Electrochemical Energy Storage
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Module - 02
Definitions and measuring methods
Lecture - 06
Introduction to EMF, Redox Potential, Faraday Law and Nernst's law

Welcome to my course, Electrochemical Energy Storage and this is module number 2 Definitions and measuring methods. So, this is lecture number 6, where I will talk about Introduction to Electromotive Force, Redox Potential, Faraday Law and Nernst Law and their application.

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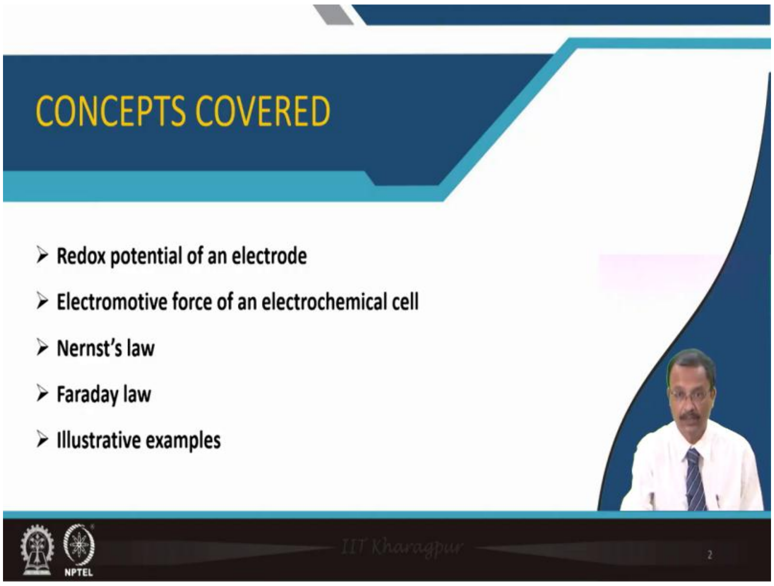

CONCEPTS COVERED

- Redox potential of an electrode
- Electromotive force of an electrochemical cell
- Nernst's law
- Faraday law
- Illustrative examples

So, the concept that I want to cover in this course is the redox potential of an electrode, then we will talk about electromotive force of an typical electrochemical cell, then I will introduce Nernst law, followed by Faraday's law and certain illustrative examples how the Faraday's laws are used in electrochemical energy storage.

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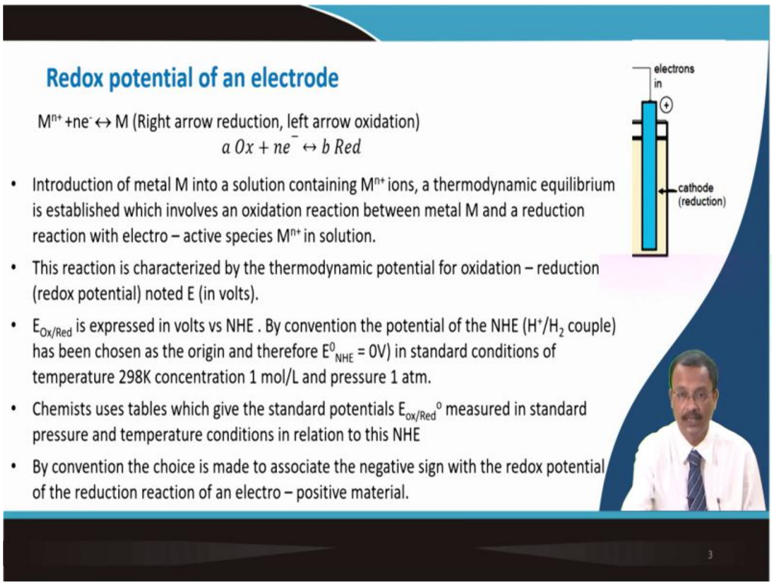

Redox potential of an electrode

$M^{n+} + ne^- \leftrightarrow M$ (Right arrow reduction, left arrow oxidation)

$$a\,Ox + ne^- \leftrightarrow b\,Red$$

- Introduction of metal M into a solution containing M^{n+} ions, a thermodynamic equilibrium is established which involves an oxidation reaction between metal M and a reduction reaction with electro – active species M^{n+} in solution.
- This reaction is characterized by the thermodynamic potential for oxidation – reduction (redox potential) noted E (in volts).
- $E_{Ox/Red}$ is expressed in volts vs NHE . By convention the potential of the NHE (H^+/H_2 couple) has been chosen as the origin and therefore $E^0_{NHE} = 0V$) in standard conditions of temperature 298K concentration 1 mol/L and pressure 1 atm.
- Chemists uses tables which give the standard potentials $E_{ox/Red}{}^o$ measured in standard pressure and temperature conditions in relation to this NHE
- By convention the choice is made to associate the negative sign with the redox potential of the reduction reaction of an electro – positive material.

So, you know that in my first week lecture we introduced the concept of the redox and here you can see a typical reaction basically if you follow the forward arrow, then it is reduction and follow the backward arrow then it is oxidation of a metal. And, in general we can write that oxidant it takes electron and eventually it get reduced and in my last week lecture, we talked about the stoichiometry should be maintained in this reaction.

$$a\,Ox + ne - \quad \leftrightarrow b\,Red$$

So, once you introduce a metal into a solution it contains let us assume that its having a valency n plus. So, M n plus ions are there. So, a thermodynamic equilibrium will be established which basically involved an oxidation reaction between metal and reduction reaction with the electro active species which is already existing as M n plus in the solution.

So, here I have shown the reduction part and this react this typical reaction is characterized by a thermodynamic potential for this oxidation reduction and we call this is redox potential and this is usually we measured in terms of volt. So, E is the terminology and it is measured in volt and this voltage which is oxidation reduction this is expressed as compared to the normal hydrogen electrode.

And, by convention as I have already explained this H plus and H 2 couple this we take as a origin and therefore, this voltage under standard condition; that means, temperature will have to be maintained at 298 Kelvin concentration is 1 mole per liter and pressure is 1 atmosphere. So, we call this is the standard condition.

So, this standard electrode potential for the reference is termed as a 0 and based on that chemist they have tabulated a table which gives the standard potential particularly the reduction potential and it is measured under standard condition standard pressure, temperature and concentration of the electrolyte.

So, by convention a choice is met the negative sign with the redox potential of the reduction reaction of an electro positive material.

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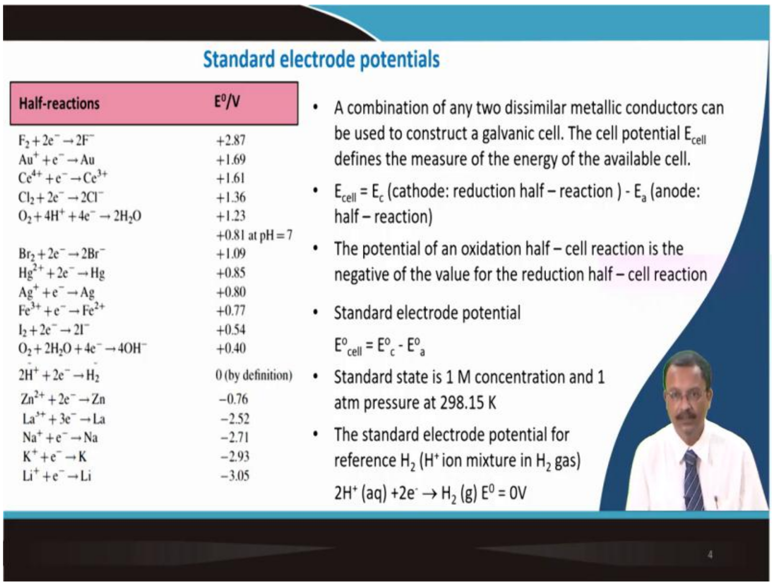

Standard electrode potentials

Half-reactions	E^0/V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23 +0.81 at pH = 7
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$2H^+ + 2e^- \rightarrow H_2$	0 (by definition)
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$La^{3+} + 3e^- \rightarrow La$	−2.52
$Na^+ + e^- \rightarrow Na$	−2.71
$K^+ + e^- \rightarrow K$	−2.93
$Li^+ + e^- \rightarrow Li$	−3.05

- A combination of any two dissimilar metallic conductors can be used to construct a galvanic cell. The cell potential E_{cell} defines the measure of the energy of the available cell.
- $E_{cell} = E_c$ (cathode: reduction half – reaction) - E_a (anode: half – reaction)
- The potential of an oxidation half – cell reaction is the negative of the value for the reduction half – cell reaction
- Standard electrode potential

  $E^0_{cell} = E^0_c - E^0_a$
- Standard state is 1 M concentration and 1 atm pressure at 298.15 K
- The standard electrode potential for reference H_2 (H^+ ion mixture in H_2 gas)

  $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$ $E^0 = 0V$

As I have illustrated in this table you can see that everything is basically a reduction reaction. So, the hydrogen is termed as a 0 potential and then you have certain material which is very strongly it is reduced and certain electro positive material which is very easy to get oxidized.

