Electroceramics

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Lecture - 15

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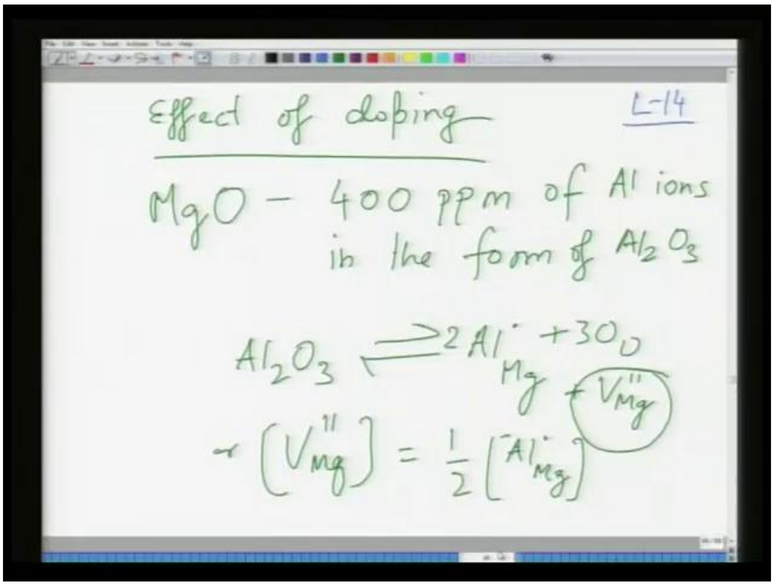

Effect of doping

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MgO – 400 ppm of Al ions in the form of Al_2O_3

$$Al_2O_3 \rightleftharpoons 2Al_{Mg}^{\bullet} + 3O_O + V_{Mg}''$$

$$\rightarrow [V_{Mg}''] = \frac{1}{2}[Al_{Mg}^{\bullet}]$$

So, in this class we will first review the last lecture and then we will go through a new concept. So, we was in the last class we looked at what is the effect of doping on the conductivity and we found that we are looking at magnesium oxide and what we found was that upon doping the conductivity changes significantly.

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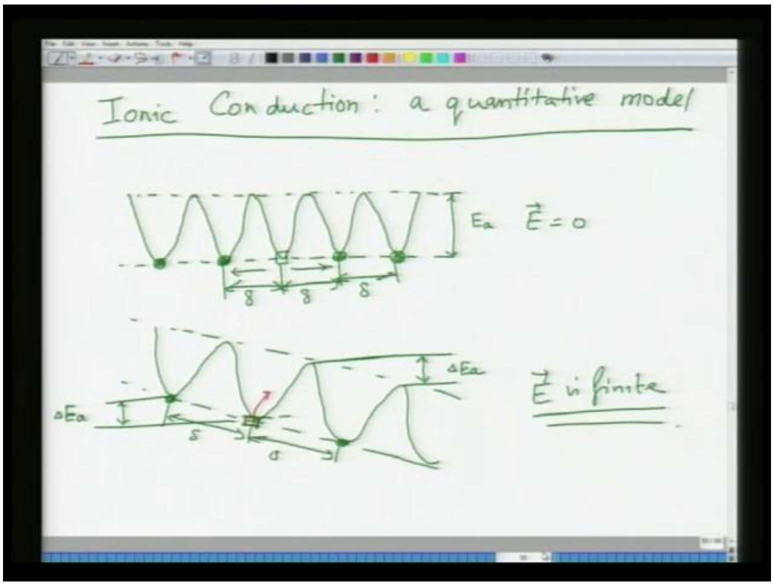

Ionic Conduction: a quantitative model

So, there is a change in the ratio of electronic to any conductivity and how the nature of conduction changes. The main thing that we discussed in the last lecture was ionic conduction and we derived a quantitative model for that. As we can see here we took for example, you can consider these positions as as at a regular ionic positions, and between these ionic positions, you have some sides which are empty which are nothing but vacant sides.

It is the migration of these vacant sides in in either direction which gives rise to conduction. So, in the absence of electric field the barrier to migration is let us say E a on either side and the probability of migrating on either side is equal. Now, when you apply your finite electric field there is a tilt in the potential well. Let us say towards the right. As a result the barrier on one side is decreased by an magnitude by a magnitude delta E a and it is increased by magnitude delta E a on the other sides, since the potential wells are symmetric.

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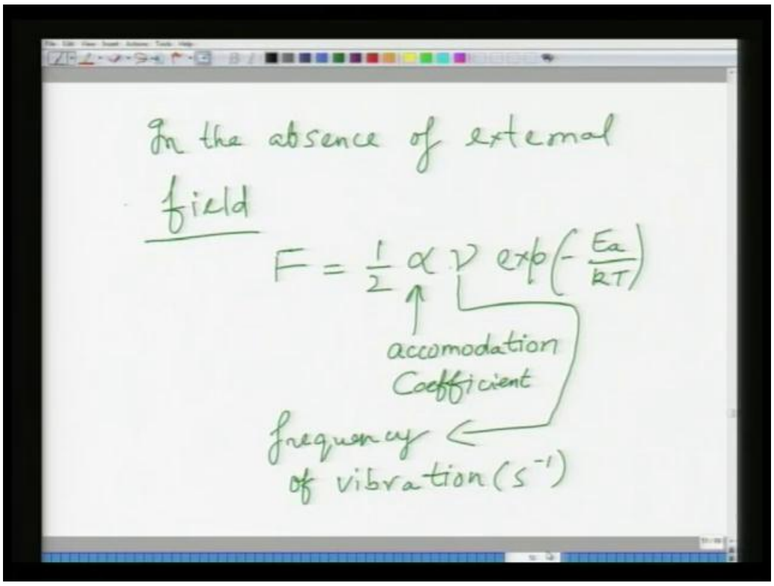

In the absence of external field

$$F = \frac{1}{2}\alpha\nu \exp\left(-\frac{E_a}{kT}\right)$$

accomodation Coefficient

frequency of vibration (s^{-1})

Now, as a result you have so as a result of application of external field. The this probability term F that gets modified.

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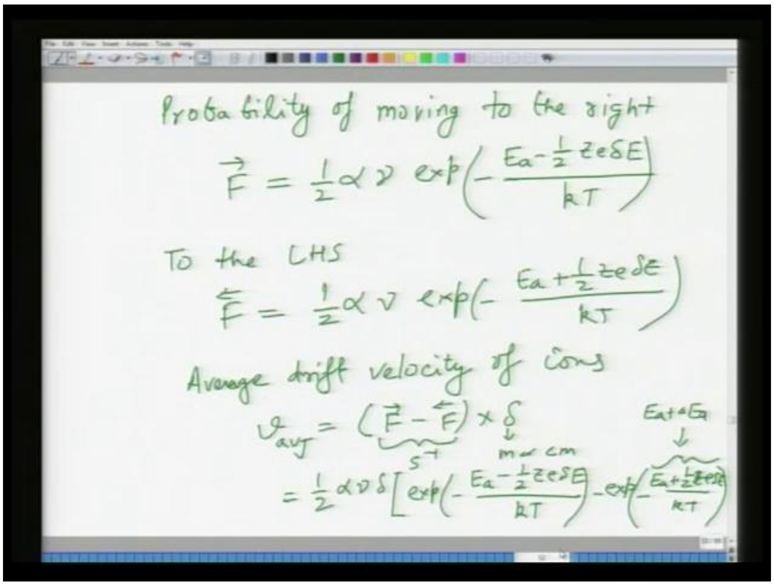

Probability of moving to the right

$$\vec{F} = \frac{1}{2}\alpha\nu \exp\left(-\frac{E_a - \frac{1}{2}ze\delta E}{kT}\right)$$

To the LHS

$$\overleftarrow{F} = \frac{1}{2}\alpha\nu \exp\left(-\frac{E_a + \frac{1}{2}ze\delta E}{kT}\right)$$

Average drift velocity of ions

$$v_{avg} = \underbrace{(\vec{F} - \overleftarrow{F})}_{s^{-1}} \times \underset{\substack{\downarrow \\ m \text{ or } cm}}{\delta}$$

$$= \frac{1}{2}\alpha\nu\delta\left[\exp\left(-\frac{E_a - \frac{1}{2}ze\delta E}{kT}\right) - \exp\left(-\overbrace{\frac{E_a + \frac{1}{2}ze\delta E}{kT}}^{\substack{E_a + \Delta E_a \\ \downarrow}}\right)\right]$$

Now, what happens is the, so as a result of unequal barrier to be crossed on either side, the probability in this case to move into right is higher as compared to moving in the left, as a result the carriers or the defects acquire a average velocity.

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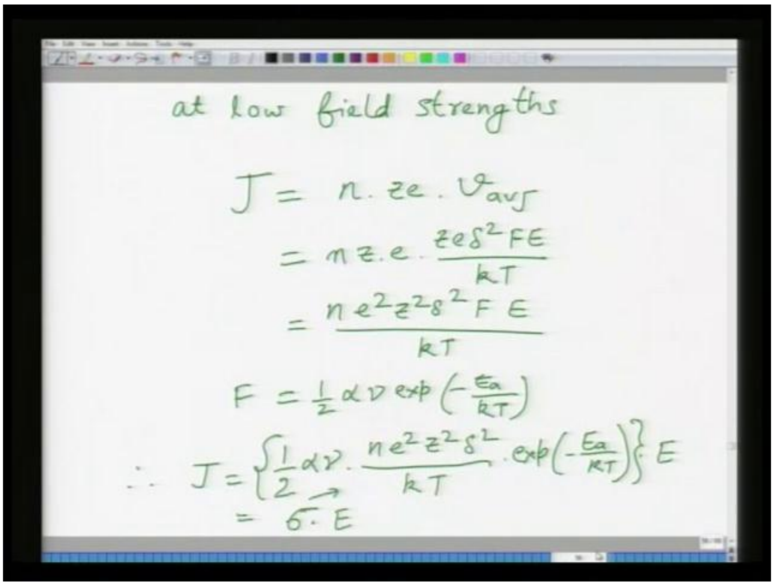

at low field strengths

$$J = n \, . \, ze \, . \, v_{avg}$$

$$= n z . e . \frac{z e \delta^2 F E}{kT}$$

$$= \frac{n e^2 z^2 \delta^2 F E}{kT}$$

$$F = \frac{1}{2} \alpha \nu \exp\left(-\frac{E_a}{kT}\right)$$

$$\therefore J = \left\{ \frac{1}{2} \alpha \nu . \frac{n e^2 z^2 \delta^2}{kT} . \exp\left(-\frac{E_a}{kT}\right) \right\} E$$

$$= \sigma . E$$

This velocity can then be in incorporated into the expression for current density, and this current density if you modify it what you get is an expression J is equal to sigma E which can be equated to J is equal to sigma E, and from this you can work out what sigma is.

