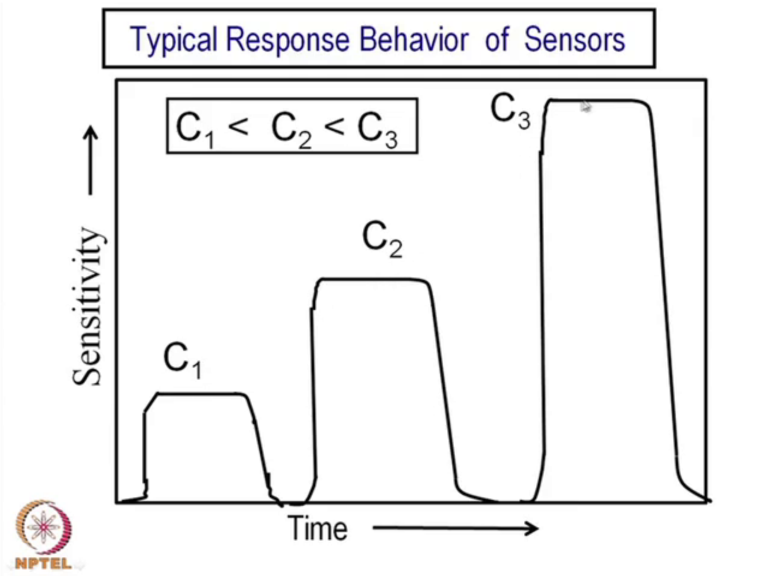
Advanced Ceramics for Strategic Applications
Prof. H. S. Maiti
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 27
Ceramics Gas Sensor
(Contd.)

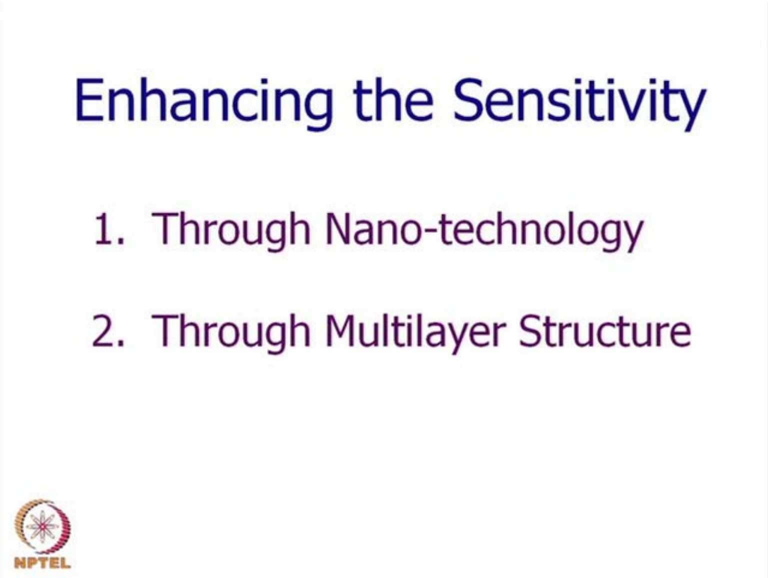
This is a continuation of our previous lecture that is on ceramic gas census. We did discuss about the response or the sensitivity of the gas sensors, semiconducting gas census.

(Refer Slide Time: 00:35)



And, that was the typical curve where different gas has been introduced at different times; and the response or the sensitivity increases as a gas concentration increases. In this case C 1 is less than C 2 and still less than C 3. So, C 3 is the highest. So, as we increase the gas concentration the total change in resistance changes increases. And as I just discussed that it may or may not be completely linear, but within a certain range certainly it is linear and one can use it for some control systems. So, this was response time.

(Refer Slide Time: 01:25)

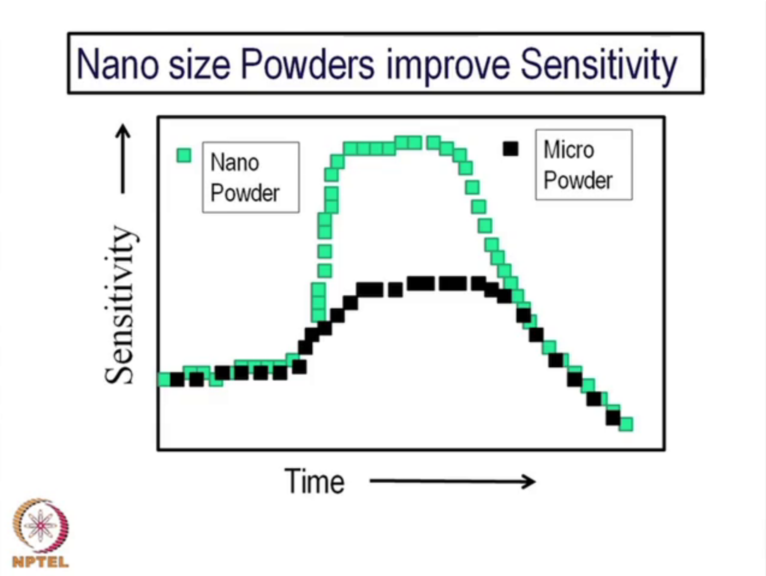


As I mentioned also the response time and the sensitivity can be changed to some extent or by a different parameters; one of course important parameter is the temperature. And temperature changes the absorption characteristics of different gases. So, you can make a relative changes in the response characteristics to specific gases that is one way of doing that. And overall once the temperature changes of course, there is a difference there is 2 different opposing factors, temperature changes oppose increases the kinetics of the process. But also it can lead to desorption of gases, desorption of oxygen in particular and that may lead to reduction in the sensitivity or lowering of the sensitivity.

So, one has to optimize which is the best temperature at which the system has to be operated. There is another way to enhance the sensitivity. This is through so called nanotechnology. Of course, this is nanotechnology in the sense here basically use nano powders, instead of micro sized powders to enhance the specific surface area; because we have seen the properties basically controlled by the surface property. So, it is adsorption desorption is the surface property and that leads to the surface conductivity and so on. So, if you can enhance the surface area, specific surface area of the material particular powder in this case one can certainly enhance the selectivity sensitivity of the sensor.

