Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 64
Hydrogen Sensing Part - 2

In the previous class we have learned the different type of sensors like the mechanical sensor, work function sensor, resistive sensor and the thermal sensor. Now in this lecture we will learn the other types of Hydrogen Sensors. We know that hydrogen sensor these are very important when hydrogen safety is being considered and from the next class we will start learning about the hydrogen safety. Now, the first type of sensors that we will learn in this class is the Optical Sensor.

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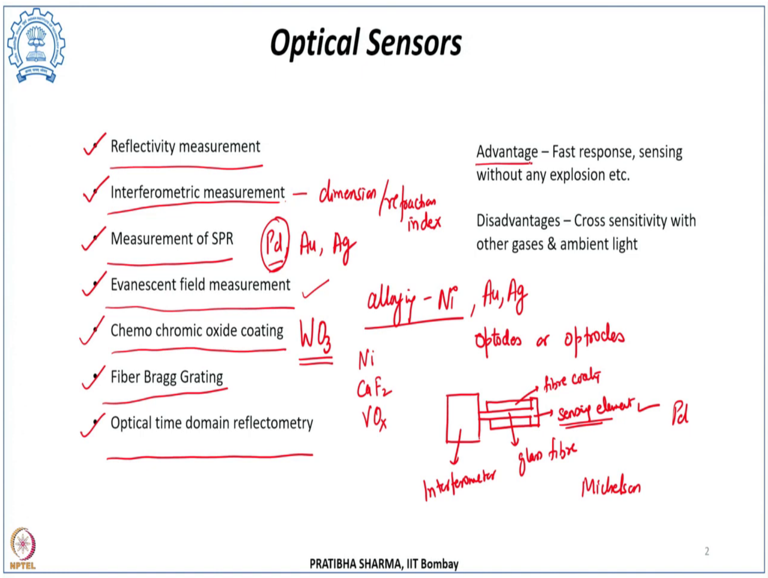

Now, as we have seen in the previous class that sensing is based on change in some of the properties of the sensing material and that can be correlated with the detection of hydrogen or the concentration of hydrogen. Now in the optical sensor, it is based on the change in the optical properties of the material.

Like some of the materials, metals or oxides when they are coated along the length of an optical fiber or on to the tip of the optical fiber in that case when hydrogen gets adsorbed onto these materials there is an expansion that will occur radially and axially and that can be monitored that can be used to identify the gas concentration.

The optical fibers which are used in these optical sensors these are known as optodes or optrodes. Now, different measurement techniques can be used for the change in the optical properties like the first one being Reflectivity measurement. Now, in this method the cleaved portion of the optical fiber to that is deposited a hydrogen sensing element. So, this is the fiber coating, the central one is the glass fiber and then we have an interferometer.

Now this sensing element thin coating of palladium it is deposited on the cleaved end of the optical fiber. And then when this sensing element which could be palladium when this is exposed to hydrogen then its reflectivity changes and that reflectivity is used to detect hydrogen and it is correlated to the hydrogen gas concentration. So, this is what is in the reflectivity measurement.

Now, the second way of measuring is or second way of gas sensing is interferometric measurement. Now in interferometric measurement, there is a change in the dimension or refractive index of the gas sensing material when it is exposed to hydrogen. So, either the dimension or refractive index of the gas sensing material it changes and in that case that change causes a phase change into the fiber optic beam and that change is measured using any interferometric technique.

Now, there could be different interferometers that can be used like the Michelson interferometer or the Fabry Perot interferometer that can be used for sensing. So, this change is correlated with the gas concentration. Now, the another method could be measurement of Surface Plasmon Resonance.

Now this surface Plasmon resonance, this is an surface electromagnetic wave which propagates parallel to the interface between the metal and dielectric and this is highly sensitive towards any structural changes of the metal surface. Now, there are several ways in which this surface plasmon can be generated like there it could be a prism coupler or it could be a grating coupler or there could be different wave guides.

Now there are few materials which support the surface plasmon resonance and they are sensitive towards hydrogen like the materials could be palladium or gold or it could be silver.

Now, when these materials are subjected to or these are exposed to hydrogen, in that case there occurs a change in the refractive index.