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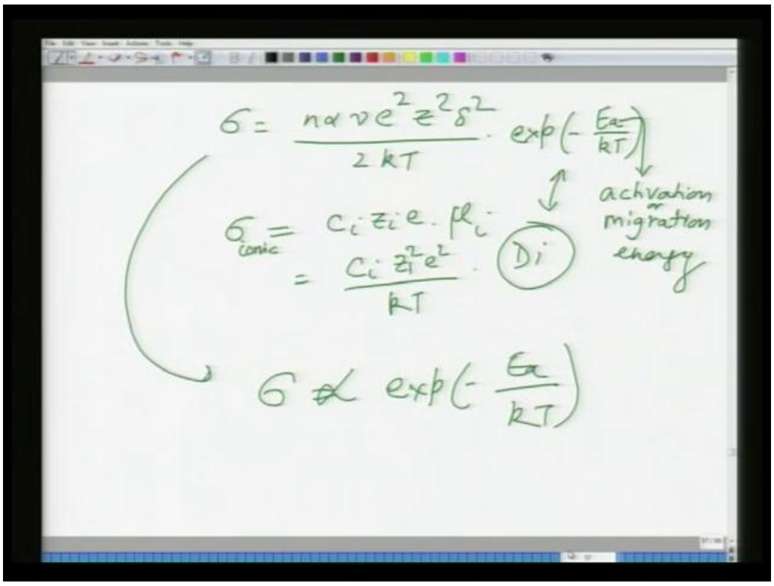

$$\sigma = \frac{n \alpha \nu e^2 z^2 \delta^2}{2kT} . \exp\left(-\frac{E_a}{kT}\right)$$

activation or migration energy

$$\sigma_{ionic} = c_i z_i e . \mu_i$$

$$= \frac{c_i z_i^2 e^2}{kT} . D_i$$

$$\sigma \propto \exp\left(-\frac{E_a}{kT}\right)$$

As you can see that sigma is nothing but some pre-exponential factor multiplied by exponential of minus E by k T and this is very similar to the expression that we derived from from the diffusivity expressions. So, these two expressions are similar so which tells that our model is not incorrect its correct model.

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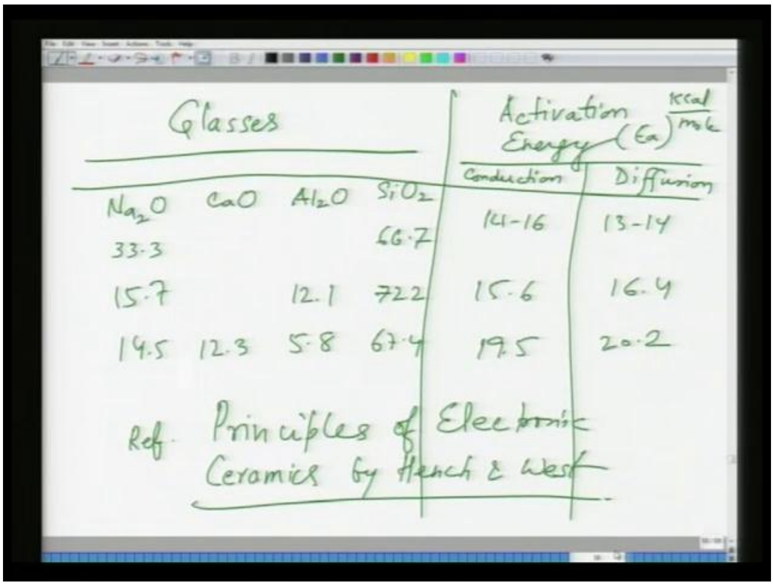

Glasses				Activation Energy (E_a) $\frac{kcal}{mole}$	
Na_2O	CaO	Al_2O	SiO_2	Conduction	Diffusion
33.3			66.7	14-16	13-14
15.7		12.1	72.2	15.6	16.4
14.5	12.3	5.8	67.4	19.5	20.2

Ref. Principles of Electronic Ceramics by Hench & West

This can be further verified experimentally, you can compare the values of activation energies, the the values obtained by diffusivity measurements are pretty similar to the values which are obtained from the conduction measurements. So, this validates again the model that we discussed.

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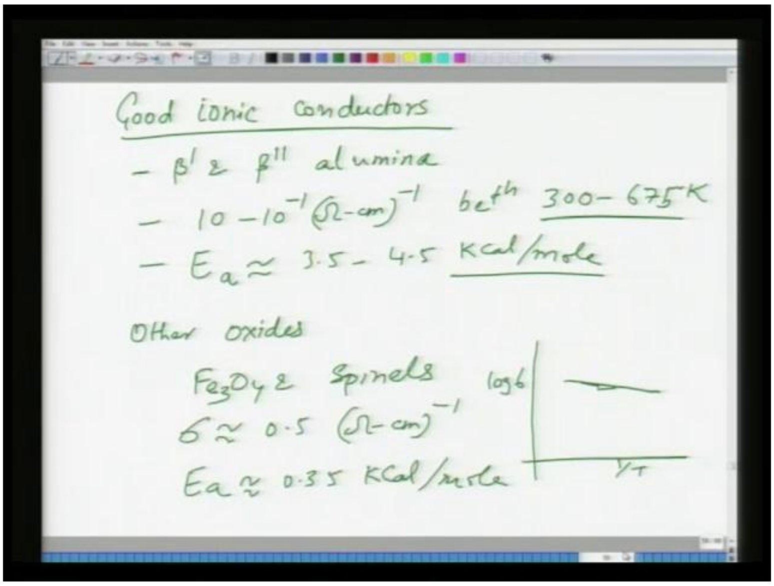

Good ionic conductors

- β' & β'' alumina
- $10 - 10^{-1} (\Omega\text{-cm})^{-1}$ be^th 300- 675 K
- $E_a \simeq 3.5 - 4.5$ Kcal/mole

Other oxides

Fe_3O_4 & Spinels

$\sigma \simeq 0.5 \ (\Omega\text{-cm})^{-1}$

$E_a \simeq 0.35$ KCal/mole

Then we looked at what are the good ionic conductors. So, one of the examples are beta aluminas. Then you have many other oxides, all of these have different activation energies, typically ionic good ionic conductors have low activation energies.

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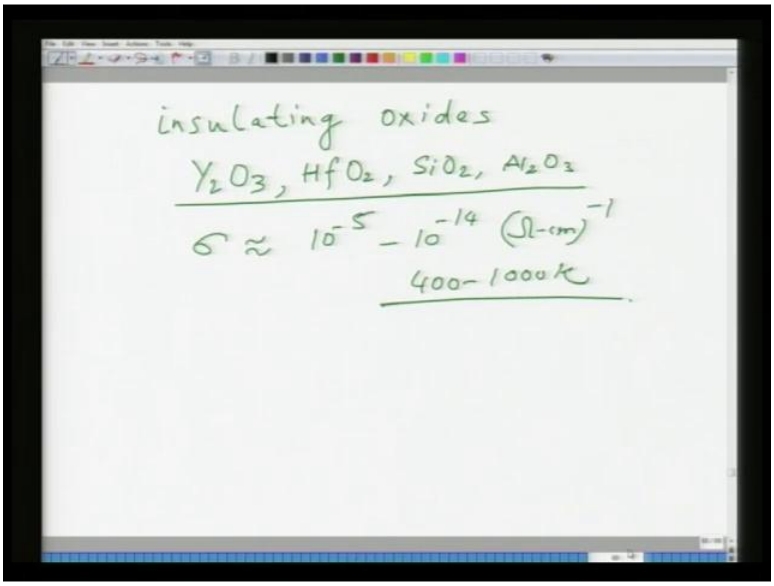

insulating oxides

Y_2O_3, HfO_2, SiO_2, Al_2O_3

$\sigma \approx 10^{-5} - 10^{-14} \, (\Omega\text{-cm})^{-1}$

400–1000K

There are other oxides which have very highly insulating corrector, such as you know aluminium oxide, yttrium oxide etcetera and these have very low connectivity values.

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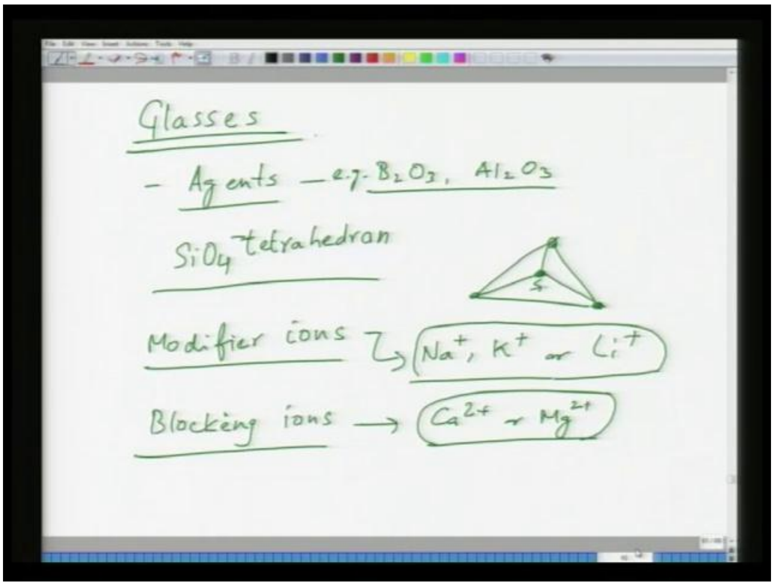

Glasses

- Agents – e.g. B_2O_3, Al_2O_3

SiO_4 tetrahedran

Modifier ions ↳ (Na^+, K^+ or Li^+)

Blocking ions → (Ca^{2+} or Mg^{2+})

Then we looked at the cases of glasses in case of glasses the resistivity or connectivity is important because glasses need to be melted in the furnace where resistivity of of the glasses can be used as a tool for resistivity of the glasses. So, that they they they are melting melted in the furnace itself to save the costs and to control the resistivity of these glasses you can add modifier ions such as sodium or potassium or lithium.

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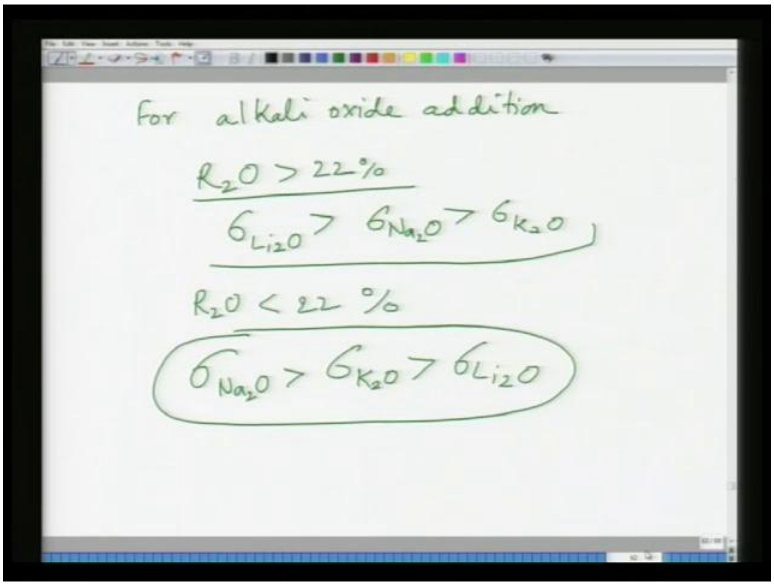

For alkali oxide addition

$R_2O > 22\%$

$\sigma_{Li_2O} > \sigma_{Na_2O} > \sigma_{K_2O}$

$R_2O < 22\%$

$\sigma_{Na_2O} > \sigma_{K_2O} > \sigma_{Li_2O}$

As well as the alkali earth ions and depending upon the size of and type of ion there will be a certain increase or decrease in the resistivity as we discussed last time.