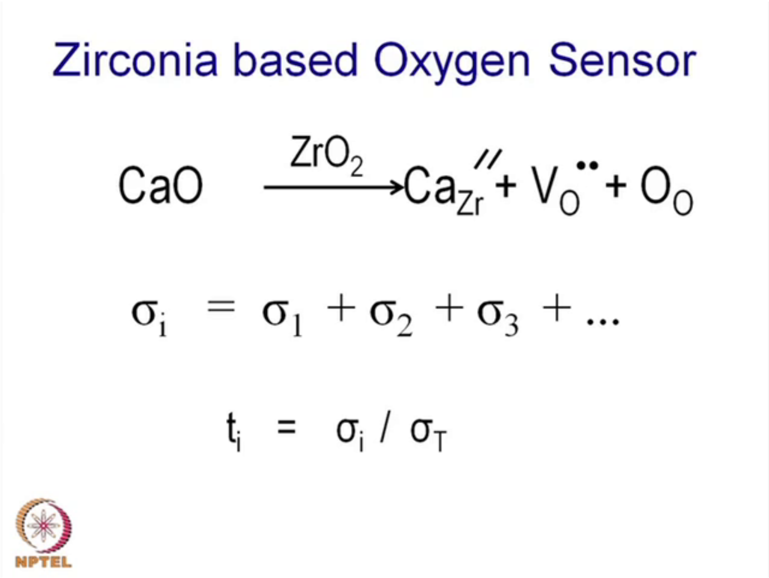
So, introduction of a nanotechnology is a very convenient way to enhance the sensitivity of the process. And most of the powders instantly are made by different kind of chemical synthetic processes either may be a soluble processes it may be process (( )), it may be prepared by hydrothermal processes and so on. So, this chemical processes always lead to very fine powders, sometimes micron sized powders, sometimes nano sized powders. So, we have some control we have some control on the surface area of this powders; which are ultimately will be used for the construction or the design design of the sensor. So, by making nano powders one can enhance the surface area and therefore, the sensitivity can also be improved.

(Refer Slide Time: 04:28)



So, there is an example, of that here just a schematic again, once again we have plotted the time or the sensitivity against time. And 2 types of powders, 2 types of same material either tin dioxide or zinc oxide sometimes maybe different other oxides nickel oxide, cobalt oxide and all that. But as I said earlier these are the 2 oxide mostly used; and this is micro sized powders, and this is nano sized powders. And you can see a fair amount of enhancement all other parameters remaining same; just by changing the particle size particle size of this ceramic powders used for the publication of sensor one can enhance into to the sensitivity property. So, that is an important criteria or important aspect must remember in designing the senses.

(Refer Slide Time: 05:30)



I think that is all before I go to another topic, I should mention that semiconducting gas, semiconducting oxide-based gas sensor are still under development. And many sensors have been already commercialized are marketed, but still further developments have been taking place. And many of the research work is still also going on in this country in different groups. Some of them for example, are ready active to develop like a the ceramic (( )); the others are discrete sensors were things like a breath sensor. Somebody consumes alcohol it can be detected from the breath how much percentage or how much if there is residual alcohol there.

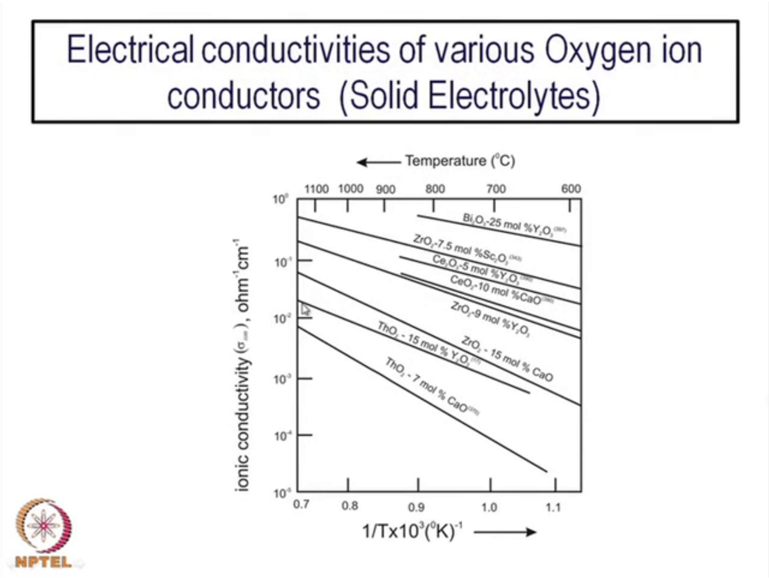
So, alcohol sensors are also available. Very recently something different is being tried acetone can be sensed. And it is understood that if somebody has a diabetic; is a diabetic patient the acetone concentration in the breath increases. And from that one can really major the diabetic diabetic state of diabetics in somebody's health. And so there is a kind of sensor or basically gas census for industrial purposes, but also can be applied for some medical treatment or medical diagnostics. So, many applications, new applications are being thought of and possibly in near future and some success will come up in those areas. With this change over from semiconducting oxide with sensors to a different kind of sensors which is called zirconia base oxygen sensor. This is basically needed for oxygen gas sensing not for any other gas. But there is tremendous importance of sensing the oxygen concentration under different situation. And in such situation particularly when it is used are in needed in slightly elevated temperature.

Then, this is one of the best sensor one can think of is more reliable and it is a wide range of applications. So, let us try to discuss what is the basic principle on which a zirconia base oxygen sensor works? Zirconia basically a high-temperature oxide, but one of the important criteria of or important property of zirconia is has a very high oxygen ion conductivity; particularly when it is stabilized with calcium oxide or yttrium oxide like that. It stabilize in fact addition of zirconium oxide, addition of calcium oxide to zirconia not only stabilizes the cubic purite phase which is normally a high-temperature phase at room temperature. But also enhances the oxygen vacancy concentration in the structure by a process like this, because zirconia is tetravalent, where as calcium is divalent. So, there is a deficient of 2 positive charge.

So, when that is what is been written in this defect equation. Calcium goes zirconium side and there is a effective 2 negative charges created. And to compensate that you have to have effectively positive charge and that is by oxygen vacancy. So, you create a oxygen vacancy by adding calcium oxide to zirconium dioxide; we actually enhance the oxygen ion vacancy concentration. And that leads to a very enhance mobility of oxygen ions and high oxygen ion conductivity. This is a very typical materials where in the solid state; you have a very high oxygen and conductivity no electronic connectivity almost nill electron conductivity.

So, the t i what you call known as the transparents number transparents number for the oxygen ions is very close to 1. And this is t i by t sigma i by sigma T that is the total a conductivity and the conductivity arising from the oxygen ion. So, this is a very close to 1 is very close to 1 more then 0.99. And that is one of the requirement for using this material as an electrolyte in some of the electro chemical systems.

(Refer Slide Time: 05:30)

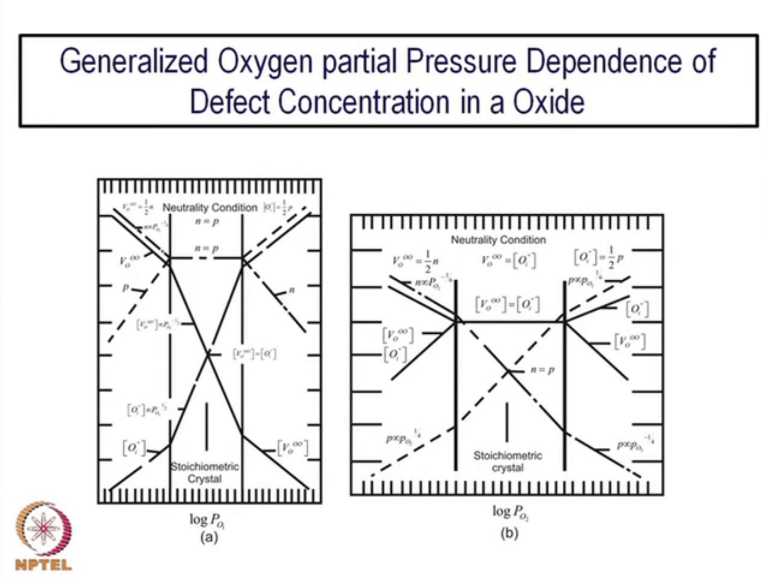


But before you come to that this are the conductivity plots. The electric conductivity of various oxygen ions and conductors; particularly which of those are known as solid electrolytes. So, they can be used as electrolyte in a solid state electrochemical cell. So, these are mostly cubic fluoride type oxides. And this starts with thorium ThO 2 also has a cubic fluoride structure and Vi 2 O 3 at a slightly elevated temperature; one of the polymorphs is also a cubic fluoride structure. So, CeO 2 is another oxide which has a cubic fluoride structure and all of them whether it is zirconia, thoria, ceria or Bi 2 O 3 bismuth oxide. So, these are all characterized by high oxygen ion conductivity. Out of the course absolute level of conductivity is a different as you can see from here; while bismuth oxide has a very high conductivity at a fairly low temperature but it is not so stable and it is little reactive chemically reactive.