Now, that change it is correlated with the resonance that is the resonant wavelength or with the change in the resonant angle of incident or with the change in the intensity of reflected light. And usually like we have seen that palladium is the material which is widely being used for gas sensing.

Now, there are certain issues that this palladium when it is used as a film; palladium is used because its properties changes. Both the electrical and optical properties it changes when it is exposed to hydrogen. Thus this can be used not only in optical sensor, but other type of sensors also. But the major problem that remains is the blistering or the delamination of the surface palladium layer and that can be protected or taken care of by alloying.

So, we can have alloying of the palladium and like this can be done with nickel. Now, alloying with nickel that what it does is it shifts the phase transformation towards higher concentration. Now, this delamination is a result of expansion that takes place on hydrogen adsorption and repeated cycling expansion and contraction that causes delamination. Now, when we alloy it with nickel it makes film more stable.

At the same time, we can also have alloying maybe with another element like with gold or with silver and this increases the stability of the palladium film and it also makes that response faster in the optical sensor. Another way to do is we can have a supporting film to the palladium layer itself and that supporting film improves onto the adhesion of the palladium layer and reduces the delamination.

Now, this supporting film could be either like it could be nickel or it could be calcium fluoride or it could be vanadium oxide. So, these layers they help in the stability of the palladium film. Now the another method could be evanescent field measurement. Now, this evanescent field this is an electromagnetic field which is generated at the border or the boundary or we will say interface of the two types of mediums.

For example in case of optical fiber it occurs at the core of the optical fiber. Now and this decays also. This evanescent field it decays from the core as we move away from the core and that decays exponentially. Now, in case of such sensors what we do is the cladding of the optical fiber is removed. Now, when the cladding of optical fiber is removed, thereafter a film of hydrogen sensitive material like palladium or palladium silver, that is deposited onto the core.

Now, what happens is when that is exposed to hydrogen, hydrogen adsorption will take place and as the hydrogen adsorption will take place in that film its refractive index will change. Now, when the refractive index will change there will be a change in the evanescent field as well that gets attenuated and that could be measured in terms of change in the transmittance of the material. So, this is how we can even use this as a way to detect hydrogen.

Now another way could be a Chemo-chromic oxide coating. Certain oxides they react with hydrogen and they change their color. Like one of the example is tungsten oxide and this tungsten oxide on reacting with hydrogen it forms tungsten bronze and this is subjected they react with hydrogen and then they change color and this happens in the chemo chromic oxide because of the change in the oxidation state.

Now, this, these oxides can be used as a means to detect the concentration of hydrogen. Another method could be Fiber Bragg Grating. Now in the grating, it is the grating it is in fact edged onto the core of the optical fiber and this provides a sort of periodically modulated refractive index. And on that grating surface is the hydrogen sensitive material like the palladium is being deposited. Now, when there is a hydrogen adsorption that takes place, we know that gratings reflect certain wavelengths.

Now, when the adsorption takes place there is a change in the characteristics and as such the Bragg wavelength changes in these type of grating and there could be even long period gratings as well where the period is long and they are more sensitive and they have a better performance when used as optical sensor. Another one could be optical time domain reflectometry. Now, in this the reflectance is measured along the entire length of the fiber optic cable instead of at a particular point.

So, in this case this is a sort of distributed hydrogen sensing and using only one device. So, the signal could be spatially resolved and then we can use it for sensing over a longer distance. Now this is about the optical sensors. They have certain advantages like they have faster response, they can be used without being exposed to certain oxidizers or being electric current being flown through that so that there are chances of less of explosions being originating from the sensors.

The disadvantage with these type of sensors is they have a cross sensitivity. Cross sensitivity would be signals from the other gases or even from the ambient light they interfere with the detection of hydrogen. Now, the another type of sensor could be acoustic sensors.