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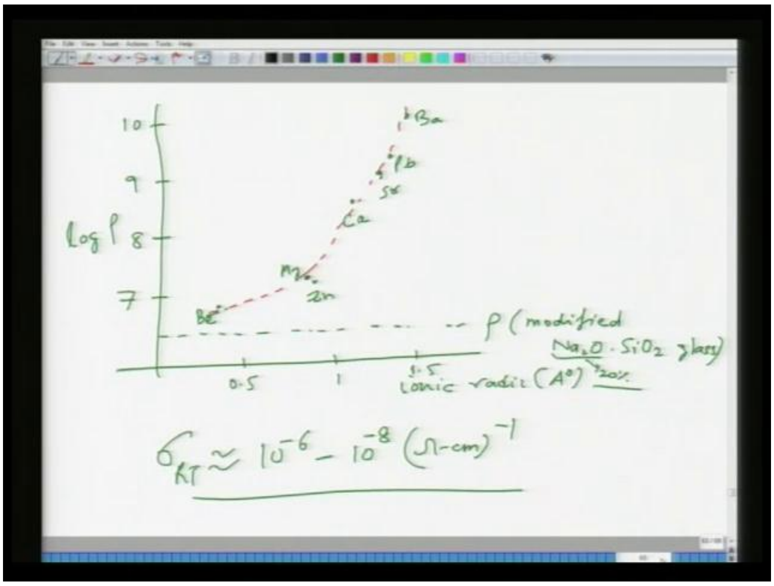

$\sigma_{RT} \approx 10^{-6} - 10^{-8} (\Omega\text{-cm})^{-1}$

Typically, what you see is that as the size of the ion increases the resistivity also goes up. So this is so the the bigger ions actually act as a blockers. So, they they block the ionic movement.

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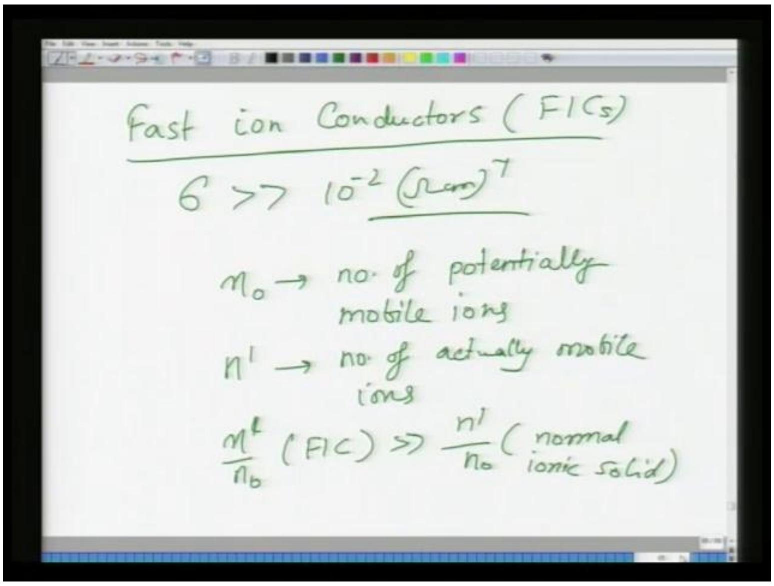

Fast ion Conductors (FICs)

$\sigma >> 10^{-2} (\Omega cm)^{-1}$

$n_0 \rightarrow$ no. of potentially mobile ions

$n' \rightarrow$ no. of actually mobile ions

$\frac{n'}{n_0}$ (FIC) >> $\frac{n'}{n_0}$ (normal ionic solid)

In the same category you have something called as fast ion conductor and these fast ion conductors are basically very highly conducting oxides or other ceramic materials, which have conductivities higher than 10 to the power minus 2 per ohms centimetre. This is because in these materials then number of actually mobile ions is significantly, is a significant proportion of number of potentially mobile ions which is very small in normal ionic solid.

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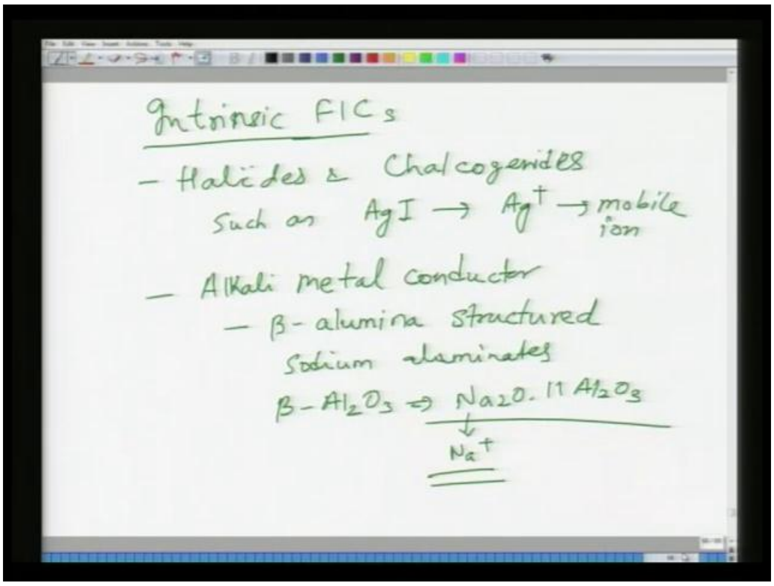

Intrinsic FICs

- Halides & Chalcogenides
  Such as $AgI \rightarrow Ag^+ \rightarrow$ mobile ion
- Alkali metal conductor
  - β-alumina structured Sodium aluminates
    $\beta\text{-}Al_2O_3 \Rightarrow \underset{\downarrow \atop Na^+}{Na_2O}.11 Al_2O_3$

So, you intrinsically the fast ion conductors which are intrinsically FIC's could be your Halides and Chalcogenides of for example, silver you can have alkali metal conductors like beta aluminas. These are intrinsically very mobile structures because of presence of a smaller mobile ions.

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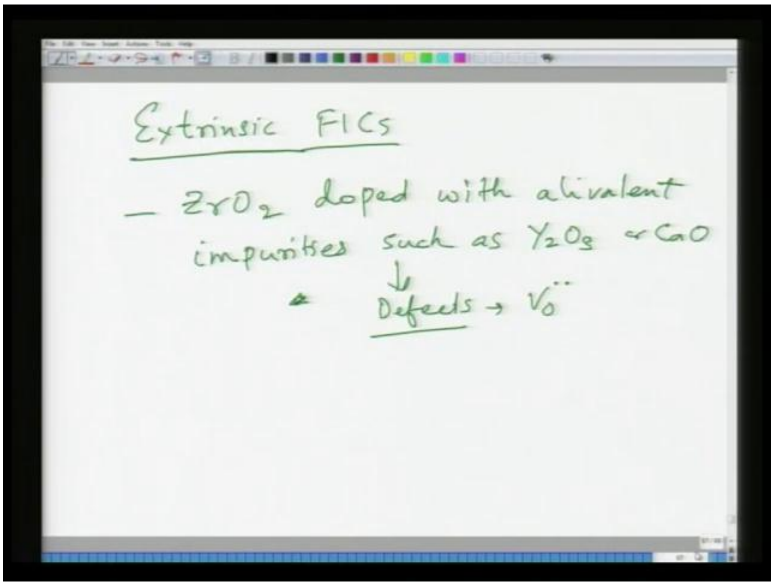

Extrinsic FICs

– ZrO_2 doped with aliovalent impurities such as Y_2O_3 or CaO

$\downarrow$

Defects → $V_O^{\bullet\bullet}$

Then you can have extrinsic FIC's where you can convert otherwise insulating material into a good conductor, such as zirconium oxide doped with yttrium oxide or calcium oxide by means of defects and also since there is a open structure in the compound.

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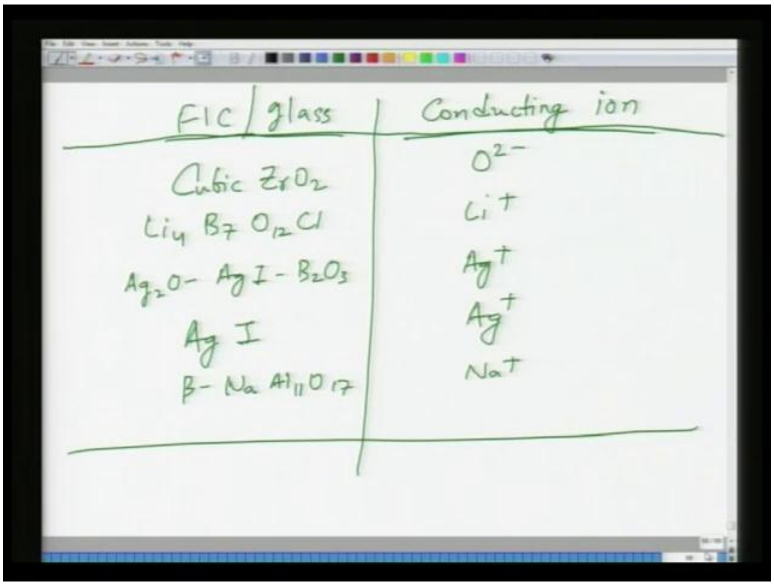

FIC / glass	Conducting ion
Cubic ZrO_2	O^{2-}
$Li_4B_7O_{12}Cl$	Li^+
$Ag_2O-AgI-B_2O_3$	Ag^+
AgI	Ag^+
$\beta-NaAl_{11}O_{17}$	Na^+

Then we looked at some of the conducting ions which participate in these oxides. Now, what will we do in in in this lecture is, we will look at some other aspects of a ionic conduction and one of these is electrochemical potential.