So, bismuth oxide is normally not used although it has a high conductivity. Zirconium oxide 7.5 more percent scandium oxide. Scandium when you dope Sc 2 O 3 scandium oxide to zirconium dioxide it produces a very high conductivity. Unfortunately, this is again a rarely used because of the very high-cost of scandium oxide and non availability of this particular oxide. Cerium oxide with 5 more percent yttrium oxide or cerium oxide 10 more percent yttrium oxide, you have a fairly high conductivities. And they can be also used as an electrolyte of course has some disadvantages may be I will discuss in a minute what are those. But the most important solid electrolyte is zirconia stabilized or doped with yttrium oxide or zirconia 15 more percent calcium oxide.

So, Yttrium is normally preferred because it has a higher conductivity than that of calcium stabilizer zirconia. Thorium on the other hand as a much lower conductivity. So, they can be used as a very high temperatures, but normally it is costly as well as there is some problem of radioactivity and so. Until and unless it is absolutely essential a one does not use thorium oxide electrolytes. So, these are the relative conductivity, ionic conductivity of all the oxygen ion conductor, of course of different electrolytes are known to us.

(Refer Slide Time: 14:23)



Well, this we have discussed. When we are discussing about the defect structure of different oxides; and this is generalized picture of partial pressure partial pressure dependence of different kind of possible defects present in a oxide. So, in general one can notice here that there are 3 partial pressure ranges; broadly, they can be divide in to 3 ranges. In the middle range, you will see either it is n equal to p neutrality condition or we can follow this particularly for the oxide ion conductors this is the more suitable diagram. Where in the intermediate partial pressure range one can see the neutrality condition is V o; that means, oxygen vacancy and oxygen interstitial. So, they become equal.

So, it becomes a kind of stoichiometric oxide. Stoichiometric oxide with antifrenkel defect. This is an antifrenkel defect kind of situation and at a very high Po 2 at a very high Po 2. Of course what is high is not mentioned here usually that will depend on the particular oxide which is high, but the characteristics changes.

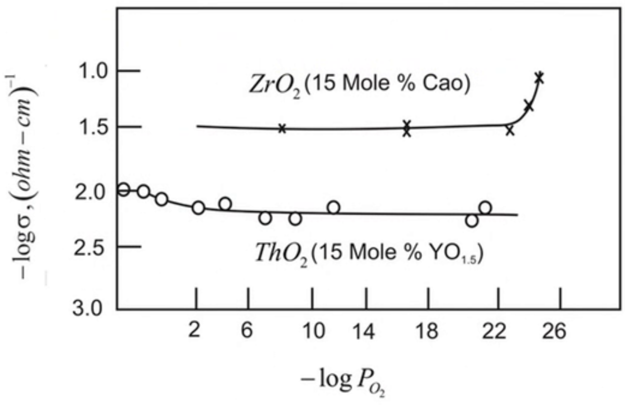
The high is basically characterized here. Because the nature of neutrality condition changes and one changes from a constant value of this defects to an increasing value of the defect. That means, this one oxygen interstitial increases beyond this point. Beyond at lower oxygen partial pressures this is remains constant independent of Po 2 whereas, beyond this point there is an enhancement in oxygen ion interstitial as a function of Po 2. So, that is how this boundary is characterized where it changes from in the Po 2 independent region to Po 2 dependent region.

On the left is also similar boundary condition is there. Once again from a Po 2 independent region it is changes to a Po 2 dependent region, but in this case it is oxygen vacancy the oxygen vacancy is the predominant defect on the left side that is lower Po 2. Whereas on their right side oxygen interstitial is the predominating defect others are lower concentration.

So, this is dominated in this region. This is dominated by oxygen interstitial whereas, in this it is oxygen vacancy. And in between both are same concentration they are same and therefore, you have a independent Po 2 independent conductivity. In fact for our purposes this is the region; most important region where it is not only a independent of Po 2 the conductivity impact the vacancy concentration and interstitial concentration are independent of Po 2. And they give rise to conductivity, so the mobile species the concentration of these actually determines what will be the conductivity.

So, the conductivity is proportional to this defect concentration either oxygen ion concentration, oxygen ion vacancy concentration or oxygen ion interstitial concentration. So, our interest is here in this we have Po 2 independent oxygen ion conductivity on this region is Po 2 dependent whole conductivity, although, interstitial is increasing in this, but the interstitial is also associated with whole conductivity. And therefore, this becomes an electronic conductivity in this case. And this is also purely n type conductivity on this case. So, this is our interest where it is independent and ionic conductivity.

(Refer Slide Time: 18:56)



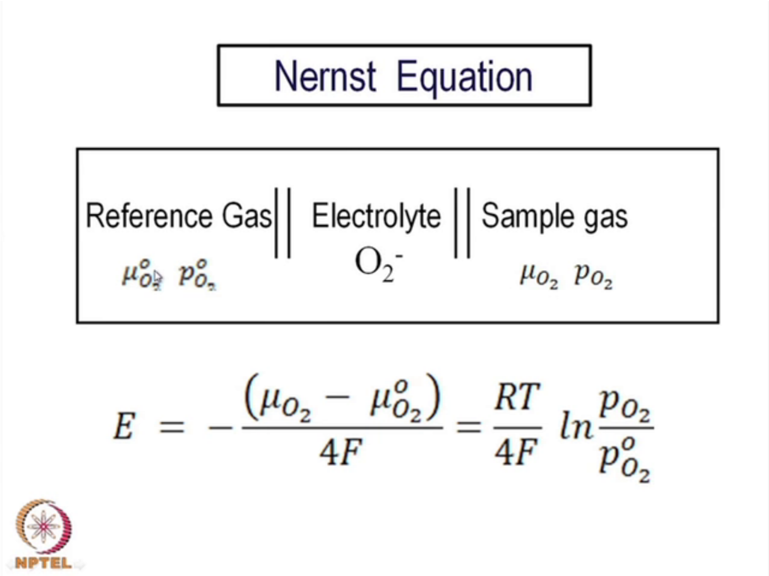
Oxygen partial pressure dependence of electrical conductivity of two most important oxygen ion conductors.