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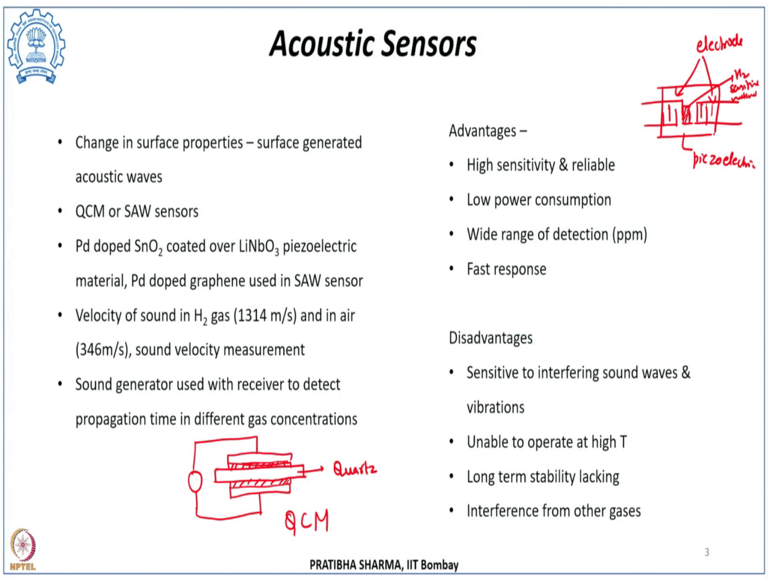

Now, these acoustic sensors they are based on the change in the surface property of the piezoelectric material and that generates a surface acoustic wave. Now, there are different devices that can be used for detecting the surface acoustic wave, like the simplest one is the quartz crystal micro balance. Now, in the quartz crystal micro balance what is done is there is a quartz there is a small thin disk of quartz to that on both sides the electrodes are printed.

Now these electrodes they cause a deformation into the quartz and that there is a resonance and that resonance frequency changes when such a deformation takes place if there is an accumulation of certain mass. Now, on the electrode there is a hydrogen sensing material also being deposited and then that is connected to external signal. So, this is like the quartz crystal micro balance.

Now in these type of materials in this type of device when there is a hydrogen or any gas accumulation onto the surface; say for example, in this case if this is a hydrogen sensitive material hydrogen gas gets adsorbed then there is a change in the resonance frequency and that change in the resonance frequency that is attributed or that can be used to detect the hydrogen concentration.

Or there could be even the surface acoustic wave sensors. These are similar to the quartz crystal micro balance and in the surface acoustic type of wave type of sensors, we have a piezoelectric material, onto it the two inter digitized electrodes they are deposited to that there is a film that is of hydrogen sensitive material. So, the there is a piezoelectric material, then there are two electrodes and then there is a hydrogen sensitive material.

Now, this one of the electrode, that converts the electrical signal into surface acoustic waves and the other one electrode that converts that signal into electrical signal. Now, the difference between the input and the output, that gives a sort of signature of the hydrogen gas concentration as there is an adsorption that takes place into the hydrogen sensitive film.

Now, there could be different materials that can be used for the acoustic sensors like the palladium doped SnO_2 which could be coated over lithium niobate $LiNbO_3$ and that is the piezoelectric material. Or it is possible that palladium doped graphene could be used in the SAW sensor; the surface acoustic wave sensors.

Another method that could be used in acoustic sensor is we know that the velocity of sound in hydrogen is much higher than the velocity of sound in air. Like in hydrogen it is 1314 meters per second while in air it is 346 meters per second and this difference can be used as a means to measure the hydrogen concentration.

So, the sound velocity measurement it is done. For that there is a sound generator which is used and then there is a receiver and this receiver is used to detect how much time it takes for the sound to propagate in different gas concentration. So, that propagation time is calibrated against the gas concentration and that can be used to detect hydrogen gas.

Now, these type of acoustic sensors they have advantages that they have high sensitivity, they are reliable, they require less of power consumption and they have a wide range of detection. So, we can have detection range of even parts per million range they have a faster response. But at the same time they have a disadvantage that they are sensitive towards the other sound waves interfering sound waves or the vibrations.

So, the noise could be an interference in these sensors. They are unable to operate at high temperatures and the stability long term stability is the biggest challenge. There could be interference that could arise from the other gases other than hydrogen and that could behave a make its use limited.