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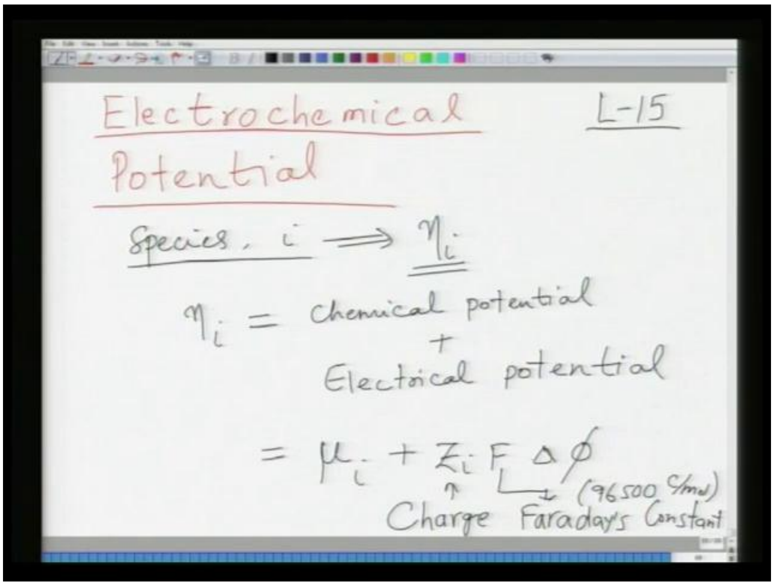

Electrochemical Potential

L-15

Species, i $\Longrightarrow \eta_i$

η_i = Chemical potential + Electrical potential

$= \mu_i + Z_i F \Delta \phi$

(96500 C/mol)

Charge

Faraday's Constant

Now, electrochemical potential as the name suggests is a is a combined effect of electrical potential and chemical potential. Now, usually what happens in ionic systems, you have both electrical as well as chemical gradients present. Now, this could be because chemical gradients is because of differences for example, in the composition etcetera and electrical gradient comes because of the charged nature of many of these defects. So, this non uniform distribution of defects in a solid which is bound to occur in any given solid in homogeneity is something, which is which occurs naturally in most of the materials this gives rise to internal electric field.

So, even if you do not apply an external electric field, you have a built in electric field within the material because of this non distribution non homogeneous distribution of electric charges, which is associated with the defects. Then you can always have chemical potential which is nothing but thermodynamic potential, which will arise because of compositional gradients. So, the total mass transport now in such a case, the total driving force behind such a mass transport is, not only the chemical force plus also this electrical force and this is what is called as total electrochemical potential. Sum is called as electrochemical potential.

So, let us assume we have a species i. Let us define this species i, which could be nothing but a defect. So, electrochemical potential of this species i is eta i. So, eta i is something which I have defined as electrochemical potential. This eta i is nothing but sum of chemical plus electrical potential and this becomes equal to nothing but mu i which is chemical potential plus electrical potential this becomes equal to Z i F delta phi. So, where Z i is nothing but your charge, F is nothing but faraday’s constant, which is nothing but 96500 coulomb’s per mole, 96500 coulomb’s per mole and delta phi is nothing but your potential gradient.

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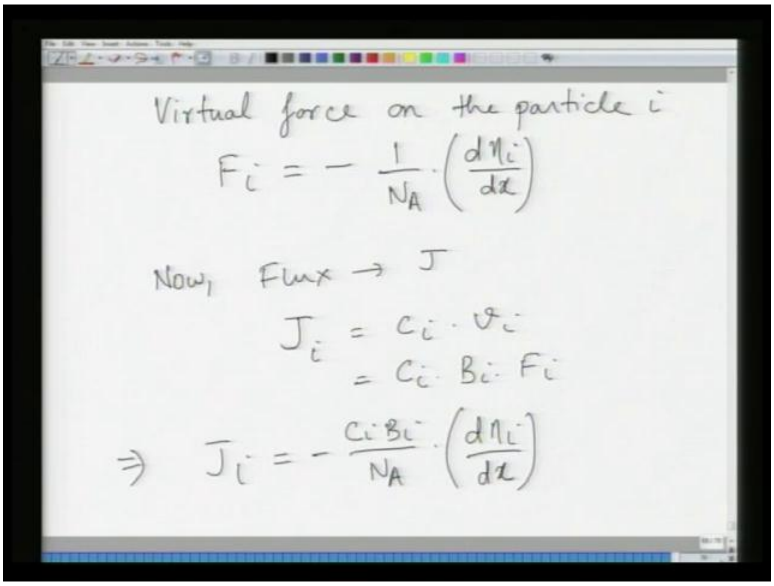

Virtual force on the particle i

$$F_i = -\frac{1}{N_A}\cdot\left(\frac{d\eta_i}{dx}\right)$$

Now, Flux → J

$$J_i = C_i \cdot v_i$$

$$= C_i \cdot B_i \cdot F_i$$

$$\Rightarrow J_i = -\frac{C_i B_i}{N_A}\cdot\left(\frac{d\eta_i}{dx}\right)$$

Now, we know that the virtual force on the particle is so the virtual force as we defined earlier on the let us say we call it as a particle. I mean you can its nothing but an entities. Virtual force on the particle i is nothing but negative gradient of eta i. So, virtual force F i is given as minus of 1 by N a into d eta i by d x. This is how we define this virtual force earlier in the beginning of this module. How do you now flux is nothing but J. So, if I write now flux J i as nothing but C i into v i it is a product of concentration per unit volume multiplied by the velocity.

This since we know how velocity is related to force C i into B i into F i. So, this this is the relation that we derived earlier flux is nothing but product of composition in velocity. This this becomes equal to your concentration multiplied by v i is equal to B i into F i which is nothing but mobility into force and this becomes your flux expression. Now, if you replace the F i from the above expression this J i can be written as minus of C i B i divided by N a into d eta i by d x. So, up to this point we are fine, so now if we look at the expression. So, this shows that what is flux made of? The flux is nothing but a, so flux is nothing but a derivative of electrochemical potential, so or related to derivative of electrochemical potential.

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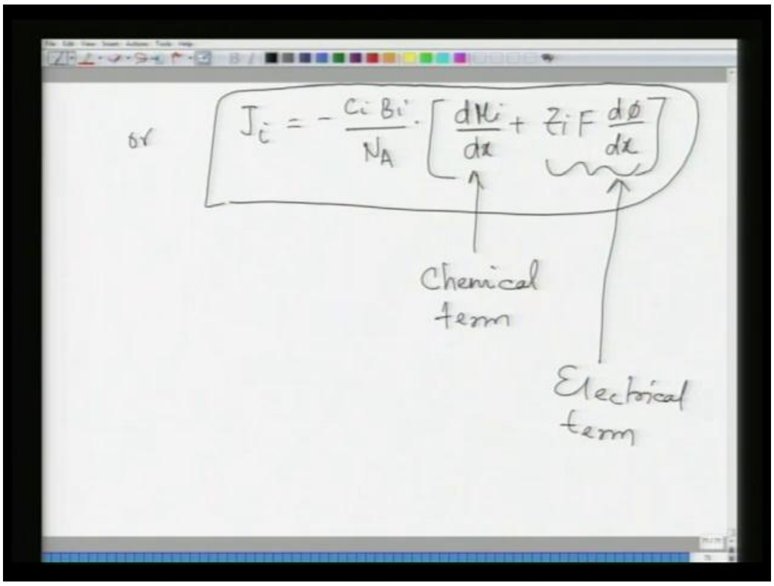

or

$$\boxed{J_i = -\frac{C_i B_i}{N_A} \cdot \left[\frac{d\mu_i}{dx} + Z_i F \frac{d\phi}{dx}\right]}$$

So, alternatively this J i can be written as minus of C i B i divided by N a into d mu i by d x plus Z i F d phi by d x. So, J i is function of d u mu i d mu i by d x as well as d phi by d x. So, this is a basic expression that we will now use to in case of any conductors. So, so this your chemical term and this is your electrical term. Now, what we will do is that we will derive a equation which is very pertinent to ionic systems and which is called as Nernst equation. So, this now now what happens is when you have such a system in which your flux is related to electric field. Now, what happens is when you have a chemical potential gradient in in a system, then this chemical potential gives rise to chemical potential.

Gradient gives rise to an electrical signal and this electrical signal can be a useful property because now you can use this electrical signal in practical devices like censors in fuel cells in in batteries as a as a tool to regulate something. So, regulate the the the chemical part of this system. So, now you have basically these two chemical parameters and electrical parameters which can be used to regulate the system. So, for now in a ionic in a ionic system you can have a system in which you have suppose you have a gradient in the oxygen concentration. So, this is very so this is something which happens very regularly in batteries or in many other devices so suppose you have a system.

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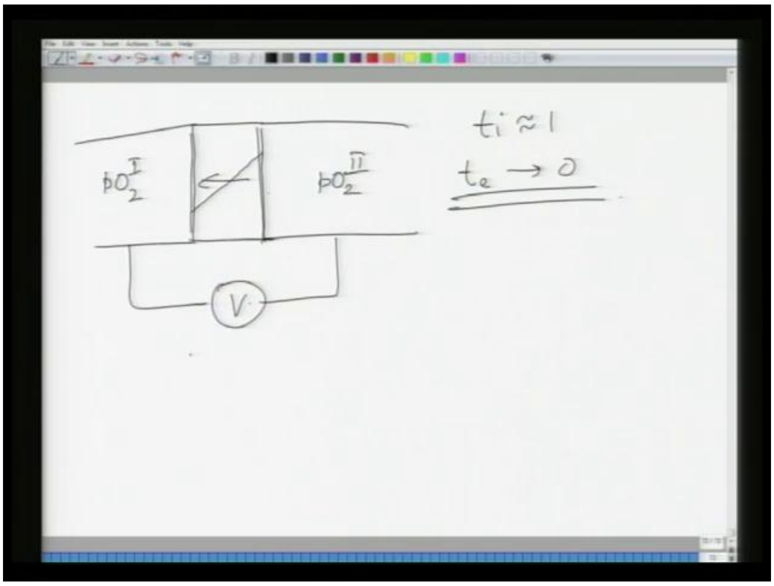

So, let us say you have some sort of device. Let us say this has this separates two regions. So, in this case you have some p O 2. Let us say p O 2 one and here you have p O 2 two and this change in partial pressure of oxygen requires, which means you have a gradient in in terms of oxygen concentration. You might have a gradient like this which means you have transport of oxygen in this direction and this transport of oxygen, since you have a chemical gradient as a function of composition, which is related to your electrical gradient. This is now this gives rise to a signal. Let us say v and this ionic transport as a result of chemical potential can now be controlled by using this electrical signal.

So, now what must happen in such a system is when you have a electrical signal as a result of this ionic concentration gradient, you must not have an electronic conduction otherwise you will have short circuiting. So, for these kinds of applications one must ensure that t i is equal to 1 which means t e is negligible. No electronic conduction you would like to prefer a system where ionic conductivity is highest, to avoid the short circuiting. So, consider now two systems where you have two sides separated by an electrolyte. So, we consider a system let us say this is an electrolyte or let us draw in the next page. So, the better picture would be something which I am going to draw now. So, you have such a system.