In fact, if you plot the 2 most important oxides which is our interest one we have sent zirconia calcia. So, the 15 more percent calcia zirconia, this is the variation of conductivity. These are experimental plots. So, one can see the conductivity remains independent of Po 2 from almost atmospheric condition; that is pure air to or down to a very low Po 2 like 10 to the power of minus 2 minus 22 atmosphere.

So, it is a very, very reducing condition even at the extremely reducing condition. The zirconia remains as an ionic conductor and it is dominated the conductivity is dominated by ionic conductivity. Same thing happens here in thorium oxide although the absolute conductivity is low. Here, this has a higher conductivity, a lower conductivity, but you do not see a after on here because the material do not become electronically conducting or n type conductor even at 10 to the power of minus 22 of atmosphere. Whereas, on this side there is a slight upturn at very close to the atmospheric oxygen partial pressure you have p type conductivity.

So, this actually needs to n type conductivity beyond certain partial pressure low in the lower range below 10 to the power of minus 22 atmosphere. Whereas, here above 10 to the power minus 2 atmosphere these becomes slightly hole conductor or a p type conductor. But otherwise from 10 to the power of minus 6 or 10 to the power of minus 4 to 10 to the power of minus 22 both of them behave as an ionic conductors. So, that is important points to be noted. So, because this is the variation or the nature of variation of conductivity as a function of partial pressure. We can assume that the within this range it acts as a good oxygen ion conductor and so it can be used as an electrolyte in an electrochemical cell or sometimes called concentration cell.

(Refer Slide Time: 21:53)

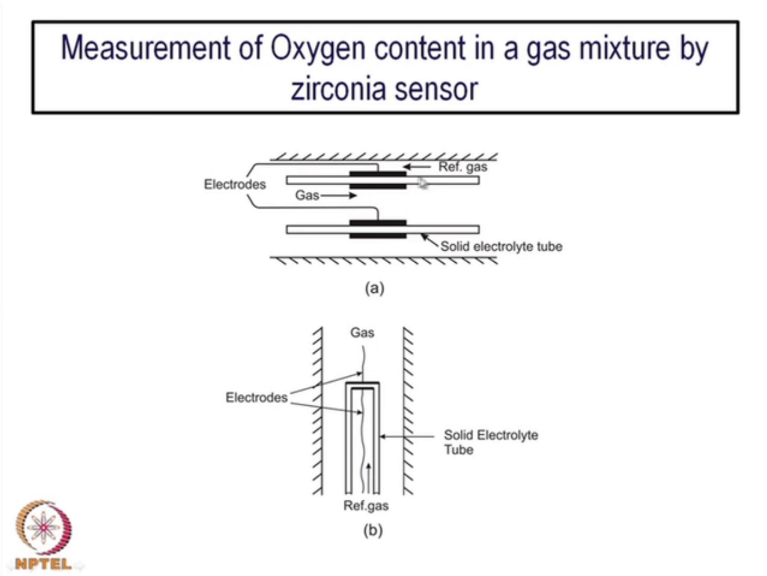


So, this is what one can represent an electrochemical cell. So, there is an electrolyte which is basically zirconia, zirconia calcium, zirconia yittria, yittria stabilized zirconium oxide. And then on either side you have a sample gas and a reference gas having 2 different partial pressures or oxygen potentials. So, reference gas whatever the oxygen partial pressure of reference gas which a it is mu 0 2; or chemical potential and that has is related to the partial pressure Po 2 0. On this side is mu o 2 and Po 2 0 and Po 2. So, this is one can say unknown Po 2 oxygen concentration or oxygen partial pressure this is a known one that is why is called reference.

Now, if you make a if you make a oxygen concentration or electrochemical cell like this. And we can find out what is the non stick from the non stick version what is the e m f generated. So, there will be an e m f generated because in a electrochemical cell it is an electrolyte and these are the 2 electrodes; one is anode and another cathode. So, by that one can find an e m f generated out of this. So, this is minus mu o 2 minus mu o 2 0 by 4 f; 4 is the number of electrons transferred during the reaction; oxidation reduction reaction. And that can be mu is nothing but RT ln Po 2. So, you have RT by 4F ln Po 2 by Po 2 0 or Po 2 naught.

So, this is the e m f. So, you by generating a electrochemical cells or constructing electrochemical cell that will generate in e m f. So, that can be measured quite easily. What is the electro electromotive force or e m f generated out of this cell? And that in this if we know all others being known the temperature of the cell has to be known and these are constants. So, if one knows this of this value then this can be determined. So, that is the basic principle when measuring the e m f and co-relating it to the partial pressure oxygen by this formula. All others being known one can find out what is the Po2 on this side this is reference and this is the sample variable.

(Refer Slide Time: 24:46).



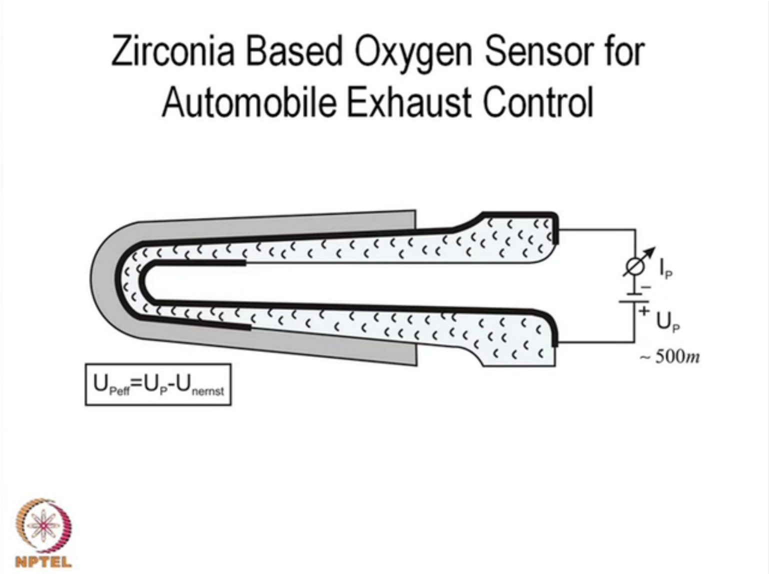
Well, how exactly one can utilize it. For example, if you want to find out the oxygen concentration or the oxygen potential, oxygen partial pressure of a gas you just simply take a tube, a ceramic tube made of zirconia, stabilize zirconia. So, these are the one, this is the one of wall and these the cross-section basically a schematic. So this is another wall same wall continuation of the other side. So, you make a cell by just putting some platinum electrodes here; this is only for the current collection. So, because gas is basically gas electrode one cannot use the gas electrode; for measurement or the e m f used a current collector here or a contact. So, this is the black area is basically a platinum electrode. And it has to be porous platinum electrode because the gas as to come in contact with the electrolyte.