So, if you combined any two dissimilar metallic conductors they can be used to construct a galvanic cell. I already introduced the concept of a galvanic cell and the cell potential that basically measures the energy which is available in the cell. So, this cell potential if I defined at E cell that you can estimate from the cathode potential that is the reduction half cell reaction minus the anode potential which is defined as anode half cell reaction.

$E^{o}_{cell} = E^{o}_{c} - E^{o}_{a}$

So, the potential of oxidation half cell reaction as I told that it is taken negative value of the reduction half cell reaction which is taken as positive. So, under standard condition the cell potential is the cathode standard potential minus anode standard potential and by standard I mean 1 molar concentration of the electrolyte and 1 atmospheric pressure and temperature is typically 298 Kelvin. And, the standard electrode potential for the reference which is hydrogen in this case that is taken as 0 and this is the so called reduction reaction so, that is taken as 0.

$2H^{+}\,(aq) + 2e^{-} \rightarrow H_2\,(g) \qquad E^{0} = 0V$

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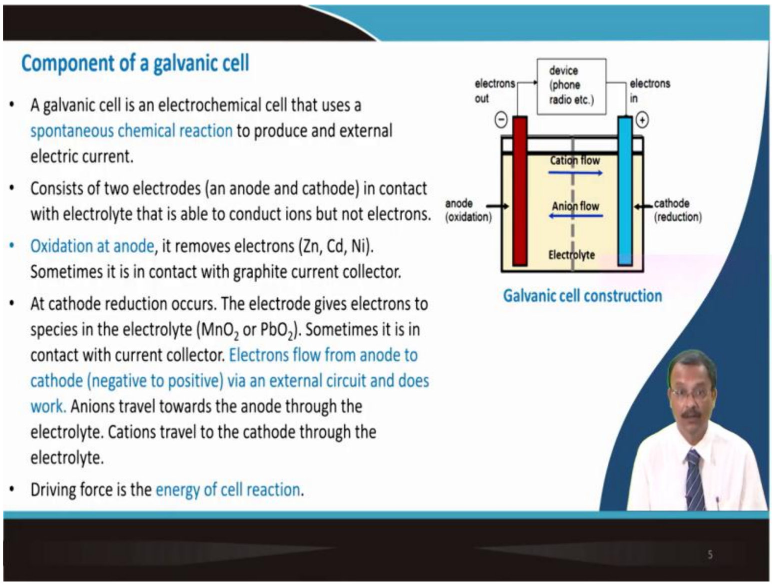

Component of a galvanic cell

- A galvanic cell is an electrochemical cell that uses a spontaneous chemical reaction to produce and external electric current.
- Consists of two electrodes (an anode and cathode) in contact with electrolyte that is able to conduct ions but not electrons.
- Oxidation at anode, it removes electrons (Zn, Cd, Ni). Sometimes it is in contact with graphite current collector.
- At cathode reduction occurs. The electrode gives electrons to species in the electrolyte (MnO_2 or PbO_2). Sometimes it is in contact with current collector. Electrons flow from anode to cathode (negative to positive) via an external circuit and does work. Anions travel towards the anode through the electrolyte. Cations travel to the cathode through the electrolyte.
- Driving force is the energy of cell reaction.

Galvanic cell construction

So, if you look at the component of a galvanic cell this is electrochemical cell that use as a spontaneous reaction. So, whenever two electrode with different standard reduction potential you dip in the electrolyte so, the reaction is spontaneous. So, it consist of two electrodes one we call anode and another one we call cathode that is in contact with the electrolyte that is able to conduct ions, but not electrons. Electron will be supplied to the external load or the device.

So, usually the anodes are typically zinc, cadmium or nickel it removes electron sometimes they are kept in contact with a graphite current collector to take the electron out into the galvanic cell towards the load. And, at cathode the reduction reaction occurs and the electrode gives electron to the species in the electrolyte sometimes it is in contact with a current collector as well.

And, electron as I said it flows from anode to cathode that is from negative to positive electrode by an external circuit and does the necessary work. So, energy is involved. And anions travel towards the anode through the electrolyte and cations travel to the cathode through the electrolyte and driving force is the energy of the cell reaction.

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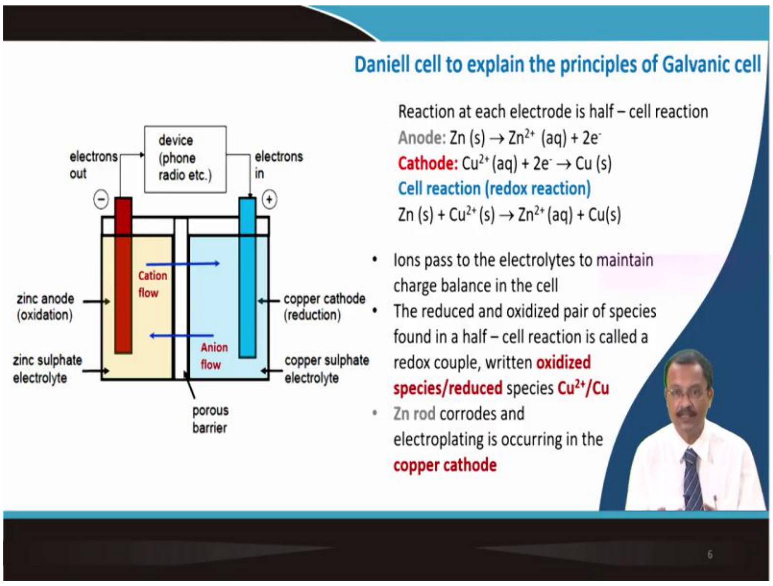

Daniell cell to explain the principles of Galvanic cell

Reaction at each electrode is half – cell reaction

Anode: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

Cell reaction (redox reaction)

$Zn\ (s) + Cu^{2+}\ (s) \rightarrow Zn^{2+}\ (aq) + Cu(s)$

- Ions pass to the electrolytes to maintain charge balance in the cell
- The reduced and oxidized pair of species found in a half – cell reaction is called a redox couple, written **oxidized species/reduced** species **Cu^{2+}/Cu**
- Zn rod corrodes and electroplating is occurring in the **copper cathode**

So, based on this I can define the Daniell cell which already I introduced and that basically explain the principle of the galvanic cell. So, the reaction at each electrode is a half-cell reaction. So, each of this part is a half-cell reaction. So, in the anode zinc is oxidized and in cathode copper ion is getting reduced to form copper metal which is eventually deposited on the cathode plate.

So, the total cell reaction this we call a redox reaction, this is defined as zinc in solid state and copper is in the oxidized state Cu 2 plus and zinc gets oxidized and copper eventually get reduced. So, as I told the ion passes to the electrolyte to maintain the charge balance of the cell and the reduced and oxidized pair of the species found in the half-cell reaction that is called as a redox couple.

Anode: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

Cathode: $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

Cell reaction (redox reaction)

$Zn\ (s) + Cu^{2+}\ (s) \rightarrow Zn^{2+}\ (aq) + Cu(s)$

So, it is written as oxidized species versus reduced species. So, this is copper 2 plus slash copper that actually defines the redox couple and in this reaction zinc rod corrodes and electroplating is occurring into the cathode electrode copper cathode.