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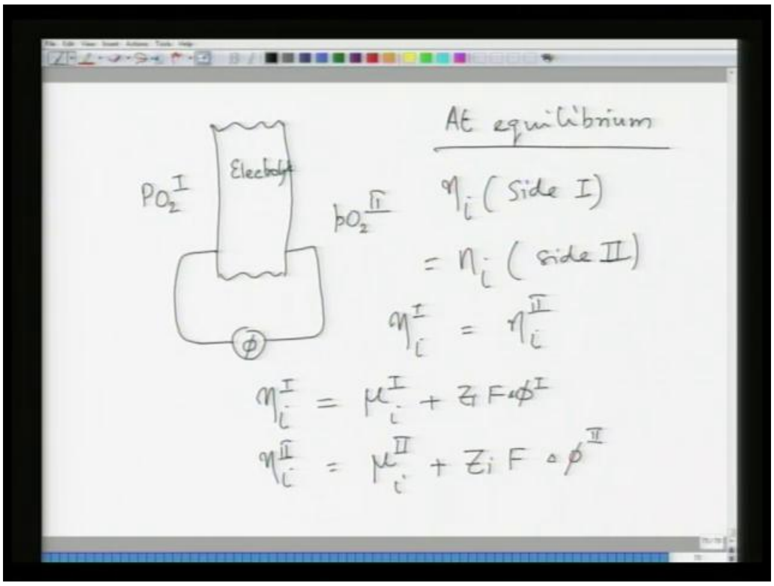

At equilibrium

$$\eta_i\,(\text{Side I}) = \eta_i\,(\text{side II})$$

$$\eta_i^{I} = \eta_i^{II}$$

$$\eta_i^{I} = \mu_i^{I} + Z_i F \Delta\phi^{I}$$

$$\eta_i^{II} = \mu_i^{II} + Z_i F \Delta\phi^{II}$$

So, this is let us say your electrolyte. It could be solid liquid does not matter in most cases in ionic solids it would be solid. So, here you have p O 2 one here you have p O 2 two. So, you have gradient in the oxygen partial pressure, you connect this with potential stat. This gives rise to a potential let us say phi. Now, what we will do is that so at so what what will happen at equilibrium. Now, at equilibrium when there is a equilibrium there so electrochemical potential of side one will be equal to electric chemical potential of side two. So, let us say which means I define eta i one is equal to eta i two because I had equilibrium that that overall electrochemical potential has to be equal. So, if this is the case now we know what is eta i one.

Eta i one if you go to previous slide it is nothing but sum of these two mu i and Z i F i. So, this becomes mu i 1 plus Z i F phi one. Delta phi one similarly, eta i two become mu i 2 plus Z i F delta phi two. So, I know the equilibrium condition. Equilibrium condition is eta i one is equal to eta i two.

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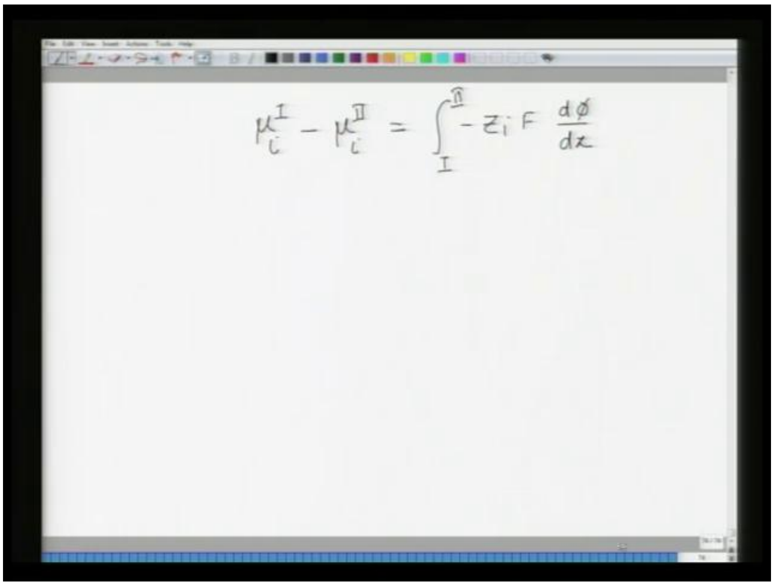

$$\mu_i^{I} - \mu_i^{II} = \int_{I}^{II} -Z_i F \frac{d\phi}{dx}$$

So, as a result now I can write mu i of side one minus mu i of side two. So, I what I do is that I rearrange the terms. I take the chemical potential term on one side electrical potential term on another side, and this becomes equal to one to two minus of Z i F d phi by d x. So, delta in the previous case this becomes equal to. let us get this sign correct.

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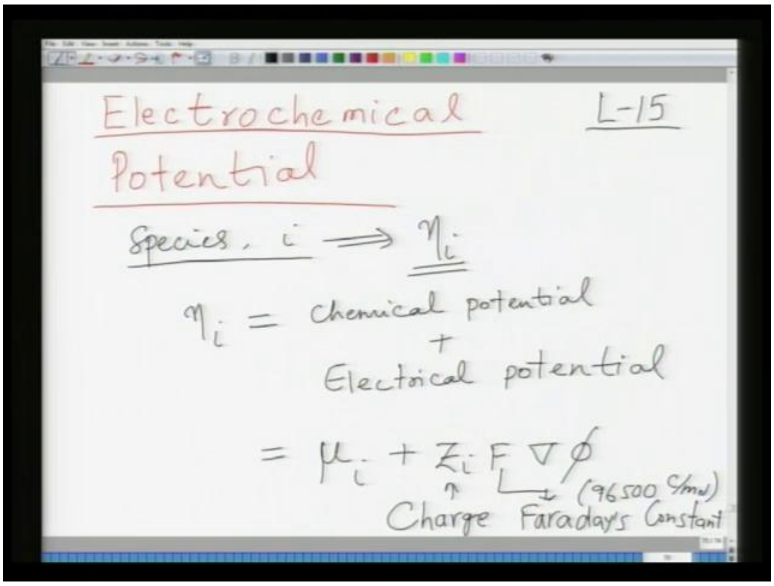

Electrochemical Potential

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Species, i $\Longrightarrow \eta_i$

η_i = Chemical potential + Electorical potential

$= \mu_i + Z_i F \nabla \phi$

This should be the alpha i, alpha i by del x.

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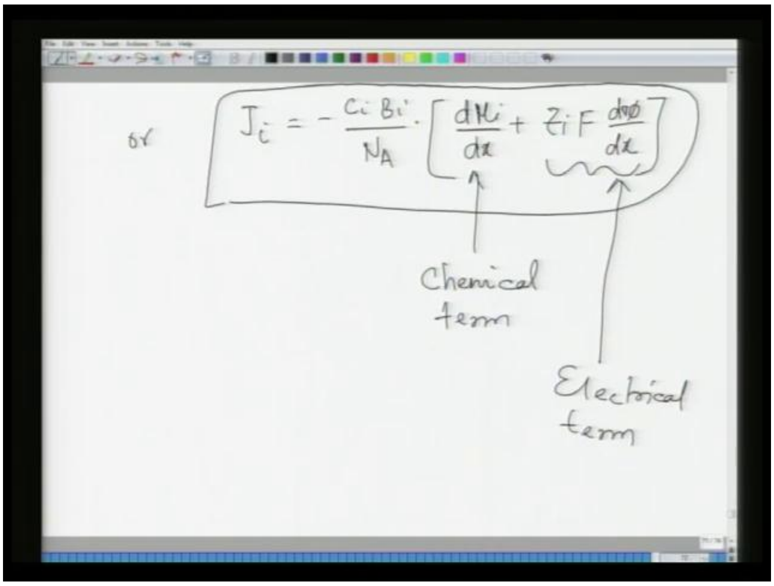

or

$$\boxed{J_i = -\frac{c_i B_i}{N_A}\cdot\left[\underbrace{\frac{d\mu_i}{dx}}_{\text{Chemical term}} + \underbrace{z_i F \frac{d\phi}{dx}}_{\text{Electrical term}}\right]}$$

Similarly, this is fine. Here it should be like this.

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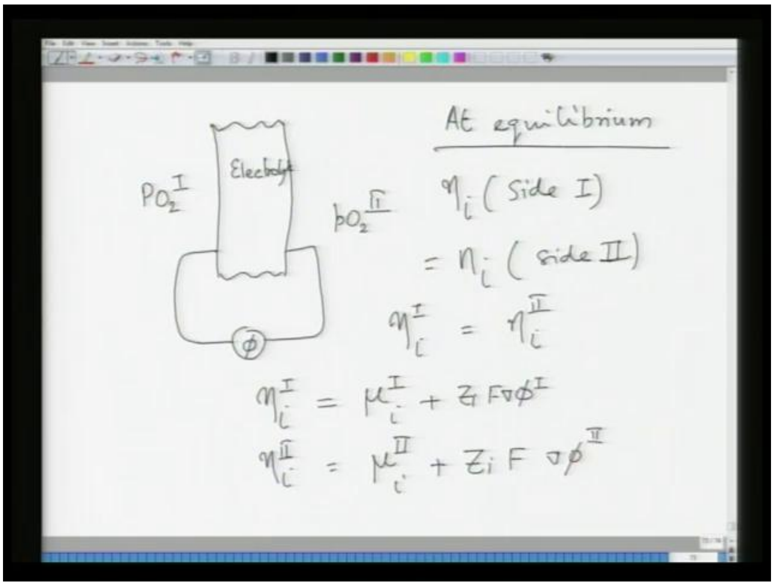

At equilibrium

$$\eta_i\,(\text{Side I}) = \eta_i\,(\text{side II})$$

$$\eta_i^{I} = \eta_i^{II}$$

$$\eta_i^{I} = \mu_i^{I} + z_i F \nabla\phi^{I}$$

$$\eta_i^{II} = \mu_i^{II} + z_i F \nabla\phi^{II}$$

Here again we will just make this lines correct, otherwise there will be confusion. So, so this becomes now you have taken both of them on one side.

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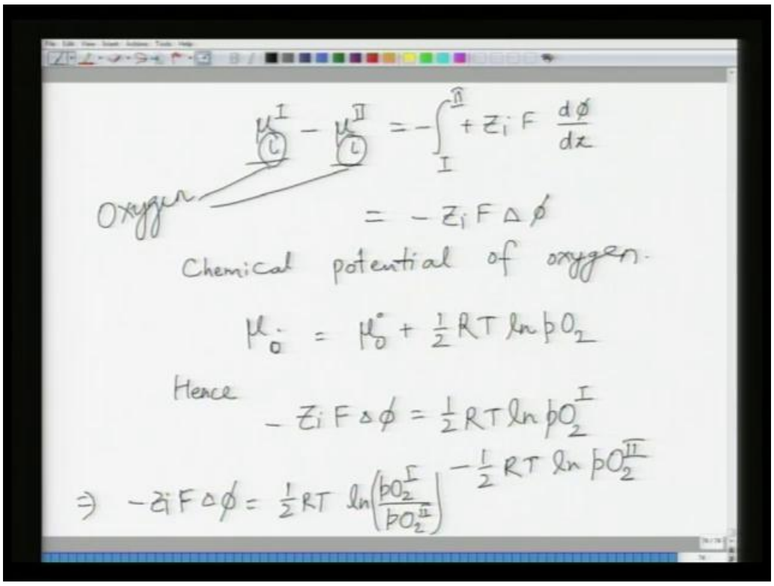

$$\mu_{\textcircled{i}}^{I} - \mu_{\textcircled{i}}^{II} = -\int_{I}^{II} + z_i F \frac{d\phi}{dx}$$

Oxygen

$$= -z_i F \Delta \phi$$

Chemical potential of oxygen.

$$\mu_{o} = \mu_{o}^{\circ} + \frac{1}{2} RT \ln pO_2$$

Hence

$$-z_i F \Delta\phi = \frac{1}{2} RT \ln pO_2^{I} - \frac{1}{2} RT \ln pO_2^{II}$$

$$\Rightarrow -z_i F \Delta\phi = \frac{1}{2} RT \ln\left(\frac{pO_2^{I}}{pO_2^{II}}\right)$$

So, chemical potential of side one minus chemical potential of side two, so here what I have done is this negative sign will come out and this has and this I have taken chemical potential of side electrical potential of side two minus electrical potential of side one. So, that is why this negative sign has come out and this becomes equal to minus of Z i F i can say if I am integrating, it it will become delta phi. So, this chemical potential now we written as so chemical potential I know mu i is equal to mu naught plus half chemical potential of any species i is equal to mu naught plus half of R T l n. If I consider it as activity then in in for for oxygen it would go as p O 2.

