentration of the species, and also the diffusion coefficient.

$$i_p = (2.69 * 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$$

So, if you consider the electrode active material, electron also flows through it within this electrode material and it is transferred to the current collector depending on whether it is a positive and negative electrode. So, in battery the diffusion coefficient signifies how easily that charge carriers that ions can move through the electrode. So, it is an important parameter to estimate.

So, if you consider the lithium ion cell, the diffusion of lithium ions through the electrode materials that determine their electrochemical performance for faster movement of lithium that will lead it to the high power discharge or it can be charged at relatively lower time. So, it is important lithium diffusion inside the electrode material.

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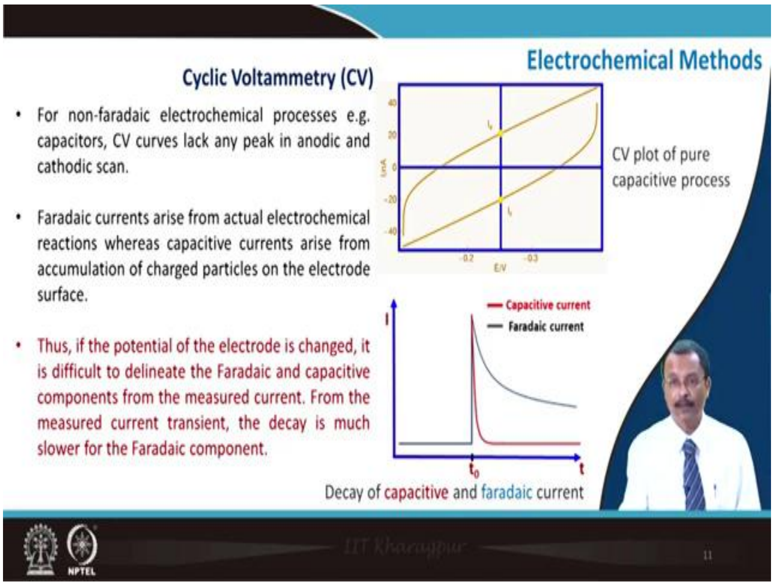

Electrochemical Methods

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, cyclic voltammetry can help you to estimate the diffusion coefficient by the equation that I mentioned. So, for a non-faradaic process, for example, in a capacitor the CV curve that lacks any anodic or any cathodic peak as obvious; because there is no redox reaction is involved.

So, the faradaic current that arises from actual electrochemical reactions and this capacitive current that arise the due to the accumulation of the charge particulate on the electrode surface, you know about the EDLC behavior and you can understand that.

So, the potential of the electrode if it is changed, it is difficult to delineate; whether it is faradaic and capacitive component from the measured current. So, from the measured current transient, if you see the decay is much slower in case of faradaic component as compared to the capacitive component; but both this mechanism may be operative in a battery material and in some instances it is required to be delineated.

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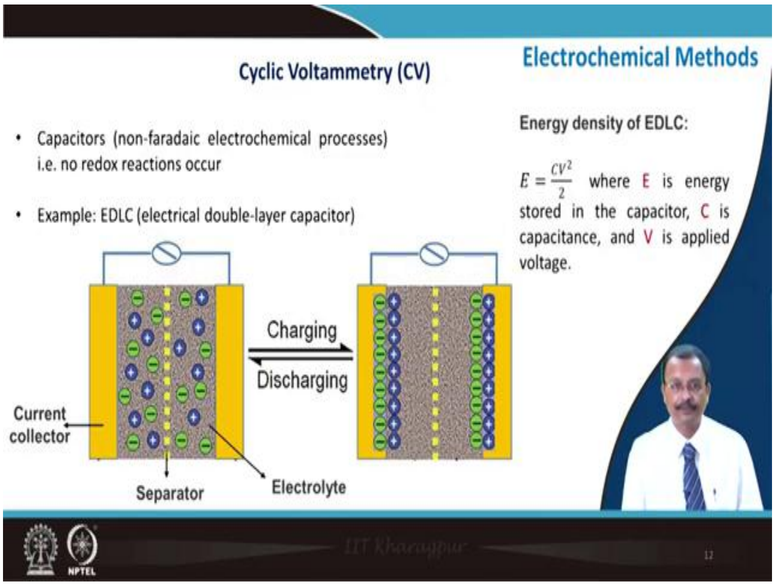

Electrochemical Methods

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.