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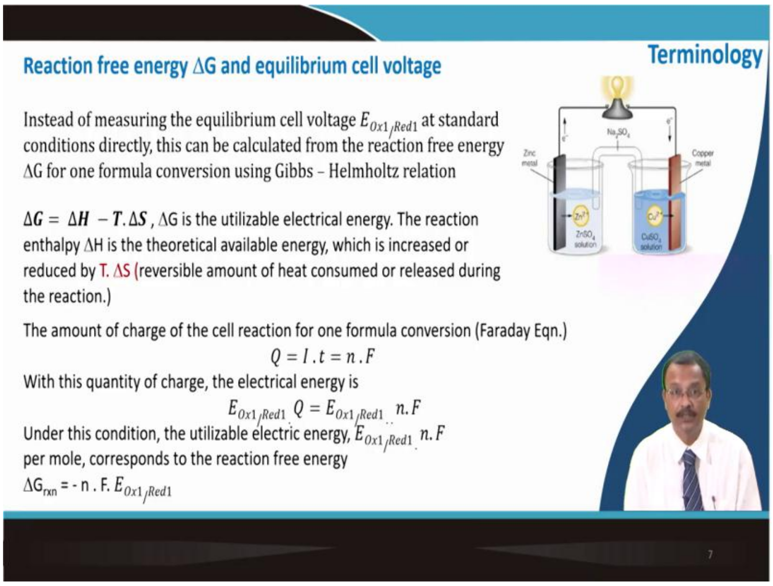

Terminology

Reaction free energy ΔG and equilibrium cell voltage

Instead of measuring the equilibrium cell voltage $E_{Ox1/Red1}$ at standard conditions directly, this can be calculated from the reaction free energy ΔG for one formula conversion using Gibbs – Helmholtz relation

$\Delta G = \Delta H - T.\Delta S$, ΔG is the utilizable electrical energy. The reaction enthalpy ΔH is the theoretical available energy, which is increased or reduced by T. ΔS (reversible amount of heat consumed or released during the reaction.)

The amount of charge of the cell reaction for one formula conversion (Faraday Eqn.)

$$Q = I\,.\,t = n\,.\,F$$

With this quantity of charge, the electrical energy is

$$E_{Ox1/Red1}\,Q = E_{Ox1/Red1}\,n.F$$

Under this condition, the utilizable electric energy, $E_{Ox1/Red1}\,n.F$ per mole, corresponds to the reaction free energy

$\Delta G_{rxn} = -\,n\,.\,F.\,E_{Ox1/Red1}$

So, now, we are in a position to estimate the reaction free energy and equilibrium cell voltage. So, instead of measuring the equilibrium cell voltage that is the oxidant and reductant this voltage at standard condition directly this can actually be calculated from the reaction free energy which is defined as del G for one formula conversion using the so called Gibbs–Helmholtz relation and while I in the first lecture we already introduced the thermodynamic concept for this course.

And one can write this relation where del G is utilizable electrical energy and the reaction enthalpy is del H and this is the theoretical available energy which is either increased or reduced depending on this T del S term. So, it is the reversible amount of heat that is consumed or released during the reaction. So, the amount of charge of the cell reaction for one formula unit conversion this is termed as Faraday equation.

$$\boldsymbol{\Delta G = \Delta H - T.\, \Delta S}$$

So, this charge is current and time product which is eventually the number of electrons per mole and the Faraday constant. So, with this quantity of charge I can estimate the electric energy by multiplying both side by oxidation E oxidation reduction this voltage into the charge.

$$Q = I\,.\,t = n\,.\,F$$

So, that gives you the energy. So, the utilizable electrical energy is E Ox reduction this voltage into the number of electrons involved usually one formula unit of the reactant material and F is the Faraday constant.

So, this is per mole and this is actually the reaction free energy and when the reaction proceeds, reaction takes place then by convention this reaction free energies is taken negative so, the energy that you can estimate from this simple relation of minus n, the product of minus n Faraday constant and this oxidation reduction potential.

$\Delta G_{rxn} = - n\,.\,F.\, E_{Ox1/Red1}$

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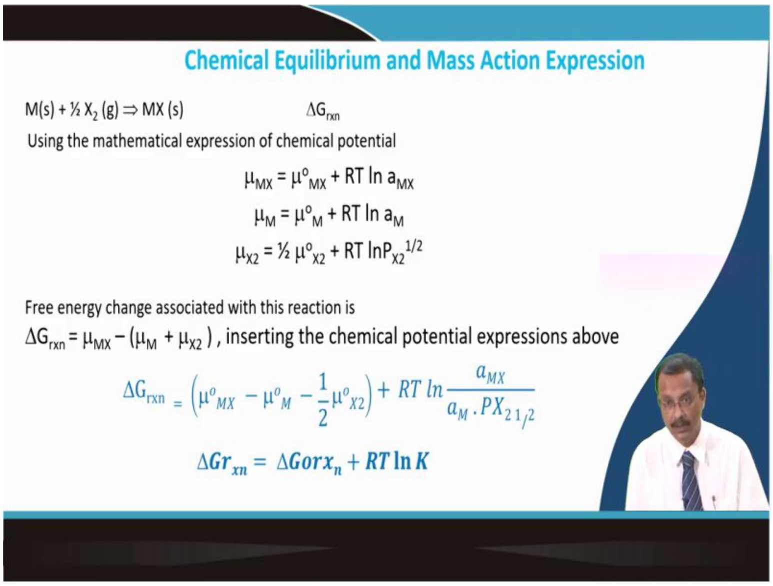

Chemical Equilibrium and Mass Action Expression

$M(s) + ½ X_2 (g) \Rightarrow MX (s)$ ΔG_{rxn}

Using the mathematical expression of chemical potential

$$\mu_{MX} = \mu^o_{MX} + RT \ln a_{MX}$$

$$\mu_M = \mu^o_M + RT \ln a_M$$

$$\mu_{X2} = ½ \mu^o_{X2} + RT \ln P_{X2}{}^{1/2}$$

Free energy change associated with this reaction is

$\Delta G_{rxn} = \mu_{MX} - (\mu_M + \mu_{X2})$, inserting the chemical potential expressions above

$$\Delta G_{rxn} = \left(\mu^o{}_{MX} - \mu^o{}_M - \frac{1}{2}\mu^o{}_{X2}\right) + RT\, ln \frac{a_{MX}}{a_M \,.\, PX_{2\,1/2}}$$

$$\Delta Gr_{xn} = \Delta Gorx_n + RT \ln K$$

So, now, chemical equilibrium and mass expression this is also related. So, if I define a simple relation that a metal in solid state that is reacting with some kind of gas to form a it could be metal oxide and this reaction free energy we take at del G reaction. So, I can define the mathematical expression of chemical potential which already I have introduced earlier part of this lecture.

$M(s) + ½ X_2 (g) \Rightarrow MX (s)$

So, for the product we can write this relation of the chemical potential and it is related to its standard state and gas constant temperature and activity of this particular species. Similarly, for the metal and for the gaseous thing also I can write the relation of the chemical potential. And, then the free energy associated with this reaction is nothing but the chemical potential of the product minus the reactant.

So, mu MX minus this term and if you insert the chemical potential expression here so, you will get this relation. So, this is for the product and these are the reactant. So, this part is the standard part and you have this RT and this is coming from this part activity of the product and divided by activity of the metal and the partial pressure of the gaseous reactant.

So, your free energy term is this is del G this 0 is actually the superscript and rxn is the subscript. So, this is the standard energy part and it is having this RT ln K, where K is the equilibrium constant.