So, since I am considering here oxygen chemical potential gradient of oxygen. So, let us say this would be mu o naught because i th species, I have taken it as oxygen here. So, as a result now all I do is that I I I make substitution. So, this minus Z i F delta phi becomes equal to half so mu naught mu naught will cancel each other because this i is nothing but oxygen in this case. So, this becomes half R T l n p O 2 one minus half R T l n p O 2 two. So, as a result this becomes equal to minus Z i F delta phi, this is equal to half R T l n p O 2 one divided by l n divided by p O 2 two.

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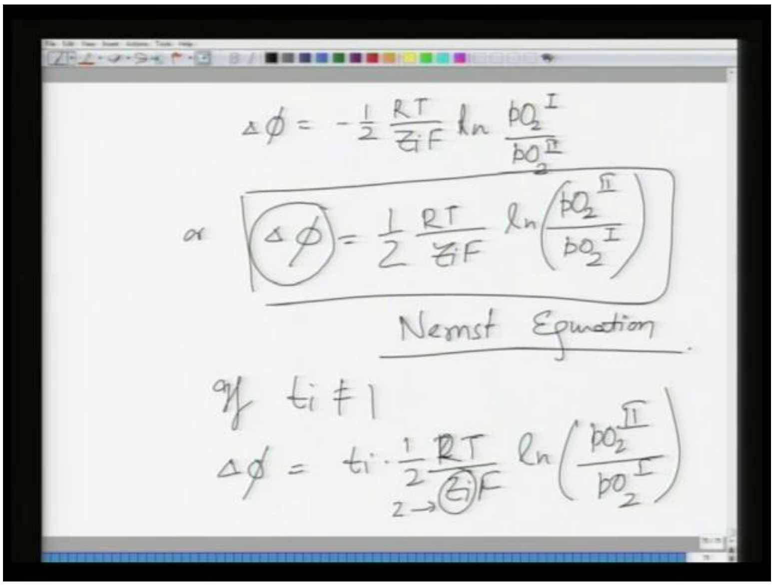

$$\Delta\phi = -\frac{1}{2}\frac{RT}{Z_iF}\ln\frac{pO_2^{I}}{pO_2^{II}}$$

or $$\boxed{\enclose{circle}{\Delta\phi} = \frac{1}{2}\frac{RT}{Z_iF}\ln\left(\frac{pO_2^{II}}{pO_2^{I}}\right)}$$

Nernst Equation

If $t_i \neq 1$

$$\Delta\phi = t_i\cdot\frac{1}{2}\frac{RT}{2\rightarrow\enclose{circle}{Z_i}F}\ln\left(\frac{pO_2^{II}}{pO_2^{I}}\right)$$

So, this is your relation or delta phi has become equal to minus of half R T divided by Z i F l n of p O 2 one divided by p O 2 two or delta phi is equal to half R T divided by Z i F l n p O 2 two divided by p O 2 one. Now, this is called as what is famously called as Nernst equation of electrochemical equilibrium.

Now, what this tells you is that if you have a system in which you have partial in which you have a gradient of partial pressure of oxygen, this partial pressure of oxygen gradient across an ionic solid will give rise. You will give rise to an electrical signal delta phi which is a voltage. So, this is a very useful thing, this can be used in for example, controlling the air to fuel ratio in automotive application which I will explain in a minute. Now, so this equation was calculated considering you have complete ionic conduction. Now, if you do not have complete ionic conduction in that case this delta phi would be modified.

So, if you have if if your t i is not equal to 1. If t i is not equal to 1, then delta phi will be equal to t i multiplied by half of R T Z i F l n p O 2 two divided by p O 2 one. So, and Z i in this case since, we are considering oxygen ion. Transport this Z i will be 2. So, for oxygen ions it would become R T divided by 4 F. If your if your ion, if that type of your ion changes in that case this Z i will also change. So, this will be your, this is the Nernst equation, which whose messages if you, in an ionic solid across the ionic solid, if you use ionic solid as an electrolyte if you have partial pressure gradient of let us say oxygen, then this partial pressure gradient of oxygen since, oxygen diffuses through the ionic solid it gives rise to an electrical potential which is delta phi. This this electrical potential can be used as a signal in various practical applications. So, I will give you one example. For example, automotive applications.

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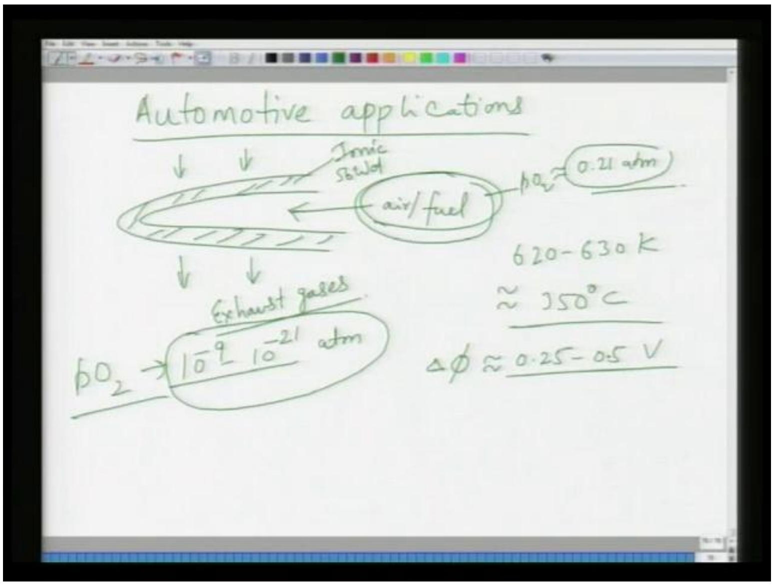

So, in automotive applications suppose you have this, something in exhaust. So, this is let us say your exhaust plug. Now, in this exhaust plug you have inside you have air to fuel supply and outside you have exhaust. Now, in the exhaust gases typically you know partial pressure of oxygen would be anywhere between 10 to the power minus 9 to and here. Inside this you will have p O 2 approximately equal to 0.21 atmosphere. So, this is a massive gradient of partial pressure of oxygen. Now, if you take at a temperature for example, at about let us say about 620 to 6, 630 Kelvin, which is roughly nothing but your 350 degree centigrade. Now, add these temperatures, this gradient of partial pressure of oxygen will give rise to delta phi of about 0.25 to 0.5 volts and this voltage is sufficient to be monitored.

It is, it can be easily monitored and this can be used in a feedback control system to regulate the air to fuel supply because we know as this pressure changes this will change. As the this ratio changes this will change because the air to fuel ratio determines efficiency of combustion would determine what is the exhaust gas composition. So, this concentration gradient across the so this is nothing but your ionic solid. So, this concentration gradient across this ionic solid can be used as a tool by means of an output which is delta phi which is reasonably large voltage to regulate the air to fuel supply in automotive systems. So, this is something which is very useful thing which can be used for variety of applications.

So, this would so at this point we are done with most of the concepts related to ionic conduction in solids. What we will do now? We will now have a look at some of the applications of these ionic conductors. So, ionic conductors can be used in variety of applications.

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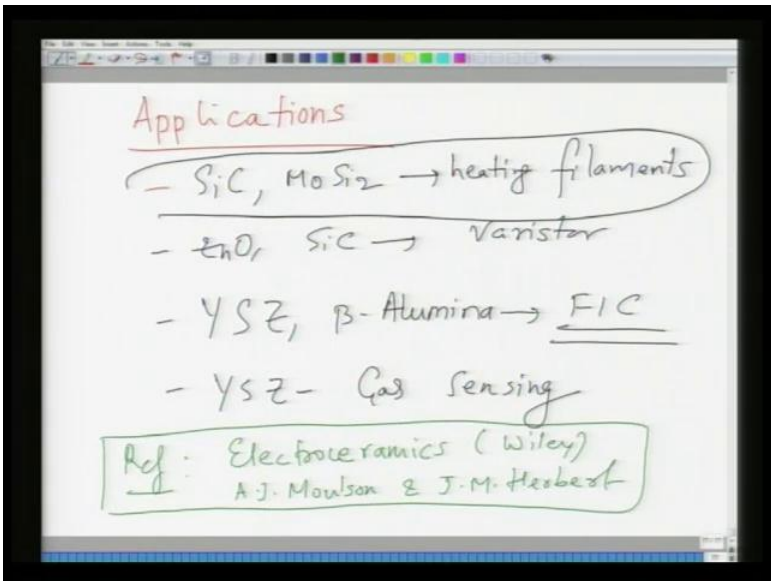

Applications

- SiC, $MoSi_2$ → heating filaments
- ZnO, SiC → Varistor
- YSZ, β-Alumina → FIC
- YSZ - Gas sensing

Ref: Electroceramics (Wiley)
A.J. Moulson & J.M. Herbert

So, for instance ionic conductors can be used in some of the common applications are silicon carbide, moly disilicide these are used as heating filaments in furnaces. The resistivity of these materials is appropriate for resistive heating in the furnaces. They are used as electrodes in some applications. Things like zinc oxide, silicon carbide they are used as varistors or devices for circuit protection. Solids like yttria stabilized zirconia, beta alumina they are used as fast ionic conductors, they are used in batteries and fuel cells. Y S Z is also used in gas sensing applications. So, there are variety of applications in which they are used while it.

Now, you can see that for in for applications like heating filaments, one is more concerned with the electronic conduction, while applications like FIC’s and gas sensing they rely more on ionic conduction.

So, depending upon the type of application you are interested either in electronic conduction part of the solid or ionic conduction part of the solid. Now, if you want to go into details of applications since, we cannot cover everything in this course, you can refer to a book. So, reference of for this part would be Electroceramics book by A J Moulson and J M Herbert and this is a Wiley publication. So, this book is a very nice book which narrates various applications of electroceramic materials in this remaining lecture we will discuss some of the applications which are pertinent to us and then we will finish this module. First example that I will take it take as is your varistors.