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So, as I said capacitor is a non-faradaic electrochemical process, particularly the EDLC type of capacitors. So, no redox reaction is takes taking place. So, this is a typical example of EDLC behavior and only I have considered the stern layer, not the diffuse double layer. So, the energy of this kind of EDLC capacitor that can be estimated by this well-known half CV square energy can be estimated from its capacitance value and it depends on the applied voltage, the energy is directly dependent on the applied voltage.

$$E = CV^2/2$$

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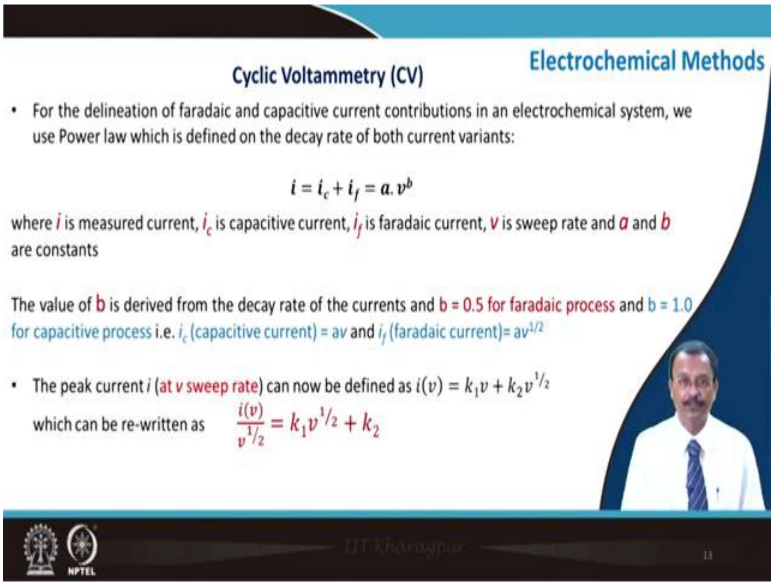

Electrochemical Methods

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)= $av^{1/2}$

- 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 $\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2$

I was talking about the delineation of this faradaic and capacitive current contribution in that electrochemical system and we can use the Power law, which is defined by the decay rate of both the current variants which I showed. So, the total current component is having a capacitive component and faradaic component and that can be related with this relation a into v to the power b.

$$i = i_c + i_f = a\nu^b$$

So, i is the measured current and i c is the capacitive current and this is the faradaic current and this is related with the voltage sweep and a and b which are the constant. Now, this b value that is derived from the decay rate of the current which is shown and typically if b is 0.5; then we call this is a faradaic process, purely faradaic process and if it is 1, then it is a capacitive process. So, for capacitive current, then it is i c is a into v and for faradaic this is a v to the power half putting the value of b.

So, the peak current at a particular v sweep rate that, now can be defined as i as a function of v at a particular sweep rate; this is sometimes I am calling it v or sometimes nu, actually it is nu, i as a function of nu is k 1 into nu plus k 2 into nu to the power half. And this can be written rewritten as this expression by dividing both side by nu to the power half and that gives this simple relation.

$$\frac{i(\nu)}{\nu^{1/2}} = k_1\nu^{1/2} + k_2$$

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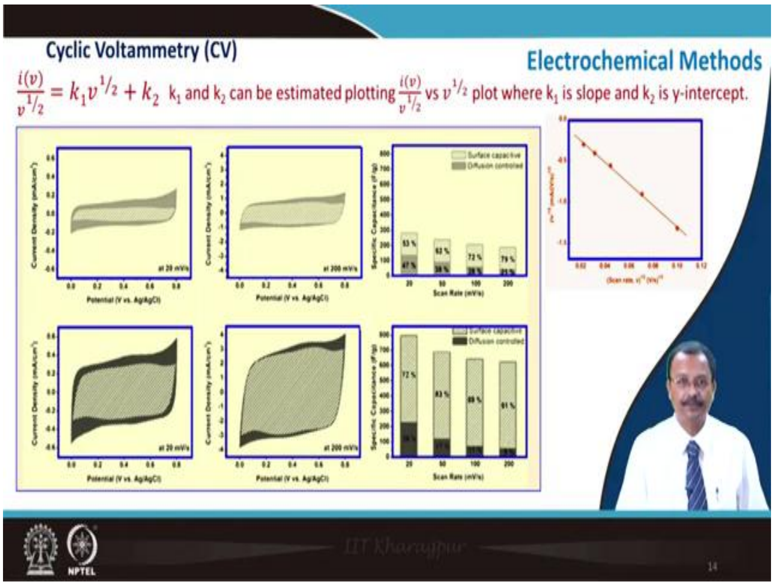