So, these becomes electrode. So, the gas has to come in contact or go to the trouble to the interface between the electrode and the electrolyte. So, it has to be porous. So, one cannot use a platinum foil, but one as to use a porous platinum pent. That means, a thick film of platinum. So, the reference gas the outside is reference gas means air is a very fairly fixed oxygen partial pressure is nothing but 0.21 from the ratio of the nitrogen to oxygen. So, this is a very stable Po 2; and if you have a gas mixture of oxygen with some inert gas then that can be varied and or any other experimental gas. So, that e m f will be generated between these 2 electrodes the inside electrode; inner electrode and the outer electrode. Inner electrode is inside the tube and outer electrode is outside the tube. So, they are exposed 2 different gases and that will generate e m f. So, you measure the e m f and knowing the partial pressure of air you know what is the partial pressure inside? So, this is a very simple setup to measure the oxygen concentration in flowing gas utilizing zirconia oxygen sensors.

So, the tube actually the tube wall acts as a sensor very simple thing. So, it is the functional electrode functional property of the tube which can be which is being exploited to make it a oxygen sensor particularly oxygen sensor. Now, there can be a another configuration the same thing. Only thing is instead of the wall being used as the electrolyte; here one end wall because it is a this was both and open tube. So, the gas is coming from one side and flowing to the other side here we have a one end closed tube. So, the closed end can be used there also can be used as electrolyte. And the partial pressure can be sensed the only differences is the gas comes in and then goes to the strikes the flat bottom or the closed end. And then the other side or goes out from the same direction where there is a outside.

You have either air or different gas. Now, which side will be the reference and which side will be experimental; it depends on the requirement in this case the air is inside and the experimental gas is outside. So, depending on the requirement and depending on the situation under which it as to be used both possibilities exist. That is the inside can be used as an experimental gas or outside can be used as an experimental gas. There will be a furnace in both the cases, because the temperature is also important here. And to reduce the impedance and normally this sensors use are used about 600 degree centigrade. So, that the impedance of the cell or the resistance of the electrolyte you can sufficiently low for accurate measurement of the e m f. So, these are the 2 configurations in which zirconia oxygen sensors can be used. To measure the oxygen partial pressure or the oxygen concentration in some of the experimental glasses.

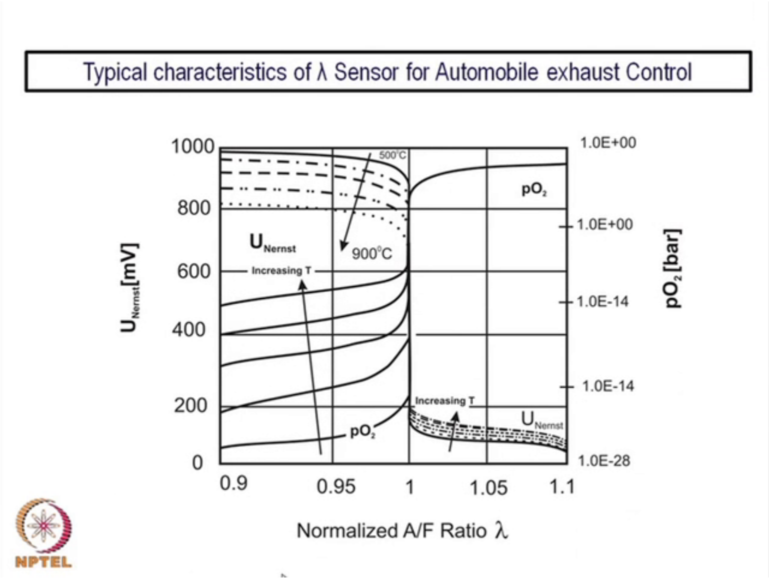
(Refer Slide Time: 30:11).



Now, this is an industrially used oxygen sensor; same thing basic principle remaining same. If the design is slightly different is this is also a one end closed tube is not a flat end, but a kind of circular end. So, this why its region is actually the electrolyte zirconia. So, it has been fabricated in the form of a thimble; a small length one end close tube, but not of uniform cross section or the wall thickness slightly varying wall thickness; these of course for mechanical advantage. And you have a slightly thicker wall towards the cold end whereas, the hot end it has a slightly thinner. And then this is a kind of porous round which protects this particular thimble and this black area is actually electrodes.

So, this is the outer electrode comes to up to this end and the lower electrode also comes through the inside of wall after this end. So, you can measure the e m f from this 2 points. So, this actually not only the whole of it is acts as a electrode, but here to the active electrode area; active cell area is basically this much. And these are and the kind of lead it can the painted portion basically acts as a lead and connection for the electrodes. So, this is very simple system, but it has a tremendous of use.

(Refer Slide Time: 32:08)



This is actually the cross section of what you call the lambda sensor for auto mobile exhaust. The basic purpose of measuring oxygen concentration in auto mobile exhaust is to control the pollution. It is the oxygen potential which becomes a measure of what is the extent of combustion, which is taking place inside the engine. And what kind of a air full ratio one has to be controlled; so that a complete combustion takes place. Because if there is a in complete combustion then lot of carbon monoxide will be generated which is a environmentally hazardous. And therefore, all automobiles these days actually uses this particular of sensor to control the combustion process. And also enhance not only the fuel utility or fuel consumption reduced the fuel consumption. But at the same time control the environmental pollution; so that, no carbon monoxide comes out of the exhaust gas.

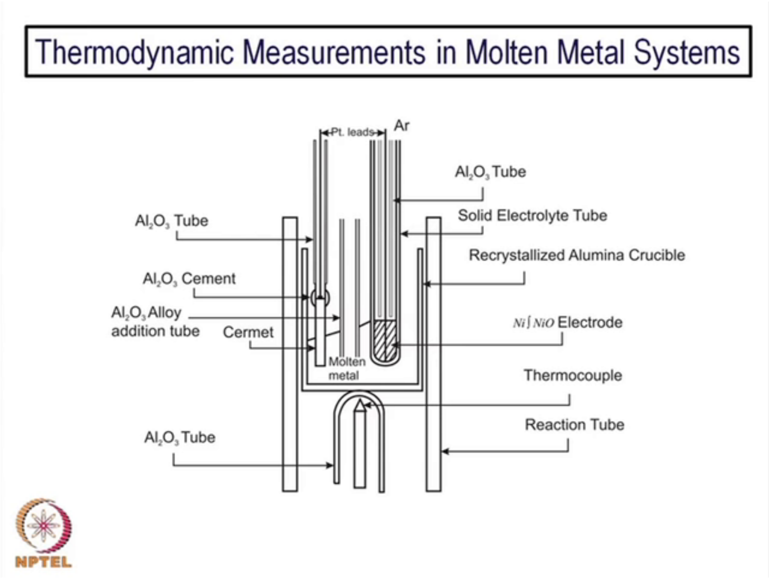
So, this kind of sensor actually is used at the end of the exhaust pipe or at the beginning of the not the end. And the beginning of the exhaust pipe as soon as the gas comes out of the engine in the exhaust pipe this kind of a sensor just like a spark plug. One can plug in this kind of sensor and measure the output. This a typical response of what we call as lambda sensor that is basically the ratio is called the lambda. And therefore, it call the lambda sensor. How it works? It operates at obviously at plotted at different temperatures you can see 500 degrees to 900 degrees.