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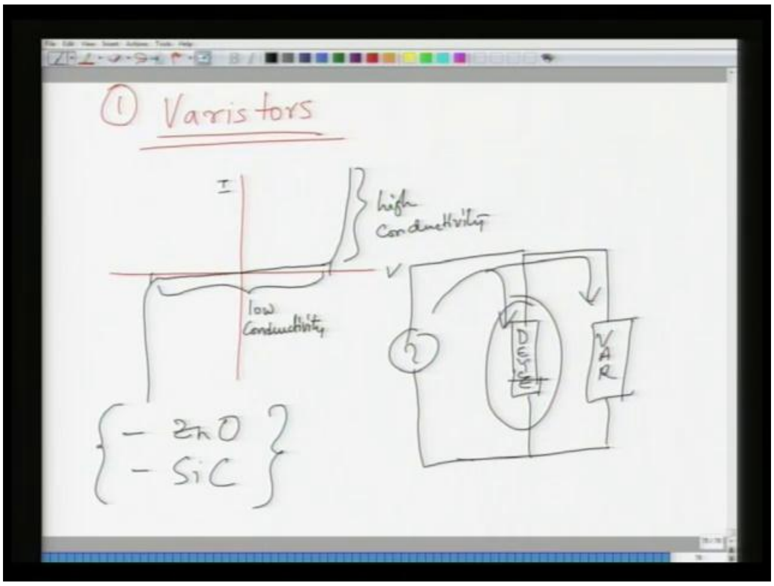

Now, varistor basically means voltage dependant resistor. Now, this a device which offers which is used for circuit protection and what it does is, it has very low, very high resistant resistance at low voltages. When the device has to be operated and when the voltage crosses a threshold. When it is, when it can fail then its resistance suddenly becomes low. So, so basically what happens is you so the operation is something like this. What it means is that your the the current which is flowing through the varistor at moderate voltages. So, this is your I V curve and then at high voltages it suddenly shoots up. So, this will be your threshold.

So, in this section you will have low sorry low conductivity or high resistance and in this section you will have high conductivity. Basically what you have is, you have a device which needs to be protected. So, this is your device you put in parallel with varistor and then you have a source. So, at moderate voltages since the resistance here is high all the current passes through here, but when the voltage becomes higher because of serge or whatever reasons, if your if your grade is not giving you reliable power supply then in that case when voltage is become high at that point this the part of the current goes through this.

So, protecting this device from things like surges in the circuit, so the typical materials that are used for these applications are zinc oxide or silicon carbide. Now, basically what you have is a zinc oxide powders which are which are pressed together. So, so majority of the medium is zinc oxide and then at the grain boundary or at the boundary between two powder particles, you have a layer which is called as a inter granular layer whose resistance is very high. This high resistance allows the material to be material to remain highly resistive at low low voltages. When the resistance, when the voltage becomes high then the conduction through these, tunneling through these inter layers or inter granular layers starts. So, I will just I will now draw the so what you have here is basically these particles.

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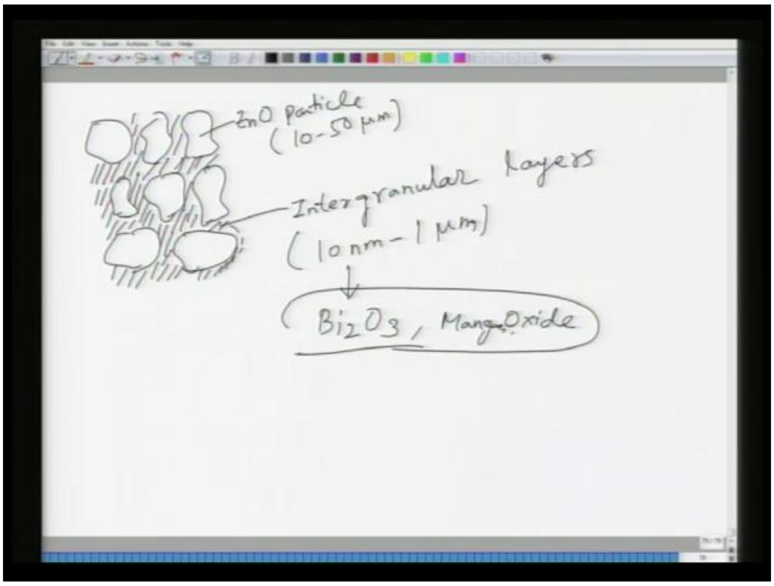

So, this is your zinc oxide particle, whose diameter is roughly 10 to 50 micron. Zinc oxide or silicon carbide and between these you have these inter granular layers. So, of course, I am making it little bit more magnified. The inter granular layers are very very thin in nature. Typically these inter granular layer could be submicron. In fact they could be nano sized range. So, these inter granular layers have roughly thicknesses of 10 nano meter to about a micron and this could be made of oxides like for example, bismuth oxide between the zinc oxide, grains bismuth oxide or manganese oxide. So, which are insulating in nature. So, basically what happens is, at so now this how it happens, you can get an understanding through the band diagram. This band diagram is something like this. So, you have in the equilibrium. So, you have a inter granular region.

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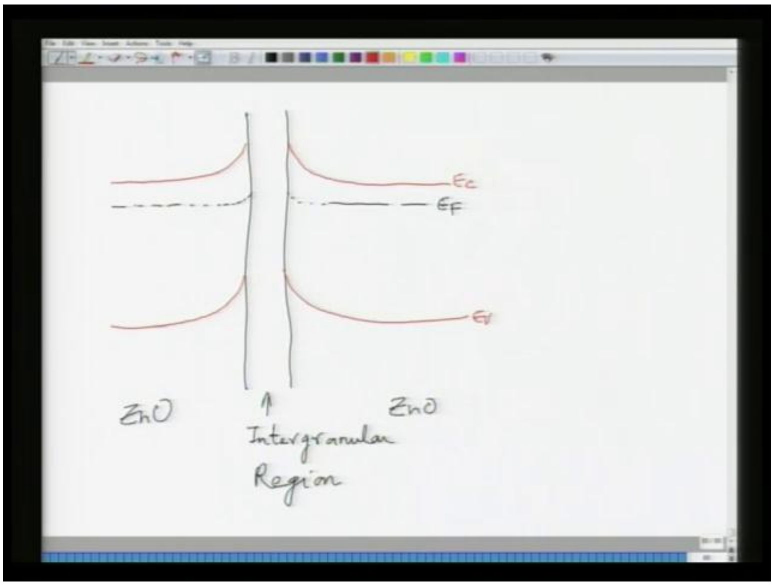

So, this is your inter granular region on either sides. You have zinc oxide grain so Z n O Z n O on either side. Now, at equilibrium you have fermi levels match so this is your Fermi level which will match at the equilibrium. Then of course, you have your connection in valence bands E V and E C. So, at equilibrium of course, nothing happens but when the when the bias is applied, when you have large bias what happens is so for instance you can assume a situation in which the grain on the right side is, let us left side is forward by us. So, let us say this is your forward biased grain this is your reverse biased grain.

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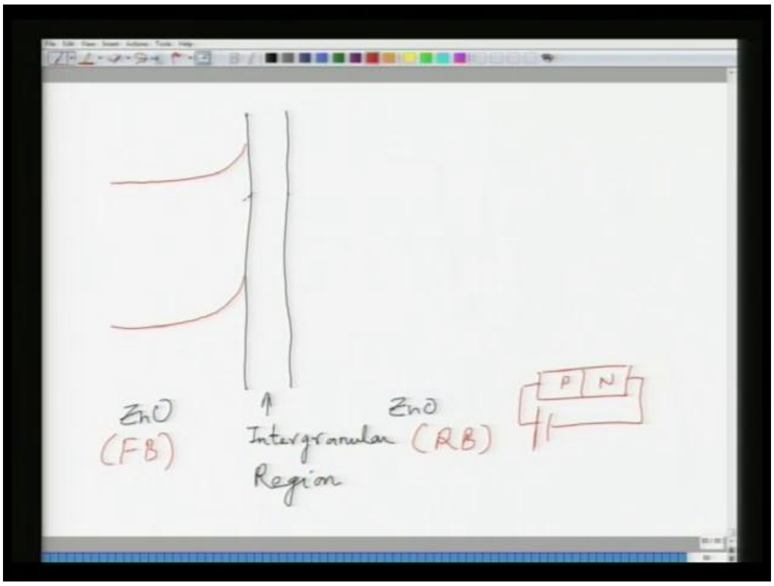

Now, forward biasing and reverse biasing you must know from the fundamentals of P N junction. So, basically in a P N junction forward biasing would mean, so this is your P N junction. P N junction forward biasing would mean you make P type more positive. So, P type becomes positive and N type becomes negative along the flow of current through the junction. So, this is forward biasing and reverse biasing is the opposite P becomes negative P is connected to negative terminal and N is connected to positive terminal.

So I will not go into details of this if you want to learn about this you you can go through any elementary solid state physics book. So, what happens in varistor is at high biases there is a forward biasing of one type of grain and reverse biasing of another set of grain. So, so one grain, so at high biases one grain is for left grains. Imagine that left grain is forward biased and right side grain is reverse biased under such condition, what will happen when this grain is forward biased the barrier on this side is will reduce and and so naturally as you know from the fundamentals of P N junction under forward biasing, the barrier go decreases and under reverse biasing, the barrier for carrier movement increases.

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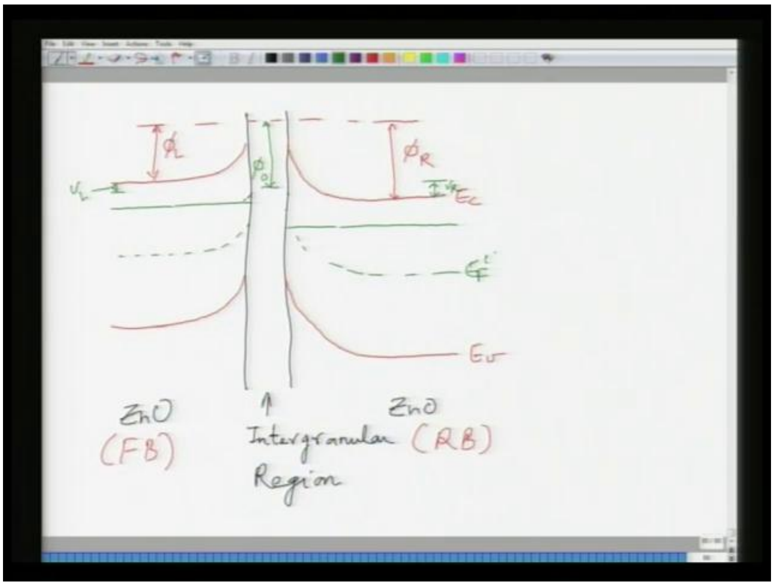

So, what happens here is the the the bands tilt on one side. The bands bend more on one side, more than other sides. So, as a result you have band bending. So, you can see that the band on one side are much more lower as compared to other side of the junction. This with respect to the so this could be defined as phi L and this could be defined defined as phi R and here the Fermi level Fermi level can be defined as. So, since you have biasing, you have shift in the Fermi level and distance of Fermi level from both of them will remain same. This is your inter granular layer in which whose work function is let us say phi naught and the bias on right side is nothing but V R unbiased on left side is nothing but your V L.