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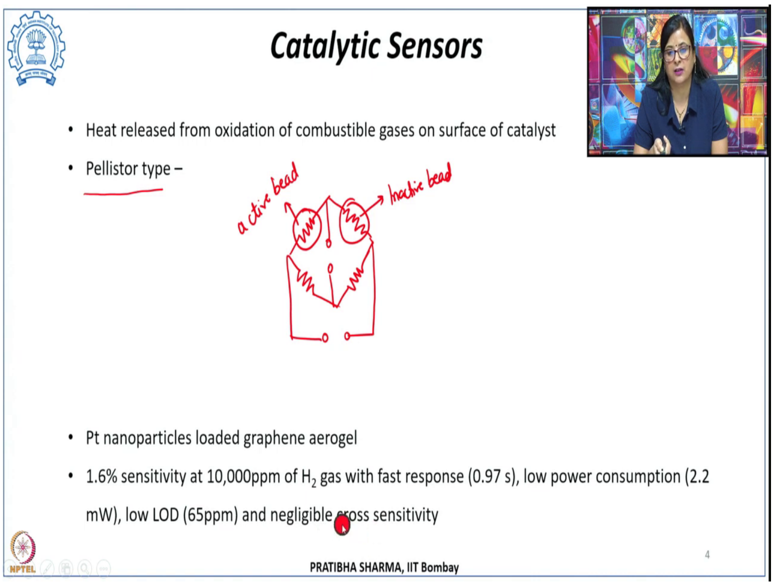

Now, another type of sensors are catalytic sensors. Now, these catalytic sensors they are based on the principle that when heat is being released because of oxidation of certain combustible gases on the surface of the catalyst, so, that will change the properties and that change in property can be used to measure the hydrogen gas concentration.

Now we know that hydrogen is a combustible gas and when it reacts with the different oxidizers it reacts exothermically and it releases depending upon the higher heating value let us say it is 142 mega joule per kg. Now that release of heat or the change in temperature can be used as a means to detect to sense the hydrogen gas concentration.

Now, one of the one of this type of sensor is Pellistor type of sensor. In pellistor type of sensor there are two platinum coils and these platinum coils are covered by ceramic beads. So, there are two platinum coils which are covered by ceramic beads and these are connected into a Wheatstone bridge.

So, there is one platinum coil with a ceramic bead that is an inactive bead. Now, this inactive bead it acts as a reference and the another one is an active bead. Now this active bead, that is coated with hydrogen sensitive material. Now, when hydrogen is absent and only air is present the Wheatstone bridge is balanced. And however when there is hydrogen present in the environment when an electric current is passed through the circuit the beads they will get heated up.

Now, this beads gets heated up and the adsorbed hydrogen, if there is hydrogen here the adsorbed hydrogen it reacts with the adsorbed oxygen exothermically and releases heat at a higher temperature. So, this occurs at a higher temperature. Now, this exothermic reaction onto the active bead that will further increase the temperature and this change in the temperature will result into change in the resistance and that change in resistance will create an imbalance in the Wheatstone bridge.

Thus we can measure that and then we can correlate it with the hydrogen gas concentration depending upon what is the temperature rise. Now, in this case like the different materials have been considered for the catalytic sensor like the platinum nanoparticles loaded graphene aerogel they have been studied and they have shown to have a good sensitivity 1.6 percent at 10000 ppm of hydrogen gas. Even the response time has been very fast 0.97 seconds.

They require very low amount of power. So, low power consumption 2.2 milli watt with a lower level of detection of even 65 ppm and they have a negligible cross sensitivity. So, this is pellistor type of catalytic sensor.

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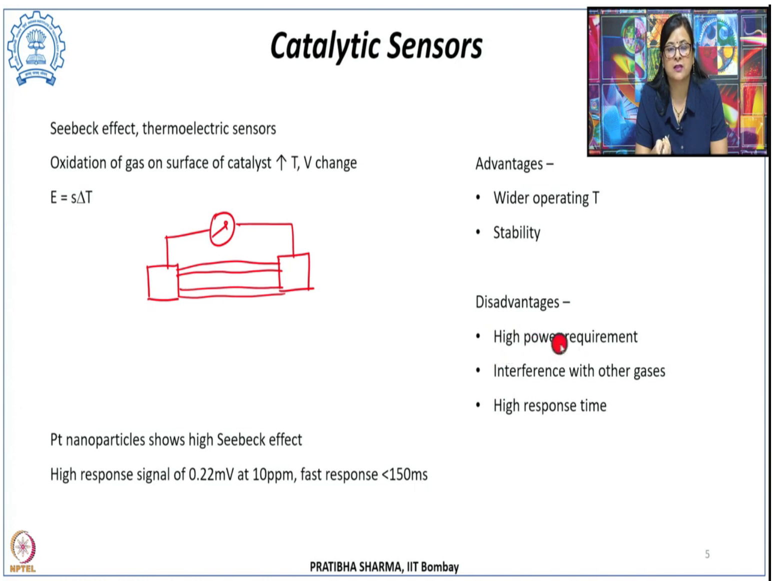