$\mu_{MX} = \mu^o_{MX} + RT \ln a_{MX}$

$\mu_M = \mu^o_M + RT \ln a_M$

$\mu_{X2} = ½\, \mu^o_{X2} + RT \ln P_{X2}{}^{1/2}$

$\Delta G_{rxn} = \mu_{MX} - (\mu_M + \mu_{X2})$, inserting the chemical potential expressions above

$$\Delta G_{rxn} = \left(\mu^o{}_{MX} - \mu^o{}_{M} - \frac{1}{2}\mu^o{}_{X2}\right) + RT\ ln \frac{a_{MX}}{a_M \cdot PX_{2\,1/2}}$$

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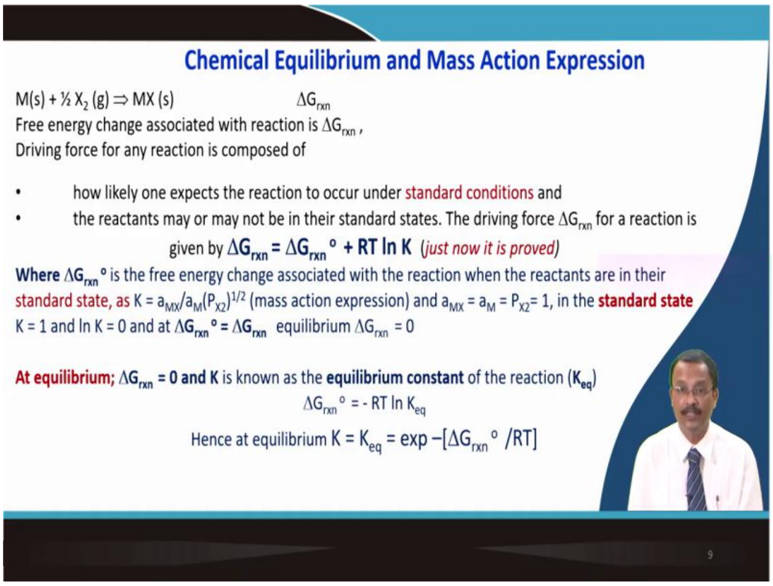

Chemical Equilibrium and Mass Action Expression

$M(s) + ½\, X_2\, (g) \Rightarrow MX\, (s)$ ΔG_{rxn}

Free energy change associated with reaction is ΔG_{rxn} ,

Driving force for any reaction is composed of

- how likely one expects the reaction to occur under standard conditions and
- the reactants may or may not be in their standard states. The driving force ΔG_{rxn} for a reaction is given by $\mathbf{\Delta G_{rxn} = \Delta G_{rxn}{}^o + RT \ln K}$ *(just now it is proved)*

Where $\Delta G_{rxn}{}^o$ is the free energy change associated with the reaction when the reactants are in their standard state, as $K = a_{MX}/a_M(P_{X2})^{1/2}$ (mass action expression) and $a_{MX} = a_M = P_{X2} = 1$, in the **standard state** $K = 1$ and $\ln K = 0$ and at $\Delta G_{rxn}{}^o = \Delta G_{rxn}$ equilibrium $\Delta G_{rxn} = 0$

At equilibrium; ΔG_{rxn} **= 0 and K** is known as the **equilibrium constant** of the reaction (K_{eq})

$$\Delta G_{rxn}{}^o = - RT \ln K_{eq}$$

Hence at equilibrium $K = K_{eq} = \exp -[\Delta G_{rxn}{}^o /RT]$

Now, again this free energy that is associated with this reaction is del G rxn and the driving force for this reaction is composed of number 1 – how likely one expect the reaction to occur under standard condition and number 2 is the reactant may or may not be in their standard state.

So, the driving force which is del G rxn for a reaction is given by this relation this just now we have proved in earlier slides. So, this is the del G rxn 0 is the free energy change associated with the reaction when the reactant are in their standard state. So, in the standard state the value of K you can see the activity of MX, activity of M and activity or sorry sorry, the partial pressure of the gaseous product can be taken as 1. So, in the standard state K is 1.

$$\mathbf{\Delta G_{rxn} = \Delta G_{rxn}{}^{o} + RT \ln K}$$

So, ln K is 0 and that tells that del G rxn 0 is actually the del G of the reaction. So, in equilibrium we know that this del G reaction is 0. So, if you put this value then K is known at the equilibrium constant for this reaction. So, this K term I will replace by K equilibrium and then this del G rxn 0 is nothing but minus RT ln of this equilibrium coefficient. So, the equilibrium coefficient you can estimate from this relation is exponential of minus of del G rxn 0 by RT.

At equilibrium; ΔG_{rxn} = 0 and K is known as the **equilibrium constant** of the reaction (**K_{eq}**)

$$\Delta G_{rxn}{}^{o} = - RT \ln K_{eq}$$

Hence at equilibrium $K = K_{eq} = \exp -[\Delta G_{rxn}{}^{o} / RT]$

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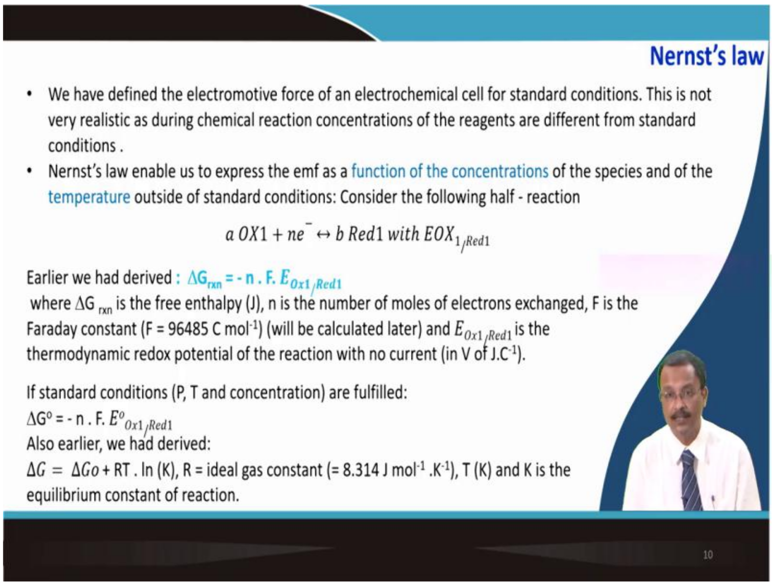

Nernst's law

- We have defined the electromotive force of an electrochemical cell for standard conditions. This is not very realistic as during chemical reaction concentrations of the reagents are different from standard conditions .
- Nernst's law enable us to express the emf as a function of the concentrations of the species and of the temperature outside of standard conditions: Consider the following half - reaction

$$a\, OX1 + ne^{-} \leftrightarrow b\, Red1 \text{ with } EOX_{1/Red1}$$

Earlier we had derived : $\Delta G_{rxn} = - n . F. E_{Ox1/Red1}$
where ΔG_{rxn} is the free enthalpy (J), n is the number of moles of electrons exchanged, F is the Faraday constant (F = 96485 C mol^{-1}) (will be calculated later) and $E_{Ox1/Red1}$ is the thermodynamic redox potential of the reaction with no current (in V of J.C^{-1}).

If standard conditions (P, T and concentration) are fulfilled:
$\Delta G^{o} = - n . F. E^{o}_{Ox1/Red1}$
Also earlier, we had derived:
$\Delta G = \Delta Go + RT . \ln (K)$, R = ideal gas constant (= 8.314 J mol^{-1} .K^{-1}), T (K) and K is the equilibrium constant of reaction.

So, we have defined the electromotive force of an electrochemical cell for the standard condition. So, this actually is not very realistic during any chemical reactions because the reagents that can of have different condition from that standard condition whatever we have defined.

So, we will introduce a Nernst’s law which will enable us to express the emf as a function of concentration of the species and of course, temperature outside the standard condition. So, again if you consider this particular relation with the potential is EOX by Red. So, this will also be in the subscript.

$$a\,OX1 + ne- \;\; \leftrightarrow b\,Red1$$

$$\boldsymbol{\Delta G_{rxn} = - n \,.\, F.\, E_{Ox1/Red1}}$$

So, we have already derived that this del G rxn is minus n Faraday constant and this potential value. So, this is the standard free enthalpy usually it is measured in Joule, n is the number of moles of electron that is exchanged during this reaction and F is the Faraday constant usually if the Faraday constant is estimated to be 96485 Coulomb per mole and we will calculate it later.

So, this potential is the thermodynamic redox potential of the reaction where no current is flowing. So, it is under open circuit condition. So, this is measured in volt or Joule per Coulomb from the dimensional analysis. So, if standard condition P, T and concentration as defined earlier are fulfilled, then we can write in standard free energy is minus n F E 0 and earlier also we have derived that del G is del G 0 which is superscript and this 0 is superscript RT ln K.

$$\Delta G^o = - n \,.\, F.\, {E^0}_{Ox1/Red1}$$

$$\boldsymbol{\Delta G_{rxn} = \Delta {G_{rxn}}^o + RT \ln K}$$

So, R is the ideal gas constant, the value is known 8.314 Joule per mole per Kelvin, T is taken as temperature in Kelvin and K is the equilibrium constant of the reaction.