Cyclic Voltammetry (CV)

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, eventually this values k 1 and k 2 from this relation can be estimated by plotting this i as a function of nu by nu to the power half versus nu to the power half. So, k 1 is the slope and k 2 is the intercept from this linear plot, a typical linear plot is shown here maintaining this. And this basically will help me to estimate the value of k 1 and k 2 and then from point by point, from a typical CV plot, I can get the capacitive and I can get the diffusion control faradaic process. And the typical example is shown for various cases

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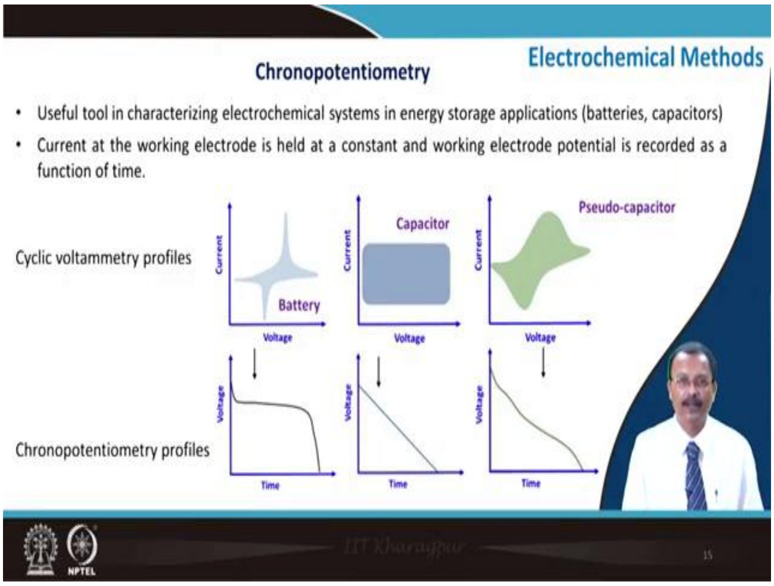

Electrochemical Methods

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.

So, next we will talk about chronopotentiometry and that is a useful tool for characterizing the electrochemical system in an energy storage application, including battery and capacitors. So, current at working electrodes it held at a constant and working electrode potential is recorded as a function of time. So, this is a constant current measurement and electrode potential is required.

So, for a battery type of material clear cut oxidation and reduction peaks are available which is absent in a purely capacitive material. And for a pseudo capacitor, where both the fraction are there; it is capacitive as well as faradaic, then you have a broad kind of behavior, this is due to this is basically mixture of this and this.

So, if you measure the chronopotentiometric profile, that means the voltage as a function of time; then for the typical faradaic material under certain condition, you know I have already defined that how you can predict the type of this voltage versus time profile using thermodynamic consideration. So, under certain condition you can get a plateau and for capacitor it is a more or less steady fall and a mixture between these two you will get in case of a pseudo capacitor material.

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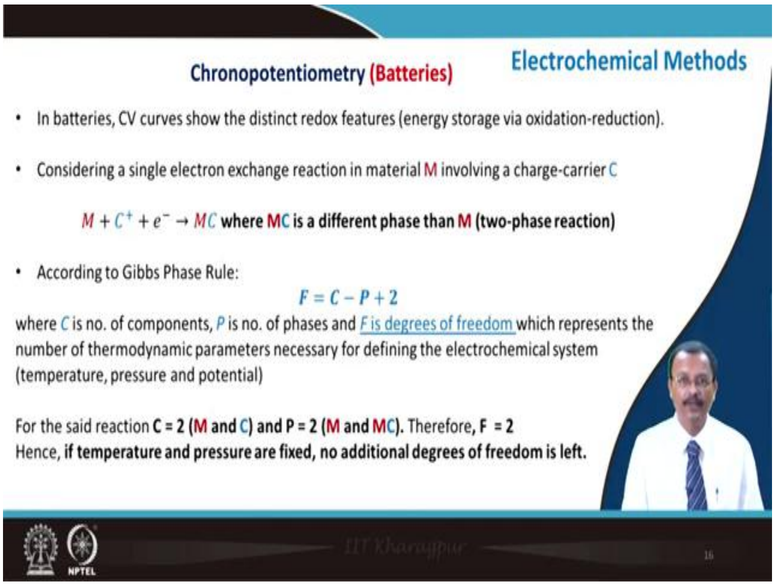

Electrochemical Methods

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.**

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So, in battery, the CV curves they show distinct redox feature and this is energy storage via oxidation and reduction reaction. So, if you consider a single electron exchange reaction in a material M involving a charge carrier C; then this part already I explained in one of my earlier lectures, so I will go a bit fast. So, this reaction takes place and here M C is a different phase than M. So, it is basically a two phase reaction.