Now, this is the normalized air full ratio. Normalize in the sense actually air to fuel ratio is about 14.5, but this has been taken as stoichiometric ratio has been taken as 1. And either it is a lean Po 2 lean fuel or a excess fuel. So, this is on the one side you can see this is the Po 2 this is the Po 2 is increasing in this passion on the side. And the e m f, e m f is plotted here. So, the e m f is very low in this region whereas, e m f is very high on this. It is basically the reference Po 2 reference Po 2 is again air.

So, compared to air if the Po 2 is very low then you have a very high e m f. Whereas, if the Po 2 is very close to air than very low Po 2, a very low e m f. So, this variation is just like this it has a very high value on the reducing condition whereas, a very low value on the oxidizing condition. So, there is a discontinuity there is a discintinuity exactly at the stoichiometric ratio. So, it is very sensitive in that is that is the reason the sensors are highly sensitive around this value. So, if a very small change in air fuel ratio the e m f drops or if it is slightly above on this side are lower side; then you have a very high Po 2. So, this is actually a very important from the sensing point of view.

So, one can electronically controlled or through the carburetor. Carburetor can be electronically controlled from taking the taking this input or taking the value from this. So, one can determine whether it is the high pure high pure ratio side or the low pure ratio side. And therefore and the carburetor can be controlled and one can find out the stoichiometric combustion. So, that that is very important from the point of various said from the elemental point of view as well as from the fuel economic point of view. So, that is the reason most of these almost all the advance cart today have this kind of a lambda sensor.

(Refer Slide Time: 37:16) .



And, that is based on zirconia sensor is a very stable and life is very long. So, there is no problem. Of course, one thing I forgot to mention that along with the lambda sensor one always uses as a catalytic converter. So, that is a catalytic converter in which the exhaust gas is allowed to flow through that. And it has certain catalysts normally some noble metal catalysts and they catalyses the carbon monoxide remaining carbon monoxide into carbon dioxide. So, no carbon monoxide actually comes out although you cannot avoid the release of carbon dioxide.

So, the only thing is that is the whatever, small amount of carbon monoxide even after this control small amount of carbon monoxide make them up, but that will get oxidized on the catalytic converter. However, if the catalytic carbon monoxide concentration is very high then the catalyst life goes down. And therefore one needs to control the carbon monoxide concentration in the exhaust gas which goes into the catalytic converter. So, these 2 devices these 2 devices; one is the sensing devices another is actually a catalytic converter these 2 has to work in tandem.

So, that the commercial efficiency as well as the environmental problems are eliminated. Now, in addition to this kind of gases measurement, now the gas measurement where one needs to measure the oxygen and concentration of different gas mixtures of different industrial gases even. In fact, another very important area where these sensors are extensively used is in furnaces.

So, just like in automotive engine you have a combustion process going on in the industrial furnaces even ceramics on a ceramic (( )). Many of the ceramics today are fitted with a oxygen sensors, zirconia sensors or oxygen measurement sensors. Again, the purpose is primarily to control the combustion. So, that you get the complete utility of your fuel there is no excess oxygen or excess air into the system. So, in automatic control of ceramic (( )). You have the senses becomes quite handy and most of the modern furnaces do have or are fitted

with this kind of sensor. So, that the combustion process the fuel combustion process can be the controlled quite efficiently. So, that is another area where besides automobile; there is huge application of zirconia oxygen sensors in combustion control of the industrial furnaces.

In addition coming back to this picture. In addition to the oxygen concentration or measurement of oxygen concentration in gaseous system; one can utilize zirconia system zirconia sensors for the liquid systems also. Many of the metals do have some dissolved oxygen or sometimes there is a oxides present in the in the metal. So, there is an oxygen potential it will be large, it will be small but oxygen concentration measurement of oxygen concentration in molten metal’s or molten alloys; is also a very great interest. And the same zirconia system can be used for measurement of for creation of a electromotive electrochemical cell and one can measure that. This is one example where this whole crucible is basically made up recrystallized alumina having some molten metal. And this is your molten metal, this is a alumina, this is an cerment.

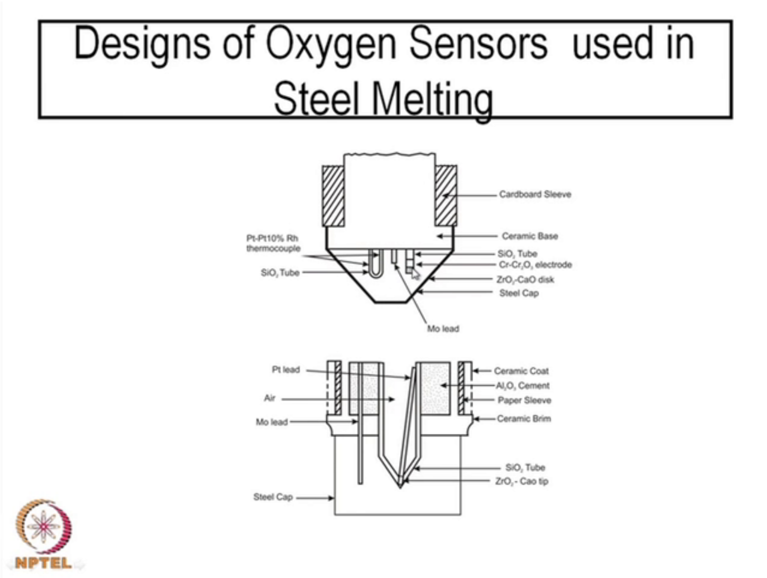
And, this is the tube; this is the one end tube, one end closed tube zirconia tube. These actually acts as the electrolyte which is dipped inside a molten metal. And this once again the wall is acting as the electrolyte inside you have a reference electrode and outside you have in contact with the molten metal. So, by that process it generates an e m f. So, that is a major of what is the oxygen potential of the molten metal; and the reference electrode here is of course of different types not in air. As a different electrodes, but a different system has been used as a reference electrode. It is a mixture of nickel oxide and nickel, nickel and nickel oxide metal, metallic nickel, and a mixture of metallic nickel and a nickel oxide.

Now, this also at a particular temperature it has a definite oxygen partial pressure. Because it is an equilibrium partial pressure between metal metal and metal oxide so, nickel when it oxidizes to nickel oxide at a particular temperature; it corresponds to a specific partial pressure of oxygen. So, whenever there is a coexistence of nickel and nickel oxide then a specific thermodynamically a specific partial pressure is maintained. So, as long as nickel any nickel oxide coexisting that partial pressure will never change. Of course it will change if the temperature changes, but otherwise that partial pressure knowing the knowing the temperature one can fix what is the exact partial pressure for nickel oxidation. And by that same technique one can use this reference this mixed oxide as the reference electrode.

So, inside you have mixture of nickel and nickel oxide which maintains a reference electrode. Outside you have a molten metal for which we want to measure the partial pressure oxygen. So, it generates an emf between reference electrode and the molten metal and the electrical contact here is through a cerment. Here this is cerment which is a conducting material and it is immersed in molten metal. So, through the molten metal it actually connects this surface. So, the inside you have a reference and outside you have the metal and the connectivity or the contact is made through this immersed cerment and molten metal being a electrically conducting material. So, it contacts up to this point. So, actually it measures if you measure a potential between this there is a platinum electrode, platinum where their which connects this surface. And therefore between this platinum and this platinum here the cerment is also connected to another platinum wire.