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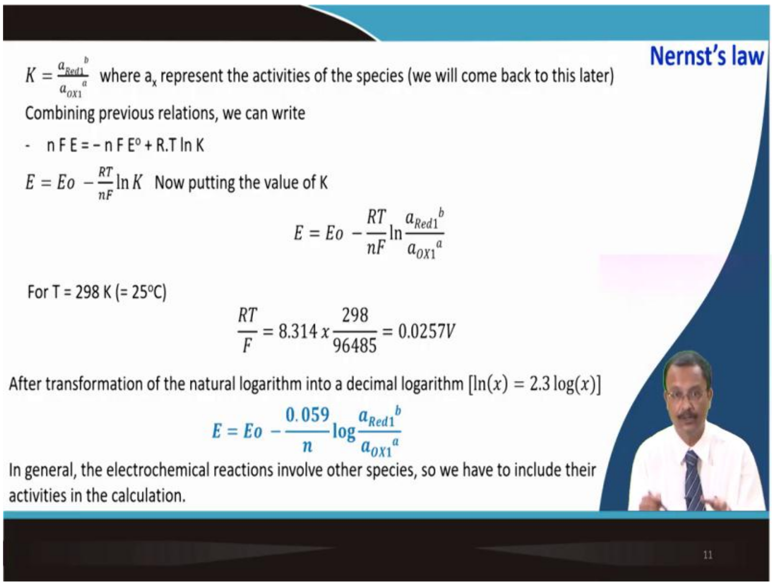

Nernst's law

$K = \frac{a_{Red1}^{b}}{a_{OX1}^{a}}$ where a_x represent the activities of the species (we will come back to this later)

Combining previous relations, we can write

- n F E = - n F E° + R.T ln K

$E = Eo - \frac{RT}{nF}\ln K$ Now putting the value of K

$$E = Eo - \frac{RT}{nF}\ln\frac{a_{Red1}^{b}}{a_{OX1}^{a}}$$

For T = 298 K (= 25°C)

$$\frac{RT}{F} = 8.314\, x \frac{298}{96485} = 0.0257V$$

After transformation of the natural logarithm into a decimal logarithm $[\ln(x) = 2.3\log(x)]$

$$E = Eo - \frac{0.059}{n}\log\frac{a_{Red1}^{b}}{a_{OX1}^{a}}$$

In general, the electrochemical reactions involve other species, so we have to include their activities in the calculation.

So, this equilibrium constant of the reaction from the earlier relation we can put it as activity of the reduct reduced species and oxidized species and this represent the activities and we will just come back to this activity concept. So, you can combine the previous relation. We put the value for del G rxn and this is the standard case plus RT ln K.

$$K = \frac{a_{Red1}^{b}}{a_{OX1}^{a}}$$

$$-\mathrm{n\,F\,E} = -\mathrm{n\,F\,E^0} + \mathrm{R.T\ln K}$$

$E = E^{0} - \frac{RT}{nF}\ln K$ Now putting the value of K

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_{Red1}^{b}}{a_{OX1}^{a}}$$

So, now, from this relation you can work out the actual value of E is E 0 minus RT by nF into ln K. So, now, you can put the value of K here from this relation. So, this is E equal to E 0 RT nF ln a reduction by a oxidant. So, if you take the temperature as 298 Kelvin that is roughly 25 degree Celsius, then this part RT by F you can estimate at 0.0257 volt.

And, you can also transform the natural logarithm to decimal logarithm with 10 base by this simple relation. So, alternatively you can write the relation for the electro motive force E 0 is sorry, E equal to E 0 into this will come about 0.059 by n and log of this activity. So, in general, the electrochemical reaction involve other species, so, we have to include their activity also in this calculation. If this reaction is a complicated one so, we will have to introduce those part as well.

$$E = E^0 - \frac{0.059}{n}\log\frac{a_{Red1}^{\,b}}{a_{OX1}^{\,a}}$$

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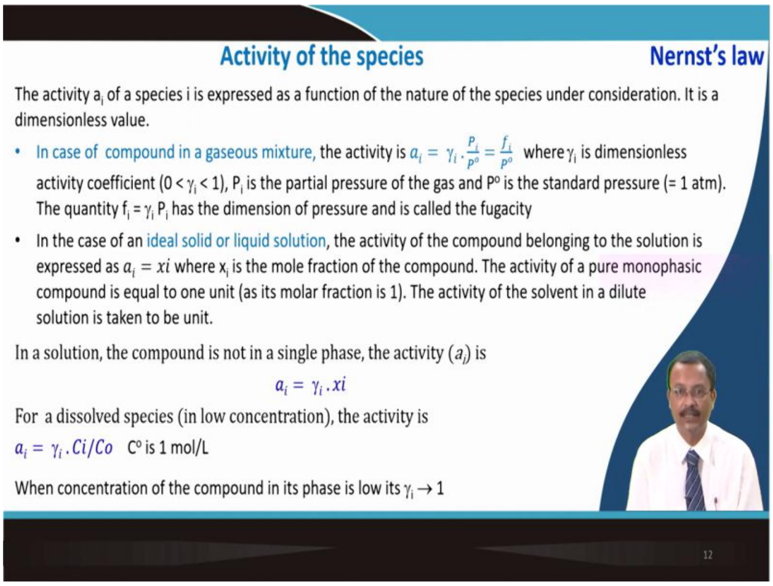

Activity of the species

Nernst's law

The activity a_i of a species i is expressed as a function of the nature of the species under consideration. It is a dimensionless value.

- In case of compound in a gaseous mixture, the activity is $a_i = \gamma_i . \frac{P_i}{P^o} = \frac{f_i}{P^o}$ where γ_i is dimensionless activity coefficient ($0 < \gamma_i < 1$), P_i is the partial pressure of the gas and P^o is the standard pressure (= 1 atm). The quantity $f_i = \gamma_i P_i$ has the dimension of pressure and is called the fugacity
- In the case of an ideal solid or liquid solution, the activity of the compound belonging to the solution is expressed as $a_i = xi$ where x_i is the mole fraction of the compound. The activity of a pure monophasic compound is equal to one unit (as its molar fraction is 1). The activity of the solvent in a dilute solution is taken to be unit.

In a solution, the compound is not in a single phase, the activity (a_i) is

$$a_i = \gamma_i . xi$$

For a dissolved species (in low concentration), the activity is

$a_i = \gamma_i . Ci/Co$ C^o is 1 mol/L

When concentration of the compound in its phase is low its $\gamma_i \rightarrow 1$

Now, the activity of the species is expressed as a function of the nature of the species under consideration. So, it is basically a dimensionless value. So, in case of a compound with a gaseous mixture, the activity you can relate with this dimensionless constant gamma i and the partial pressure of that particular gas and P 0 is the standard pressure which is taken as 1 atmosphere and the quantity that if that is equal to this gamma i and this partial pressure of this gaseous product that is called fugacity.

$$a_i = \gamma i . \frac{Pi}{Po} = \frac{fi}{Po}$$

So, in case of a ideal solution or liquid solution the activity of the compound that belongs to the solution is expressed as this relation a i is x i, where this is the mole fraction of the compound. So, the activity of pure monophasic compound that is equal to 1 because the fraction is equal to 1. So, activity of the solvent in a dilute solution can be taken as unit.