So, if you apply the Gibbs phase rule, then degree of freedom is number of component minus number of phase and this 2, plus 2 is coming one due to pressure and another one temperature. So, this degree of freedom represents the number of thermodynamic parameter that is necessary to define this electrochemical system, particularly temperature, pressure and also potential.

$$F = C - P + 2$$

So, for this reaction, this particular reaction you know there are component is 2 M and C are there, phase is also 2 M is there and MC is there. So, degree of freedom is 2. So, the temperature and pressure if you fix it, then no additional degree of freedom is left.

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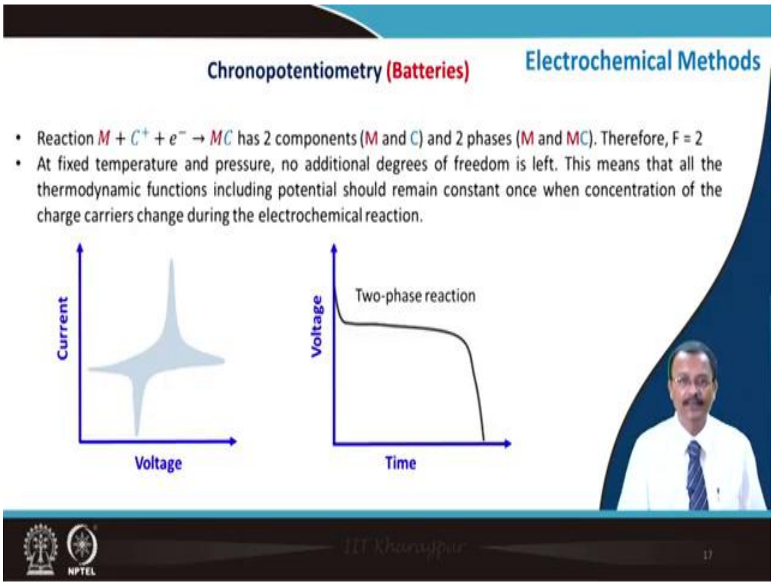

Chronopotentiometry (Batteries)

Electrochemical Methods

- 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.

And therefore, for this type of reaction, it has 2 component, 2 phase, degree of freedom 2. At fixed temperature and pressure, there is no additional degree of freedom is left. And this means that, all the thermodynamic function including a potential that should remain constant once the concentration of the charge carrier change during the electrochemical reaction. So, you get a flat kind of plateau for this two phase reaction.

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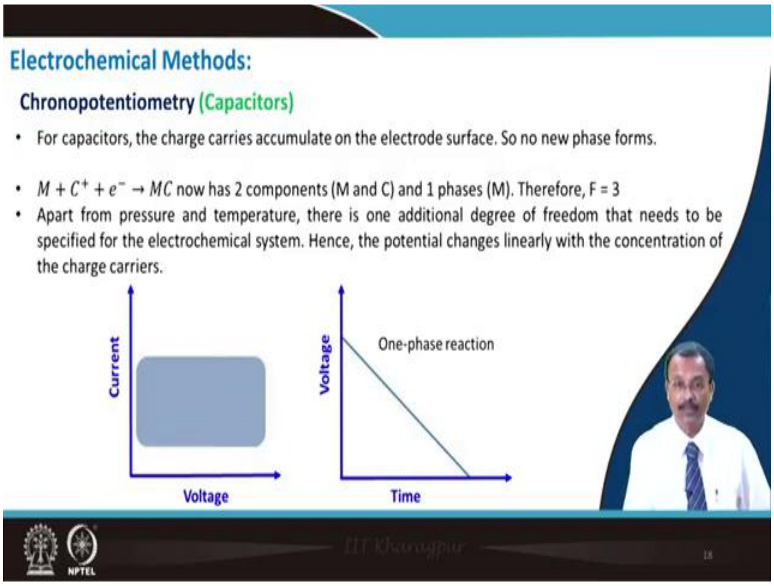

Electrochemical Methods:

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.