So, and of course, you can plot the intrinsic. Intrinsic would be like this. So, this could be E F i. So, what happens here is the in the inter granular region you have filled acceptor states. Now, as a result what you can see is since you have band bending taking place you have tilting of bands on you have bands on the one side raised, another side you have bands lowered. As a result you have tunnelling of carriers through the inter granular junction, which allows the current to flow in one direction. So, across the and across the inter granular layer as the what happens as the as the voltage as you increase the voltage bias the phi L decreases because these bands go up and phi R increases, because these bands go down and this leads to lowering of barrier on one side and this leads to conduction towards your in this direction. So, so basically a whole mass of material looks like as if you have you have network of diodes in a circuit and with each so and you have pair of diode.

Basically one pair of diode is one is an out of out of this pair one is forward bias and one is reverse bias. So, that is what happens in whole material all across. So, when you have very low bias supplied then nothing happens because the barriers are not very the change in the energy levels is very small. As a result nothing happens no current flows and when voltages are high then junction breaks down as a result you have thermionic animation, due to tunnelling across the junction due to band bending. So, this what is basically a varistor. Now, second application which which is there is a solid oxide fuel cell.

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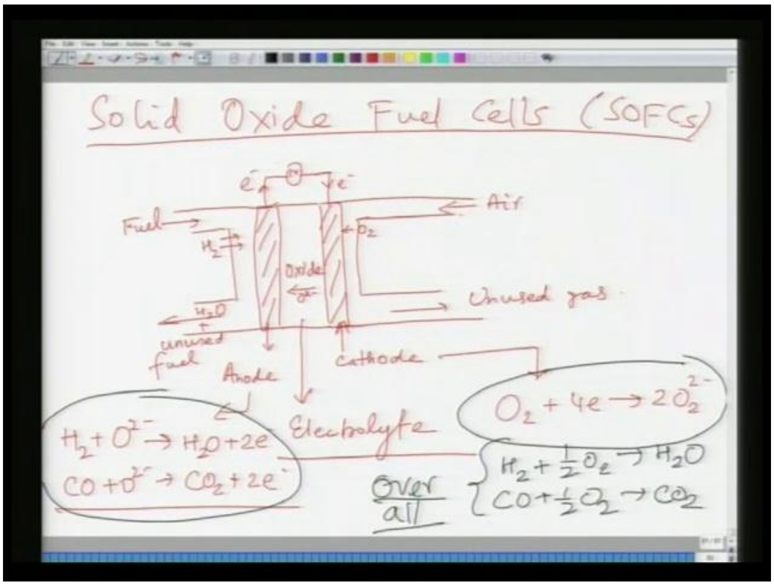

Solid Oxide Fuel Cells (SOFCs)

$H_2 + O^{2-} \rightarrow H_2O + 2e$
$CO + O^{2-} \rightarrow CO_2 + 2e^-$

$O_2 + 4e \rightarrow 2O_2^{2-}$

Over all
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$

So, you have solid oxide fuel cells or they are also called as SOFC’s. Now, these SOFC’s are nothing but your energy conversion devices, which are based on electrochemical principle. So, basically you have a what happens here is you have, you introduce a fuel which gets oxidized and which gives rise to production of electricity. So, one of the like the principle of operation based basically is based on, you have so this is an electrolyte or an oxide. Let us say on either side of this oxide you have electrodes. So, this is your in case of oxide fuel cell you will have an oxide.

So, and this is your let us say anode this is your cathode. Now, what happens in these is. So, you introduce air from this side and this air provides basically the oxygen. Through this oxide you have O 2 minus conduction and you provide fuel from this side and and the typically let us say, the fuel is hydrogen. This hydrogen reacts with oxygen, giving rise to excess water, so H 2 O plus unused gases because gases may not be burnt completely. Let us say in this case unused fuel and here you will have unused gas which could be nitrogen as well as oxygen, not all of it is completed. This is your this acts as your electrolyte which is nothing but a hard porous ceramic, which allows the ionic transport.

Now, so the reactions here which take place are so if you have for instance anodic reaction. So, reactions at anode if you have hydrogen as a fuel then H 2 plus O 2 minus giving rise to H 2 O plus 2 electrons and if you have C O then this is, C O 2 plus 2 electrons. This is a anodic reaction and your cathodic reaction would be in this case O 2 plus 4 e 2 O 2 minus. So, now you can see if you put this in an electrical circuit so you have creation of electrons here. At at this anode side and electrons go like this and electrons are consumed on the cathode side when they react with oxygen to give rise to oxygen ions which are then transported through electrolyte towards the anode to complete the whole circuit. So, this is the basically the circuit diagram.

You can now write the overall reaction, the overall reaction is nothing but production of water. You have C O plus half O 2 giving rise to C O 2. So, these are the overall reaction but electrochemical reactions are these. So, this is your anodic reaction and this is your cathodic reaction on anode electrons are liberated on cathode electrons are consumed. So, this is what is the principle of solid oxide fuel cell operation. Now, a device of so naturally when you have now, this device does not give rise to high voltage. So, in order to have reasonably large power, you need to connect many more devices in with together so as a result you have lot of technological issues like how the devices are connected, how they are packaged? So, in in in the device form, what you have is basically you have something like this, the cross section looks like, so you have an outer shell and this outer shell is nothing but the outer electrode.

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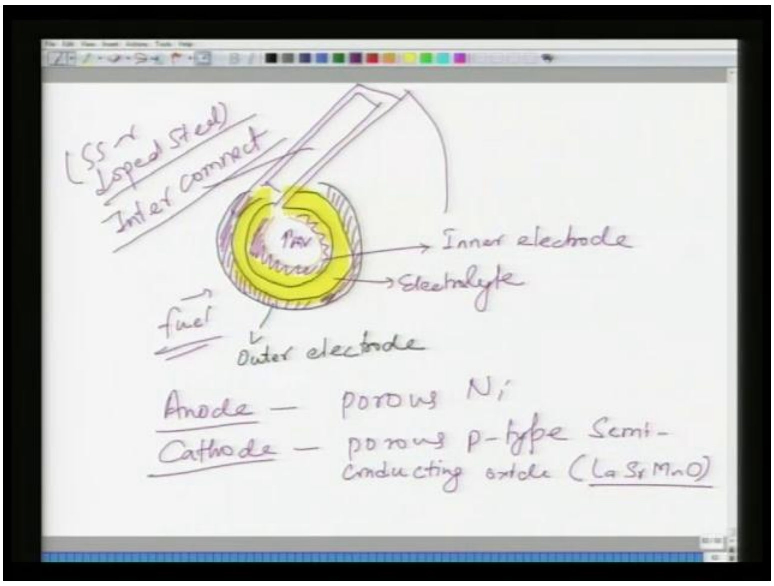

Anode — porous Ni

Cathode — porous p-type Semi-conducting oxide (La Sr Mn O)

Then you have so if I shade it like this. This would be your outer electrode and then in the middle you have electrolyte. So, this will be our electrolyte and then inside you have another layer of so this will, so yellow thing is your electrolyte and this outside inside thing is your inner electrode. So, what basically you have is on one side you have fuel flowing another side you have air flowing if air goes here then fuel goes on outside. So, this is a cylindrical body so it would be like this and on top of this cylindrical body you will have a interconnect which would which would connect with other devices. These interconnects are in such a manner so that they improve the device performance.

So, basically you can use various kinds of materials for such purposes, your anode material is typically, anode is typically porous, nickel, cathode is typically another it has to be so porosity is very important here. So, cathode is typically a porous P type semiconducting oxide. Such as lanthanum strontium manganese oxide L S M O, it is called as and interconnects are typically your either it could be stainless steel or it could be a doped oxides. So, interconnects are typically S S or doped steel. These devices are very useful devices, they can work over large temperature range and at but they work at higher temperature. So, typically the working range is somewhere between 700 to 1100 degree centigrade and they have a they could have a aerial resistance of roughly 1 to 2 micro ohm per meter per square, and they work on a very large range of oxygen partial pressure down to 10 to power minus 20 atmosphere and the efficiency of these devices is roughly 60 percent at 1000 degree centigrade.

This gives you out put power of about 100 kilo volt hour. So, these are some facts related to these devices but this is a very useful application of conducting oxides. Now, the third and last case that we will discuss here is the oxygen sensor. So, oxygen sensor as we discussed it has a design like this.

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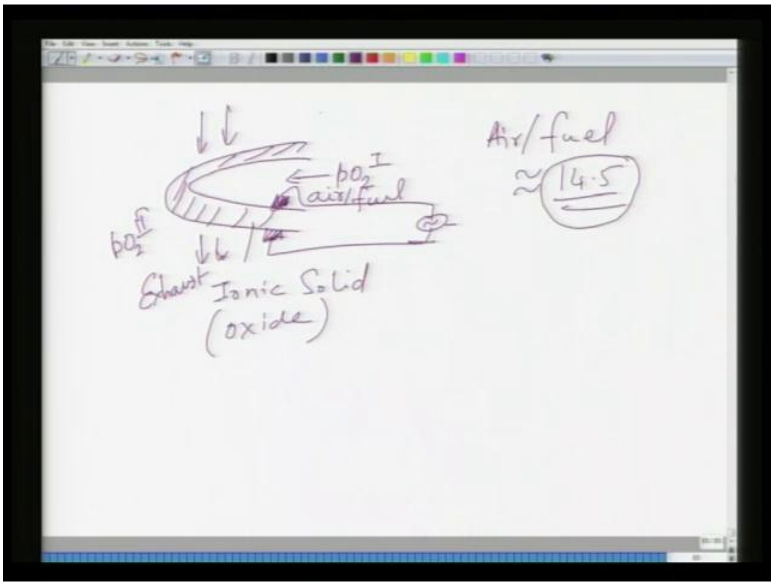

This is your ionic oxide or ionic solid. Basically which has high so you have partial pressure of oxygen one here p O 2 two here. Typically you will have air to fuel supply here and outer side is exposed to exhaust gases and this differential oxygen partial pressure because now, air to fuel ratio in case of automobiles 14.5 is optimum. Now, what happens is that above this ratio the the burning in such a manner so that hydro carbons and carbon monoxides decompose efficiently. But below this you have nox gases which burn efficiently, but carbon monoxides and the others do not.

So, as a result you need to maintain this ratio quite reasonably well. Now, this is where when you put when you take the signal between these two sides. So, you put contracts on these two sides, connect two electrical circuit, maintain the potential, measure this potential, use this potential through a feedback loop circuit to regulate the air to fuel supply by because you would know when you have absolutely efficient burning. What should be the ideal or reference point? Compare that with the reference point and correct the air to fuel ratio accordingly. So, this is this can be used in a fuel injection system, the principle is based on electrochemical potential and this can be used to regulate the fuel supply.

So, these are some of the applications of ionic solids from their conduction point of view. So, this ends the module three. In the next so what we have discussed in this module is basically the we have tried to relate parameters like diffusivity with the conductivity and we have looked at a model of conductivity, looked at various conducting ionic solids and some of the applications. So, this gives you a reasonably good summary of or overview of ionic conduction in solids.

Now, this finishes the module three here. In the next module which will be in our module four we will start looking at completely other side of the spectrum. Now, in the next class what we will learn is what is called as insulating oxides, which are nothing but your dielectrics or capacitors.

Thank you.