In a solution where the compound is not in a single phase, then the term gamma will have to be included and this lies in between 0 to 1. So, for a dissolved species in very low concentration the activity is gamma i where gamma is tends to 1. So, almost it is 1. So, it is basically concentration of that species with respect to C 0 which is 1 mole per liter and accordingly, you can just exchange the activity with the concentration for a very dilute solution.

$$a_i = \gamma_i . x_i = \gamma_i \frac{c_i}{c_0}$$

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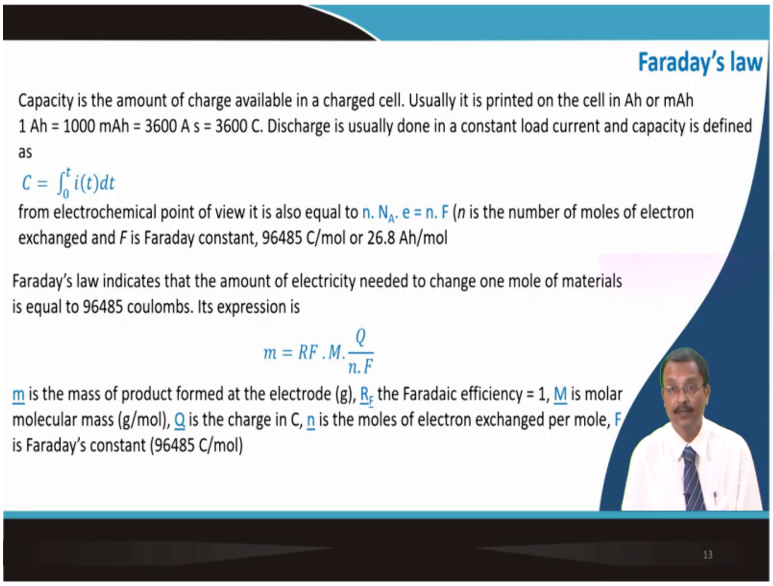

Faraday's law

Capacity is the amount of charge available in a charged cell. Usually it is printed on the cell in Ah or mAh
1 Ah = 1000 mAh = 3600 A s = 3600 C. Discharge is usually done in a constant load current and capacity is defined as

$C = \int_0^t i(t)dt$

from electrochemical point of view it is also equal to $n.\, N_A .\, e = n.\, F$ (*n* is the number of moles of electron exchanged and *F* is Faraday constant, 96485 C/mol or 26.8 Ah/mol

Faraday's law indicates that the amount of electricity needed to change one mole of materials is equal to 96485 coulombs. Its expression is

$$m = RF\,.\,M.\frac{Q}{n.F}$$

m is the mass of product formed at the electrode (g), R_F the Faradaic efficiency = 1, M is molar molecular mass (g/mol), Q is the charge in C, n is the moles of electron exchanged per mole, F is Faraday's constant (96485 C/mol)

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So, next I will talk about the Faraday law the that the capacity as I told is the amount of the charge that is available in a charged cell. So, usually if you see a battery it is printed on the cell as Ampere hour or sometimes for smaller battery as milli Ampere hour. So, 1 Ampere hour is 1000 milli Ampere hour and then you transfer into the second. So, it is 3600 Ampere second. So, this is nothing but 3600 Coulomb.

$$C = \int_0^t i(t)dt$$

So, discharge is usually done in a constant load current and capacity can be defined as the integration of the current involved in this reaction from 0 to t and from the electrochemical point of view this is also equal to the number of moles of electron exchange and Avogadro number and electronic charge.

So, this N A and e is defined as the Faraday constant. So, n is the number of moles of electron that is exchanged and F is the Faraday constant. So, if you multiply the electronic charge with the Avogadro number then you get this Faraday constant as 96485 Coulomb per mole and which can be transferred from the earlier relation it can be transferred as 26.8 Ampere hour per mole.

So, the Faraday law basically that indicates the amount of electricity that is needed to change 1 mole of material and that is equal to 96485 Coulomb. So, the expression is the mass of the product that is formed and that is related with the Faradic efficiency which is usually taken as 1, M is the molar or molecular mass in gram per mole, Q is the charge that is usually taken in Coulomb and n is the number of moles of electron exchange and F is the Faraday constant the value is 96485.

$$m = R_F \, . \, M . \frac{Q}{n . F}$$

So, this relation is actually estimated from the Faraday law and that is basically the amount of electricity that is needed to change 1 mole of material and equal that is equal to 96485 Coulomb.

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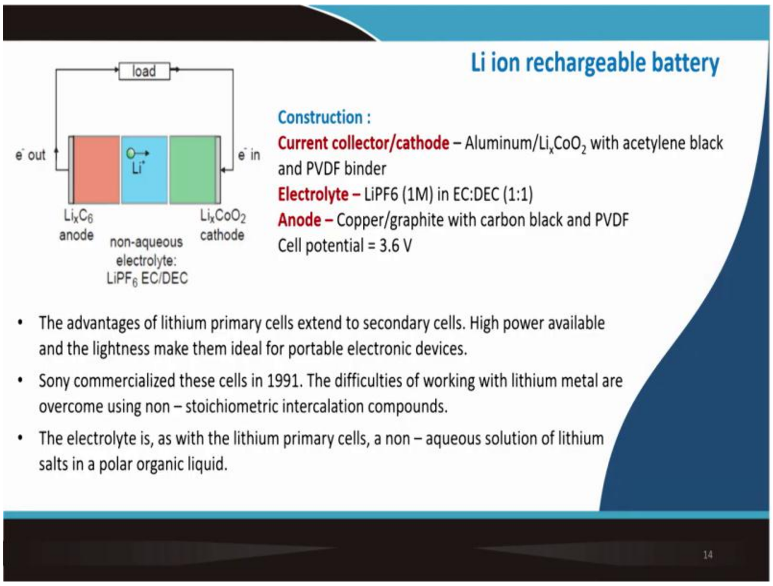

Li ion rechargeable battery

Construction :

Current collector/cathode – Aluminum/Li_xCoO_2 with acetylene black and PVDF binder

Electrolyte – LiPF6 (1M) in EC:DEC (1:1)

Anode – Copper/graphite with carbon black and PVDF

Cell potential = 3.6 V

- The advantages of lithium primary cells extend to secondary cells. High power available and the lightness make them ideal for portable electronic devices.
- Sony commercialized these cells in 1991. The difficulties of working with lithium metal are overcome using non – stoichiometric intercalation compounds.
- The electrolyte is, as with the lithium primary cells, a non – aqueous solution of lithium salts in a polar organic liquid.

So, now, I will come back to lithium rechargeable battery which already I have I had introduced in part of my earlier lectures. So, the construction is you have a current collector and cathode usually aluminum is a current collector and let us take the example of lithium cobalt oxide. And, actually acetylene black is added is a electron conductor inside the composite electrode and PVDF binder is also mixed so that it is properly adhered to the current collector.

Usually a lithium based salt in a solvent ethylene carbonate or diethyl carbonate it is 1 is to 1 mixture it is taken as electrolyte and anode is copper foil that is coated with graphite. So, that actually constitute the first prototype and also commercialized lithium ion battery.

So, the advantage of lithium primary cell which already I defined that is extended to the secondary cell and high power is available and the lightness make them ideal for portable device and Sony commercialized dated 1991. And, electrolyte, as with lithium per primary cell that is usually a non-aqueous solution of lithium salt in polar organic liquid.

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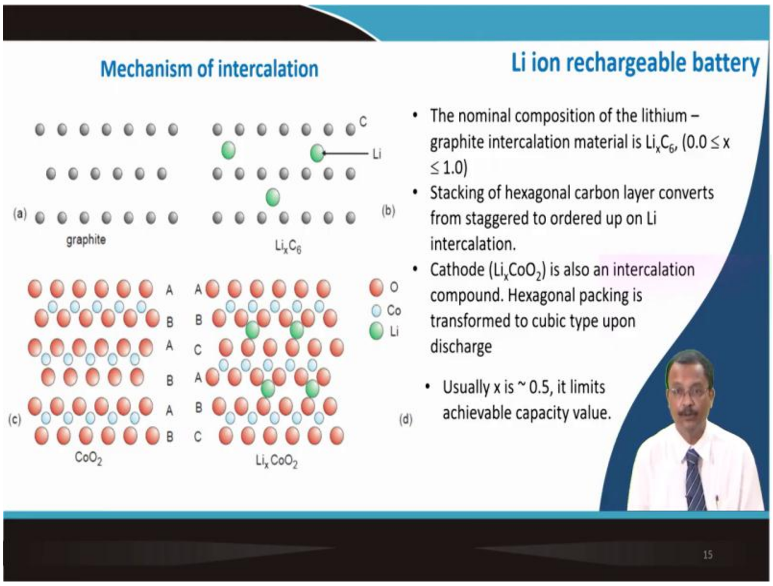

Mechanism of intercalation

Li ion rechargeable battery

- The nominal composition of the lithium – graphite intercalation material is Li_xC_6, ($0.0 \leq x \leq 1.0$)
- Stacking of hexagonal carbon layer converts from staggered to ordered up on Li intercalation.
- Cathode (Li_xCoO_2) is also an intercalation compound. Hexagonal packing is transformed to cubic type upon discharge
- Usually x is ~ 0.5, it limits achievable capacity value.