Now, if you consider chronopotentiometry measurement for capacitors, then the charge carrier they basically accumulates on the electrode surface. So, there is no new phase that forms. So, this relation is the similar type of reaction relation, but this MC has 2 component M and C and 1 phase that is only M, there is no two phase condition is there. So, degree of freedom is 3.

So, apart from pressure and temperature, there is one additional degree of freedom that needs to be specified for this electrochemical system. So, in the potential change basically linearly with the concentration of the charge carrier; therefore for the purely capacitive behavior, you get a straight line kind.

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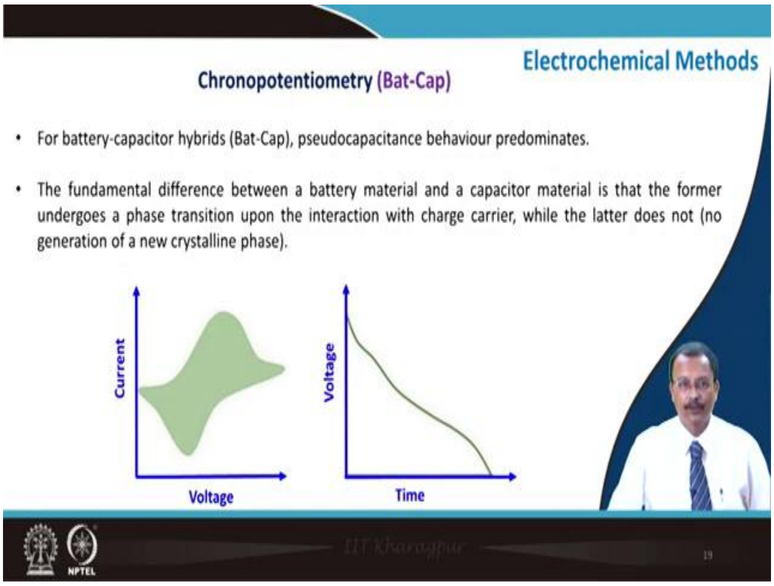
Electrochemical Methods

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, now the concept for this voltage transient, voltage versus time for at least the battery and capacitor type material is clear to you.

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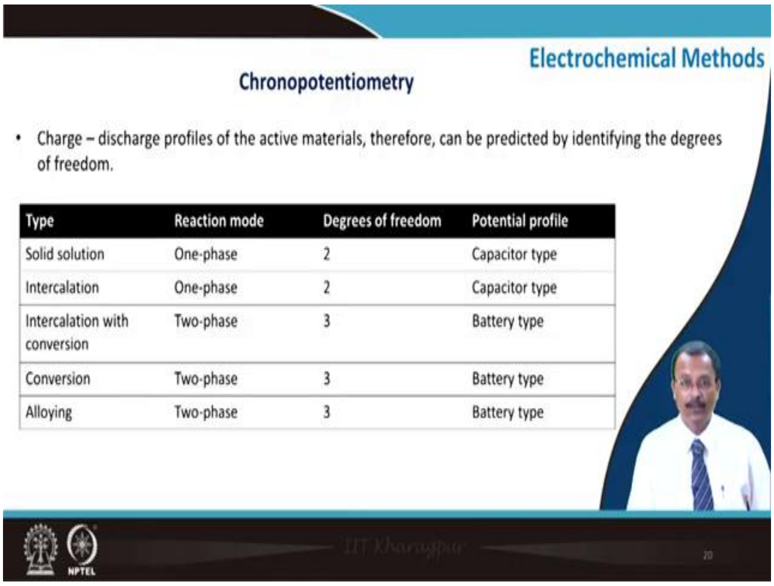

Electrochemical Methods

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, although I will talk about different types of electrode material, where various types of reaction takes place; not everywhere it is intercalation type or solid solution type. So, in those cases you can see I have tabulated most probable case. In solid solution case, you can work it out, it is a one phase reaction mode and degree of freedom is 3 and it is capacitor type.

Similarly, intercalation this is also one phase that will yield capacitor type. Now, when intercalation with some kind of conversion reaction is involved; so then it is two phase and that the same thing applies for pure conversion and pure alloying type of electrode material, then degree of freedom is 2 in all these three latter case and they behave as a battery type of material.