So, between these 2 platinum wire you will get a emf which represents the oxygen potential of the metal. So, the dissolved oxygen or some other oxygen potential in some other way there will be a thermodynamic equilibrium and certain oxygen partial pressure are normally available. Sometimes is very important to measure those partial pressures for different puposes. And this is another set up by which one can use zirconia for measurement of oxygen sensor, measurement of oxygen concentration. And this is thermocouple we just measure the temperature because if you remember the Nernst equation you also need to know the temperature. So, the precise measurement of temperature is also important, if you want to measure the oxygen partial pressure by this process.

(Refer Slide Time: 46:40).



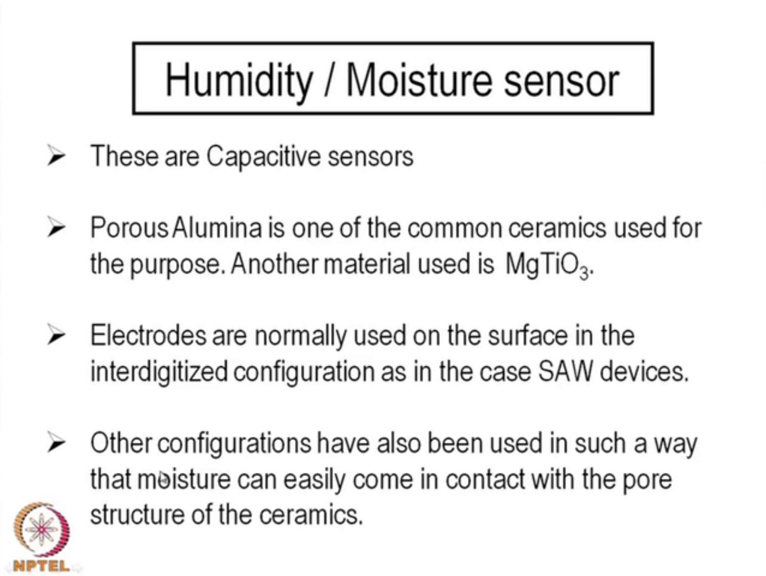
This kind of system is extensively used were extensively used extensively used in steel melting. Steel melting is nothing but an oxidation process. From pig iron you are oxidizing carbon very high concentration of carbon and then you are making steel with very low concentration of carbon. So, from 3 to 4 percent of carbon we are bringing it down to about 0.2, 0.3 percent may be still lower. So, actually you have to oxidize the carbon by that process you make steel. So, to monitor monitor the oxidation process of the pig iron within the ld convertor. You will always need to monitor the oxygen concentration or oxygen potential available in steel.

So, these are some design of oxygen probes called in oxygen probes for to measure the oxygen concentration in steel. These are of course slightly different design and you have a small molybdenum wire. Then this is actually a very small tablet of zirconia calcia fitted inside a quartz tube. So, it has been sealed actually it has been sealed the whole tube is not made of zirconia oxygen because it becomes costly. So, instead of that certain ceiling technology has been used. So, that at the end of a pure silica tube one can have a tablet of zirconia; that tablet zirconia acts as the electrolyte. It is one side, it is connected to the steel molten steel. The other side there is a electrolyte; there is a reference electrode. And in this case the reference electrode is not nickel nickel oxide it is actually chromium chromium oxide.

So, it depends on what kind of partial pressure of oxygen you are expecting in steel. Since, the partial pressure oxygen in steel and at a very high-temperature is fairly low. You need a not nickel nickel oxide, but a chromium chromium oxide. So, a chromium chromium oxide acts as a reference electrode inside the silica tube and at the end of the silica tube zirconia calcium disk as been fitted. And that is exposed to steel molten steel of course that is a stroud to start with. This is a steel stroud it is actually immersed in the liquid steel at a temperature about 1600 degree centigrade. And at that temperature this cover this cover melts and molten steel comes in contact with this surface. Otherwise it is protected by a steel cap.

So, it is a steel cap which melts at the molten liquid temperature, molten steel temperature. And exposes this electrolyte to the molten steel and then there is another silicate in the form of silicate you tube which contains the thermocouple. So, this measures the temperature. And there is a molybdenum rod which actually comes in contact the liquid steel and makes the contact on the on this surface. So, this becomes a contact. So, it goes up and finally, you measure the emf between inside and outside. That is how one can measure it is actually a disposable type of sensor because it cannot stand for too long at that very high aggressive temperature. So, it is a kind of disposable sensor. Once it measures both the measures the temperature and the emf and it gets melted away in the molten liquid. This is a another design, but let me not discuss this particular design is very similar purposes is used.

(Refer Slide Time: 51:02)



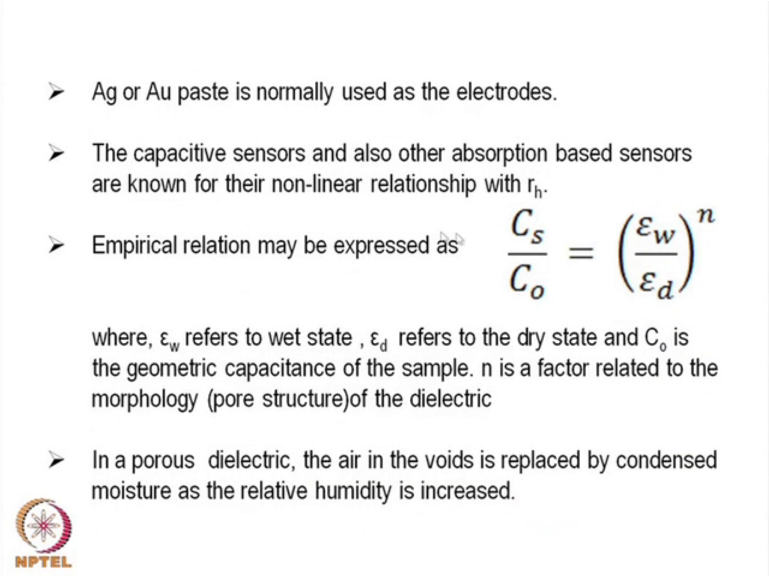
So, those are the various applications, principal the principal of operation of zirconia oxygen senses in basically is an electrochemical system. Electrochemical cell which produces some emf between the 2 different partial pressures; one partial pressure being known other partial pressure can easily be determined. The last topic in this series is humidity sensor or moisture sensors.

Well, we have use we have discuss 2 varieties of senor; one utilizes the variations of the conductivity as a function of gas concentration that is the semiconducting oxides. Other we have seen the oxygen ion conductivity or electrolytes. So, it measure the emf and emf it becomes proportional to the partial pressure of oxygen. Here, we do not measure the conductivity or the emf, we measures a capacitance. It is basically an insulating variety of oxide at a porous oxides in general a porous oxide. So, within the a pore depending on the percentage of condensed condensed moisture the capacitance changes. Basically, the moisture has one kind of dielectric constant and ceramic material have a different kind of dielectric constant.