So, the mechanism although I will come back to the mechanism later, but here the nominal composition of lithium graphite intercalation material is in graphite is in intercalated the lithium goes inside the graphitic layer here the inside that lithium is intercalated. And, the stacking sequence of hexagonal carbon layer converts from staggered to a ordered of upon lithium intercalation so that takes place.

And, cathode is actually lithium cobalt oxide and that is also an intercalation compound having a layer structure. And, hexagonal packing is transformed into the cubic type upon discharge. Already while I was talking about the crystal structure so, I introduced this. Usually you can take about 0.5 moles of lithium from this structure, if you take more lithium out of the structure the structure collapses.

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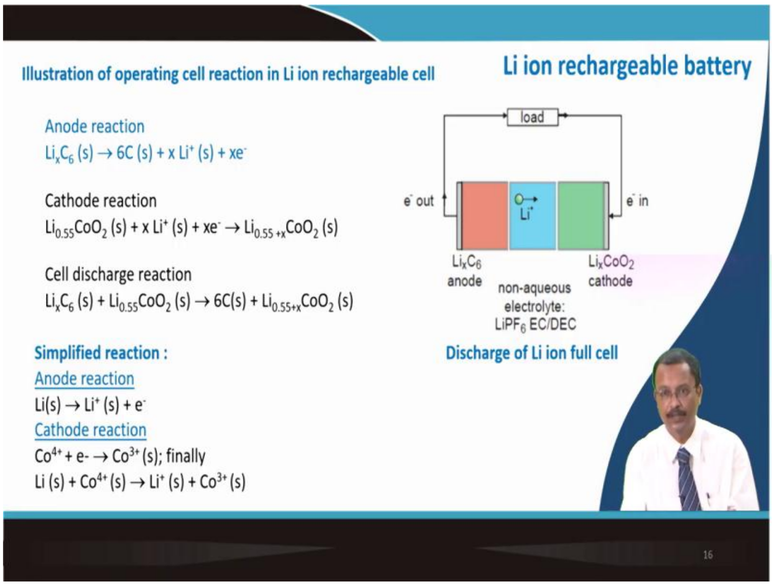

Li ion rechargeable battery

Illustration of operating cell reaction in Li ion rechargeable cell

Anode reaction

$Li_xC_6\ (s) \rightarrow 6C\ (s) + x\ Li^+\ (s) + xe^-$

Cathode reaction

$Li_{0.55}CoO_2\ (s) + x\ Li^+\ (s) + xe^- \rightarrow Li_{0.55+x}CoO_2\ (s)$

Cell discharge reaction

$Li_xC_6\ (s) + Li_{0.55}CoO_2\ (s) \rightarrow 6C(s) + Li_{0.55+x}CoO_2\ (s)$

Discharge of Li ion full cell

Simplified reaction :

Anode reaction

$Li(s) \rightarrow Li^+\ (s) + e^-$

Cathode reaction

$Co^{4+} + e- \rightarrow Co^{3+}\ (s)$; finally

$Li\ (s) + Co^{4+}\ (s) \rightarrow Li^+\ (s) + Co^{3+}\ (s)$

So, the anode reaction you can take that lithium is getting oxidized coming into the electrolyte and cathode reaction is this lithium is basically intercalated into the partially delithiated lithium cobalt oxide. The cell reaction is this one coming from this anode and cathodic reaction.

So, you can have a simplified reaction as well. So, where lithium is basically oxidized at lithium plus and in cathode reaction this cobalt ion which was in plus 3 plus 4 valence state that is reduced to plus 3 valence state. So, that is the simplified full cell reaction which is occurring during the discharge of the battery where electron is being fed to the load to do the work.

Anode reaction

$Li_xC_6\ (s) \rightarrow 6C\ (s) + x\ Li^+\ (s) + xe^-$

Cathode reaction

$Li_{0.55}CoO_2\ (s) + x\ Li^+\ (s) + xe^- \rightarrow Li_{0.55\ +x}CoO_2\ (s)$

Cell discharge reaction

$Li_xC_6\ (s) + Li_{0.55}CoO_2\ (s) \rightarrow 6C(s) + Li_{0.55+x}CoO_2\ (s)$

Simplified reaction :

Anode reaction

$Li(s) \rightarrow Li^{+} (s) + e^{-}$

Cathode reaction

$Co^{4+} + e- \rightarrow Co^{3+} (s)$; finally

$Li (s) + Co^{4+} (s) \rightarrow Li^{+} (s) + Co^{3+} (s)$

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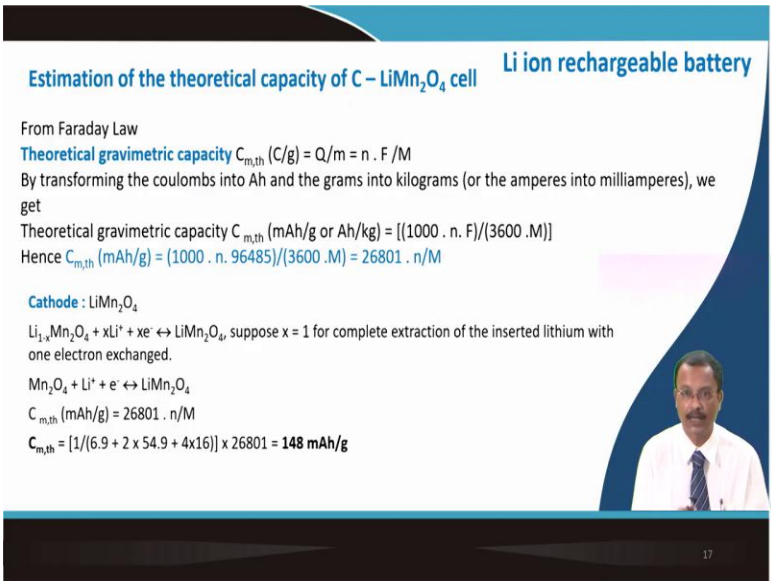

Estimation of the theoretical capacity of C – $LiMn_2O_4$ cell

Li ion rechargeable battery

From Faraday Law

Theoretical gravimetric capacity $C_{m,th}$ (C/g) = Q/m = n . F /M

By transforming the coulombs into Ah and the grams into kilograms (or the amperes into milliamperes), we get

Theoretical gravimetric capacity $C_{m,th}$ (mAh/g or Ah/kg) = [(1000 . n. F)/(3600 .M)]

Hence $C_{m,th}$ (mAh/g) = (1000 . n. 96485)/(3600 .M) = 26801 . n/M

Cathode : $LiMn_2O_4$

$Li_{1-x}Mn_2O_4 + xLi^{+} + xe^{-} \leftrightarrow LiMn_2O_4$, suppose x = 1 for complete extraction of the inserted lithium with one electron exchanged.

$Mn_2O_4 + Li^{+} + e^{-} \leftrightarrow LiMn_2O_4$

$C_{m,th}$ (mAh/g) = 26801 . n/M

$C_{m,th}$ = [1/(6.9 + 2 x 54.9 + 4x16)] x 26801 = **148 mAh/g**

So, I can apply the Faraday law. So, theoretical gravimetric capacity that is the total charge per mass and that is n into F by molecular weight. So, we can transform the coulomb into ampere hour, the way I introduced earlier and grams into kilograms or amperes into milli amperes.

$C_{m,th}$ (C/g) = Q/m = n . F /M

So, the gravimetric capacity we can get as 1000 into n F and 3600 into capital M. So, the capacity in this unit milli Ampere hour per gram is 1000 into n into Faraday constant divided by 3600 into capital M. So, if you just simplify it you will get this simple relation 26801 number of electrons that is involved in this reaction by molecular weight.

$C_{m,th}$ (mAh/g) = (1000 . n. 96485)/(3600 .M) = 26801 . n/M

So, if you take cathode instead of lithium cobalt oxide I have taken an example of lithium manganese oxide. So, lithium manganese oxide this reaction takes place while discharge. So, here I have taken x equal to 1 for complete extraction not like lithium cobalt oxide where only 0.5 moles you can take out and the relation is basically Mn 2 O 4 lithium is intercalating there and it is taking electron which is coming from the anode part and basically it forms back Li Mn 2 O 4.