When I will talk about this electrode material separately and correlate with their respective voltage profile, then this concept will become more clearer to you.

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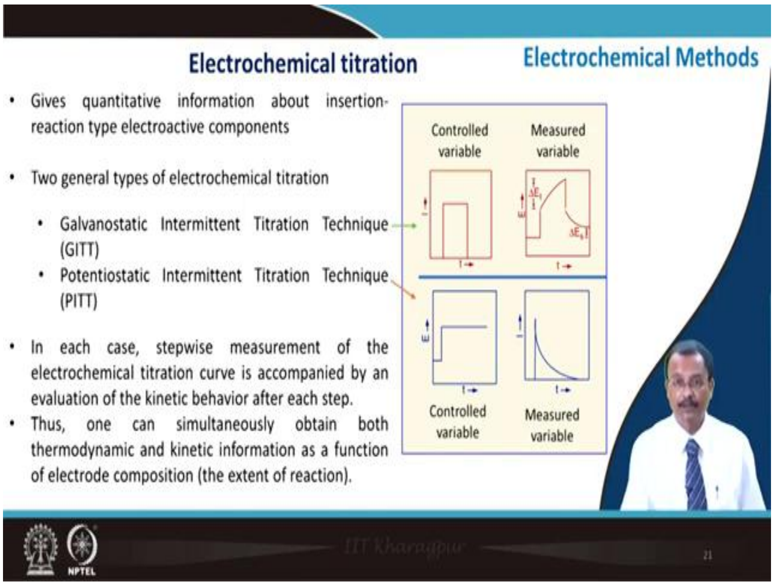

Electrochemical Methods

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).

Now, electrochemical titration, that is an important tool that gives you quantitative information about the insertion reaction type electroactive component. So, usually there are two general type; one is galvanostatic intermittent titration technique, which is shown in the upper panel, which is given abbreviated as GITT and the lower one is potentiostatic intermittent titration technique.

So, in each of this case, a stepwise measurement of the electrochemical titration curve that is accompanied by an evaluation of the kinetic behavior after each step. So, one can basically obtain both thermodynamic and kinetic information as a function of electrode composition; that means the extent of the reaction that can be determined by this two technique.

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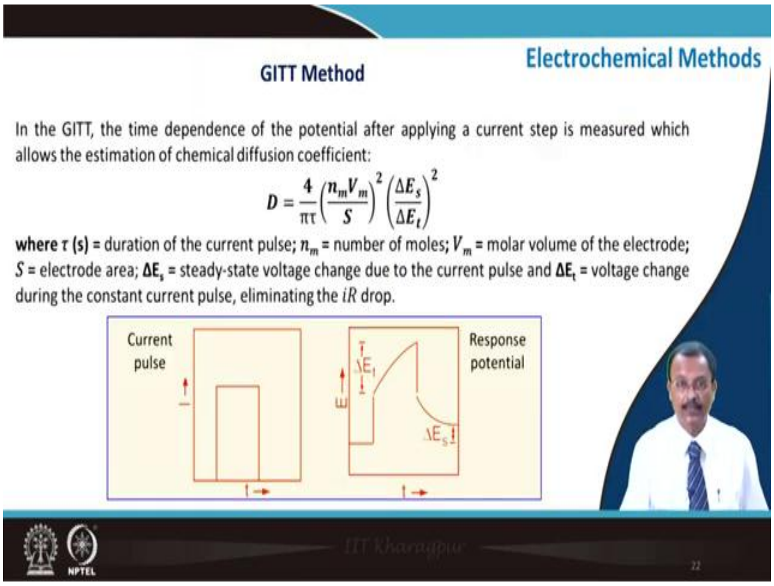

Electrochemical Methods

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, in GITT you apply a current pulse and measure voltage as a function of time. So, time dependence of the potential after applying a current step is measured and this also allows to estimate the chemical diffusion coefficient by this relation, where the term this tau s, this tau that is in this is the duration of the current pulse and del E s that is the steady state voltage change during this current pulse and this del E t that is the voltage change during the constant current pulse.

$$D = \frac{4}{\pi\tau}(\frac{nV}{S})^2\,(\frac{\Delta E_s}{\Delta E_t})^2$$

So, this part and remaining fall and then this steady state part. So, that can be measured simultaneously and putting this value, one can estimate the chemical diffusion coefficient for a lithium ion full cell.