So, the capacitance value changes as a function of moisture content which is getting deposited into the pores of the ceramics. So, this is the reason it is a capacitive type of sensor. We are not measuring either the emf or the resistance. Porous alumina is one of the common ceramics used for the purpose. Other material of course is magnesium titanate. So, there are few just like a porous alumina can very well used as a sensor of humidity sensor just the capacitance changes. And one can have the variation of capacitance as a function moisture content the electrodes are normally used on the surface. It is not the bulk again is not the bulk capacitance what one measures is basically inter digitized configuration as you have seen in case of the SAW device.

So, it is on the surface the electrodes are on the surface in a inter digitized form. And that measures the capacitance, but below that you have a porous structure. And that porous content different quantities of moisture depending on humidity condition outside. So, that changes the capacitance and the variation of capacitance actually is directly proportional to the moisture content. Other configurations have also been use in such a way; that the moisture can easily come in contact with the pore structure of the ceramics. So, it is basically once again a kind of porous, porous configuration of the electrodes because otherwise, the moisture cannot come in contact with the pores below the electrodes. And therefore, it cannot function properly. So, the design is important here one of the designs is inter digitized, but then isolated pockets can also be used.

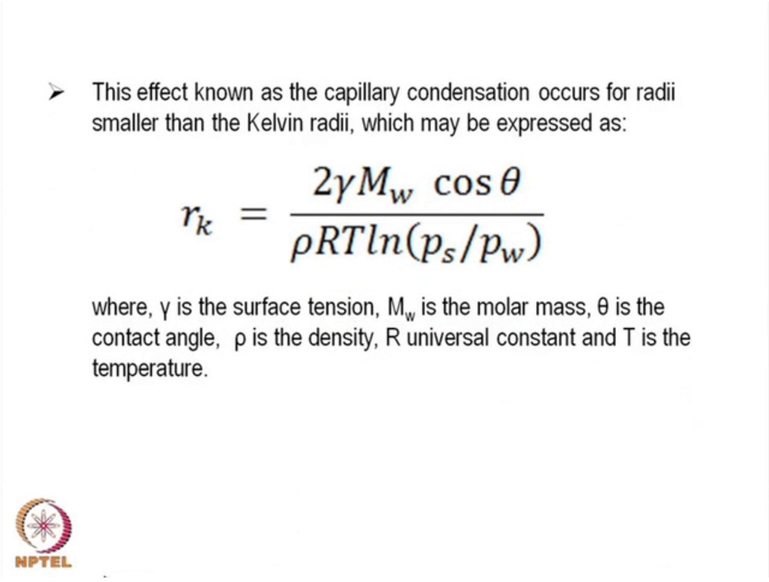
(Refer Slide Time: 55:02)



I am not going to details of those structures, but basically I am going to discuss the principal gold or platinum paste is normally used as a porous electrode. The capacitance capacitive sensor and also other absorptions based sensors are known for their non-linear relationship with rh is relative humidity. So, one of the difficulties once again is a kind of nonlinearity once one we get. The empirical relation may be expressed as C s by C 0 equal to epsilon W by epsilon d. So, W is a wet condition and ed refers to the dry condition. C0 is a geometric capacitance of the sample depending on the overall geometric size and shape.

You have a capacitance value and n is a factor related to the morphology the pore structure of the dielectric. So, depending on the morphology, fineness of the pore the overall porosity and that this n is dependent on those parameters. In a porous dielectric the air in the voids is replaced by condensed moisture as the relative humidity is increased. So, higher is the relative humidity more and more condensation takes place inside the pores and that changes the capacitance value of the ceramics.

(Refer Slide Time: 56:40)

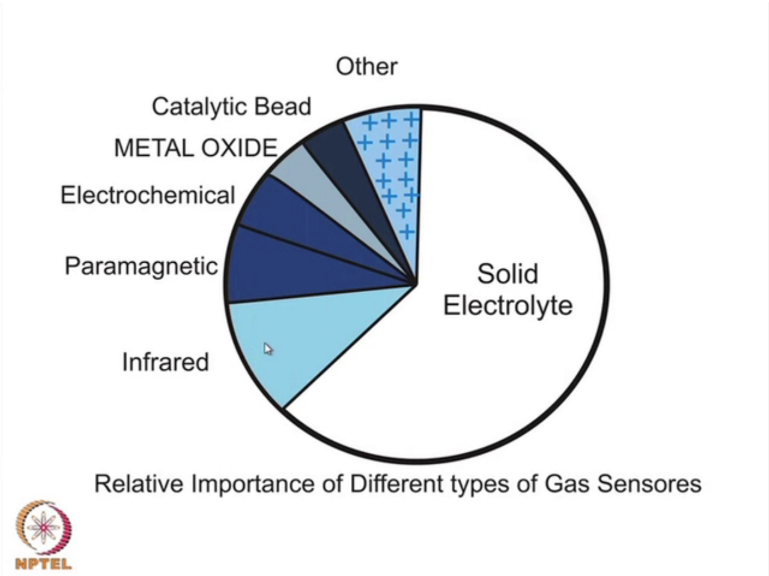


And, in simple in a empirical formula this effect know as the capillary condensation occurs where radii is smaller than the kelvin radii. So, everywhere condensation cannot take place. It is a large pore the condensation may not take place and therefore, there will much not much effect of on the capacitance. So, the pore size particularly the pore structure has to be in controlled in such a way that there is a condensation takes places in the within the relative humidity range of our concerned.

So, our interest whatever the relative humidity you want to measure depending on that the pore structure has to be designed properly. Because rk is the kelvin radii is related to different parameters. 2 gamma M w cos theta by rho RT ln (P s by P w); where gamma is the surface tension; and M w is the molar mass; theta is the contact angle of that particular pore. And then and the that depends on the material of the pore or the material in which the pores are there; row is the density; R is the universal gas constant; and T is the temperature. So, there is relationship with the surface tension, cos theta, theta is the contact angle of that surface low density and so on. So, depending on that you have a particular size of the pore in which the condensation will take place. If the row if this one is too large or too small then condensation will not take place and the material will not be used cannot be used as a sensor.

So, just if you have a insulating material and the pore structure can be controlled in such a manner that the condensation takes place. You have a variation in capacitance; by measuring the variation capacitance it can be related to the relative humidity of the environment. So, this is how one can also use ceramic materials for the sensing of moisture one kind of gas in that sense. So, we have discussed various types of gas sensors based on ceramic materials, whether it is a reducing gas or a combustible gas. In fact I forgot to mention that the lpg sensors have been used in practice quite extensively based on tin dioxide sensors. So, tin dioxide sensors have been use quite extensively to measure the combustible gases including the cooking gas. So, gas leakages can be gas leakages can be determine this. So, I think you have come to the close of our discussion.

(Refer Slide Time: 56:52)



This is the kind of this is the kind of distribution of different of sensors, solid electrolyte zirconia sensors is the maximum. And then you have metal oxide sensors here catalytic bead sensor, we have not electrochemical sensor these are not of course, the solid electrolyte sensors the liquid electrolyte sensor, paramagnetic sensors are also available in the infrared sensors are also different gases and many others. But you can see the zirconia sensor is the largest volume of sensors available in the industry. So, with this we come to the end of this discussion on ceramic gas sensors.

And thank you for your attention.