$Li_{1-x}Mn_2O_4 + xLi^+ + xe^- \leftrightarrow LiMn_2O_4$,

So, again I apply the Faraday law 26801 number of electron by M. So, here you can see that this part number of electron is here 1 and this value this molecular weight of lithium manganese oxide I can estimate this is for lithium, this is for manganese and this is for oxygen and I get the capacity about 148 milli Ampere hour per gram.

$C_{m,th}$ = [1/(6.9 + 2 x 54.9 + 4x16)] x 26801 = **148 mAh/g**

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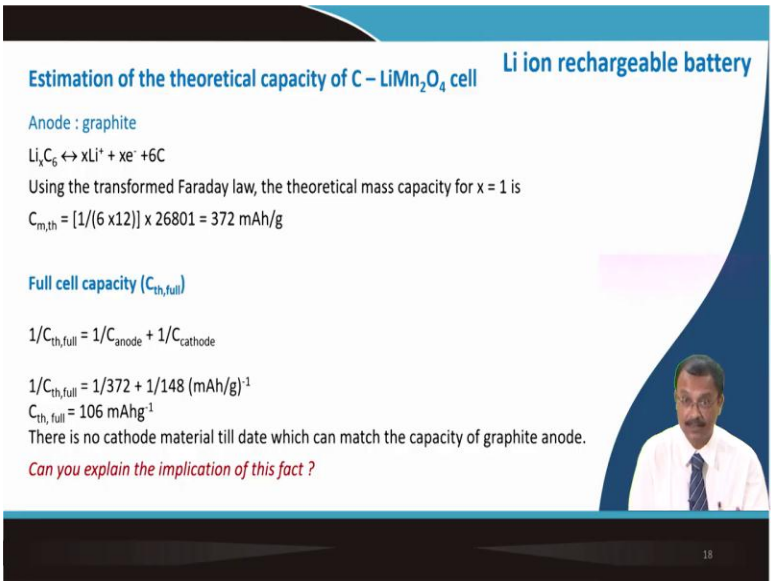

Li ion rechargeable battery

Estimation of the theoretical capacity of C – $LiMn_2O_4$ cell

Anode : graphite

$Li_xC_6 \leftrightarrow xLi^+ + xe^- + 6C$

Using the transformed Faraday law, the theoretical mass capacity for x = 1 is

$C_{m,th}$ = [1/(6 x12)] x 26801 = 372 mAh/g

Full cell capacity ($C_{th,full}$)

$1/C_{th,full} = 1/C_{anode} + 1/C_{cathode}$

$1/C_{th,full} = 1/372 + 1/148\ (mAh/g)^{-1}$

$C_{th,\ full} = 106\ mAhg^{-1}$

There is no cathode material till date which can match the capacity of graphite anode.

Can you explain the implication of this fact ?

Similarly, for graphitic reaction also I can do the same thing and calculate from the Faraday law this capacity is 1 full electron is exchanged and this is for the carbon molecular weight and multiply this term 26801 and it gives me 372 milli Ampere hour per gram. So, the full cell capacity this two individual capacitor as if they are connected in series.

$Li_xC_6 \leftrightarrow xLi^+ + xe^- + 6C$

$C_{m,th} = [1/(6 \text{ x} 12)] \text{ x } 26801 = 372 \text{ mAh/g}$

So, from the normal series capacitance law I can get the capacity of the full cell as 1 by 372 and 1 by 148 milli Ampere hour per gram. So, it is coming about 106 milli Ampere hour per gram. So, there is no cathode material till debt which can match the capacity of the graphite anode. So, you can see their graphite anode is 372 and the for cathode the capacity the half-cell capacity is 148 milli Ampere hour per gram.

$1/C_{th,full} = 1/C_{anode} + 1/C_{cathode}$

$1/C_{th,full} = 1/372 + 1/148 \text{ (mAh/g)}^{-1}$

$C_{th,\ full} = 106 \text{ mAhg}^{-1}$

So, once you have a full cell constructed the actual capacity is less than the individual capacity. So, I am leaving it to you to explain the implication of this fact ok. So, that, we will discuss in part of an assignment problem later.

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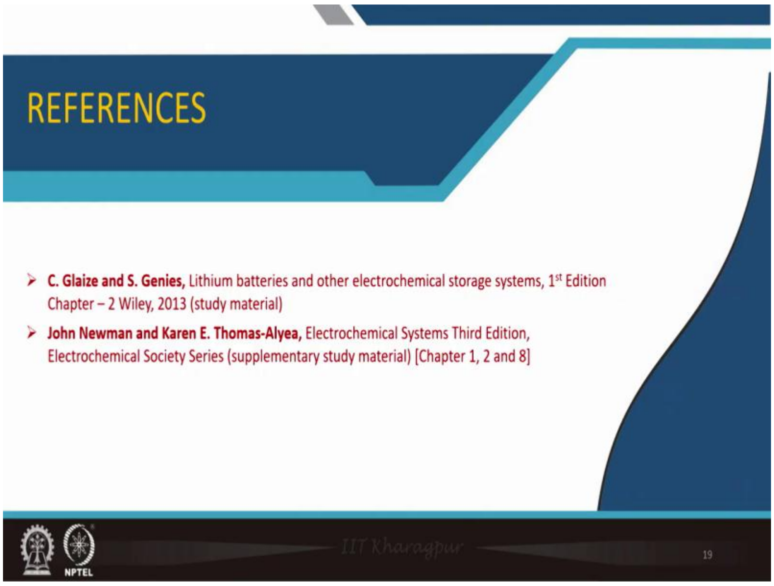

REFERENCES

- **C. Glaize and S. Genies,** Lithium batteries and other electrochemical storage systems, 1st Edition Chapter – 2 Wiley, 2013 (study material)
- **John Newman and Karen E. Thomas-Alyea,** Electrochemical Systems Third Edition, Electrochemical Society Series (supplementary study material) [Chapter 1, 2 and 8]

So, the reference for this particular lecture is the book by Glaize and Genies, Lithium batteries and that you can use chapter 2 as study material and this is excellent book by John Newman this also can be used several chapters 1, 2 and chapter 8 in particular which will clarify the basic idea.

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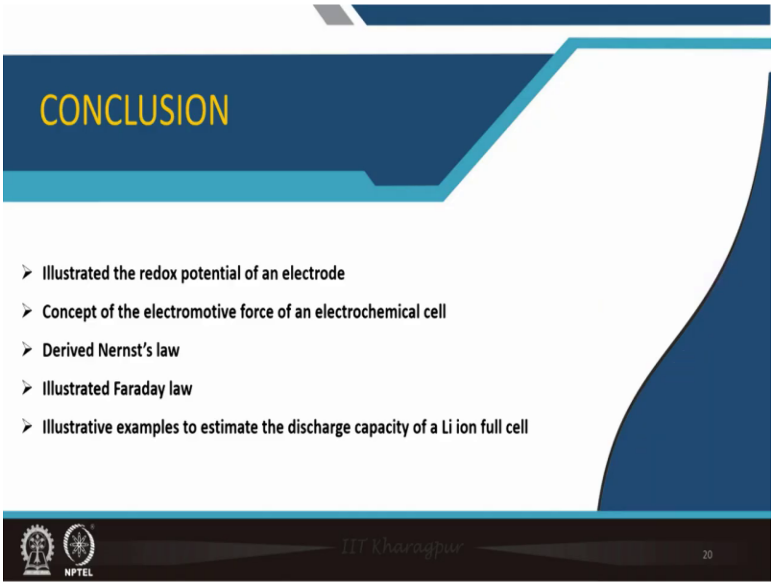

CONCLUSION

- Illustrated the redox potential of an electrode
- Concept of the electromotive force of an electrochemical cell
- Derived Nernst's law
- Illustrated Faraday law
- Illustrative examples to estimate the discharge capacity of a Li ion full cell

So, let me conclude this lecture. So, first I illustrated the redox potential of one single electrode the concept of redox potential; then we talked about electromotive force of a particular electrochemical cell.

Then, derived Nernst law which will allow you to estimate the voltage under non-standard condition, and subsequently we also talked about Faraday law illustrated the Faraday law and finally, we use Faraday law to estimate the discharge capacity of a typical lithium ion full cell taking graphite as the so called negative electrode and lithium manganese oxide spinel that as positive electrode.

Thank you for your attention.