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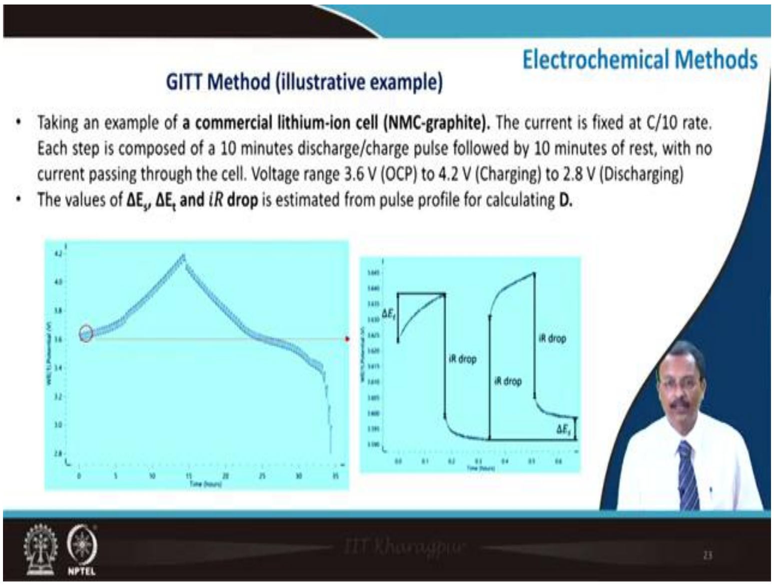

Electrochemical Methods

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.**

So, this is the typical example taken from a commercial lithium ion cell NMC graphite. So, the current is kept fixed at C by 10 rate, you know that one C means discharge it taking place is 1 hour. So, C by 10 is 10 hours it takes. So, it is a slow process and each step is composed of a 10 minutes of discharge charge pulse, which is followed by a 10 minutes of rest, well no current is passing through the cell.

And voltage range is kept 3.6 Volt, that is the open circuit potential to 4.2 Volt during the charging and then during the discharging, it was discharged till 2.8 Volt. So, you apply the current pulse and then you see in this particular region and then you measure the value of this E s, here this delta E t, and the i R drop the volt the drop due to internal resistance. And this values are put in the earlier relation to estimate the chemical potential.

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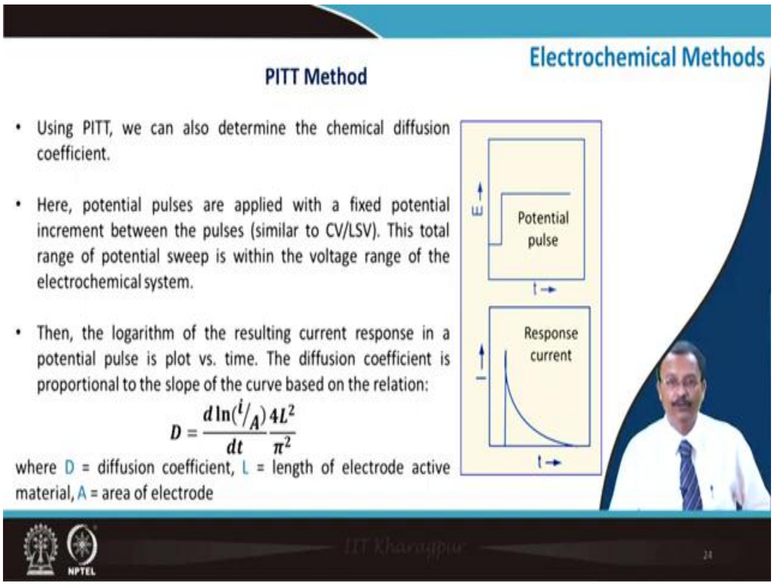

Electrochemical Methods

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

Finally, using PITT, we can also determine the chemical diffusion coefficient. So, here a potential pulse is applied with a fixed potential increment between the pulse; similar to that we talked about in CV and LSV case. The total range of potential sweep is within the voltage range of the electrochemical system, so that voltage window is important. Then the logarithm of the resulting current response in a potential pulse is plot, this is plotted versus time. So, this current transient is plotted.

And the diffusion coefficient is proportional to the slope; we will show the actual measurement and this D value diffusion coefficient that depends on the L, which is the length of the electrode active material and it depends on the area of the electrode.

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

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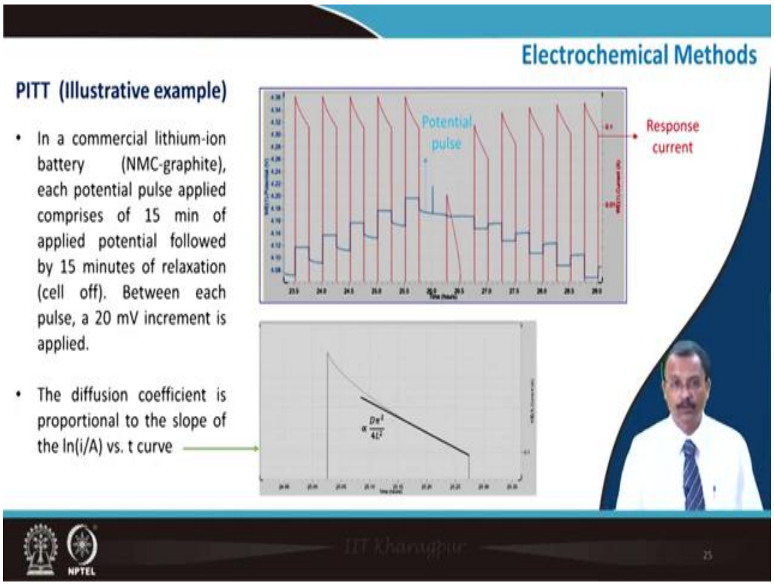

Electrochemical Methods

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, if you see the example in a commercial lithium ion battery, which is again nickel manganese cobalt based positive electrode and graphite based negative electrode, each potential pulse that comprises 15 minutes of applied potential.

And that followed by 15 minutes of relaxation, between each pulse a 20 milli volt increment is applied so, progressively this increase. And then from the current pulse, you can see a particular current pulse the linear part; this linear part is identified and the diffusion coefficient is proportional to the slope of this log i versus A versus t curve.

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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 that is mostly taken by the book by Bard as a reference book and also book by Huggins Advanced Batteries and basically application database of various manufacturer of this type of potentiostat galvanostat, Metrohm is one of them and Gamry Instrument is another. So, the application notes which is there in their site can be quite useful.

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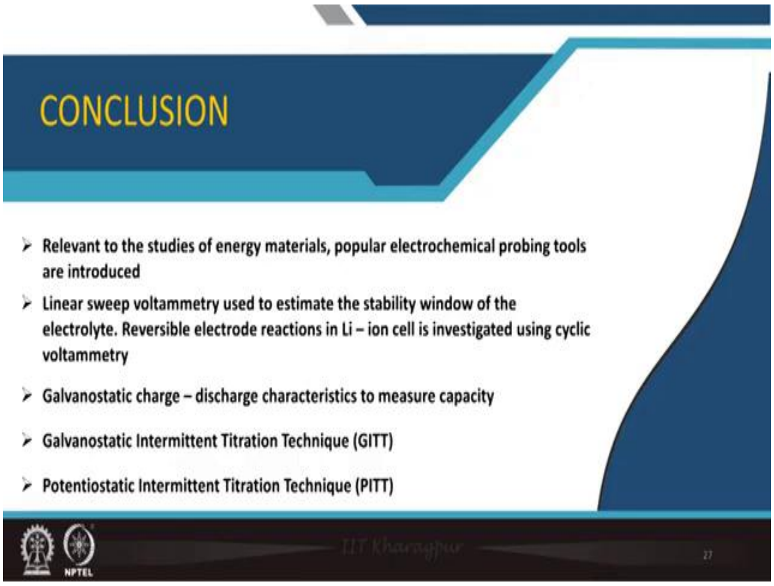

CONCLUSION

- 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, in this particular lecture, relevant to the study of energy materials, popular electrochemical probing tools are introduced and which we will keep on using when I will define the case studies, then basically this will be more clearer. Linear sweep voltammetry is used to estimate the stability window of the electrolyte mostly. And reversible electrode reactions in lithium ion cell that is investigated using cyclic voltammetry.

Then we talked about how to delineate the capacitive and faradaic part in a battery material from the cyclic voltam voltam voltammogram taken at different sweep rate. And galvanostatic charge discharge characteristics to measure the capacity, that is introduced and finally, this Galvanostatic Intermittent Titration Technique and Potentiostatic Intermittent Titration Technique is illustrated how to estimate the chemical diffusion coefficient.

Thank you for your attention.