Another type of catalytic sensor could be one which is based on the Seebeck effect and that type of catalytic sensor they are also known as thermoelectric sensors. Now, we know that Seebeck effect if there is a temperature difference between two points in a conducting or a semiconducting material then there is a voltage which is generated.

So, if there is a point which is at a higher temperature another point which is at a lower temperature and then if these two points they have a difference of temperature a corresponding voltage is generated. Now, what is considered in the catalytic sensor is similar to what we have seen in the pellistor sensor the oxidation of the gas that takes place on the surface of the catalyst what it does is it increases the temperature and that increase in the temperature will result into a change in the voltage.

Now, this change in voltage is related to the hydrogen gas concentration. So, this change in voltage is the Seebeck coefficient times the change in the temperature and that is correspondingly related to the hydrogen gas concentration. Now there could be different materials like even the platinum nanoparticles they have been studied for such type of catalytic sensors and they have shown that they have a high Seebeck effect.

So, they have shown that it is like the response signal that we can get from these platinum nanoparticles was observed to be 0.22 milli volt at 10 ppm and also a faster response of less than 150 milliseconds. So, there are advantages like they have a wider operating temperature range and they are stable.

But at the same time the disadvantage is because we require higher power, so, the power requirement in these type of sensor it is higher. At the same time there could be interference with the other gases present. And sometimes the response time could be even higher.

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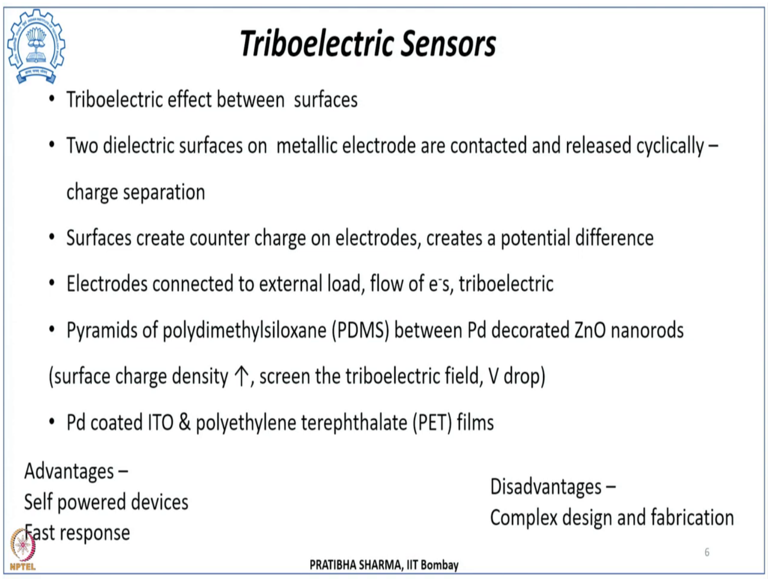

The another class of sensors is Triboelectric sensors. Now in the triboelectric sensor, these are based on the triboelectric effect that is between say two different surfaces. So, if there are two dielectric surfaces on a metallic electrode they are contacted and then released cyclically and because of that there occurs a charge separation.

Now, depending upon the electron affinity one of the surface may acquire certain charge and get negatively charged and the another surface may lose certain charge or electrons and then it may get positively charged. Now, this charge separation that occurs on these dielectric surfaces that create a sort of counter charge onto the electrodes and that counter charge on the electrodes that creates a sort of potential difference.

Now, when these electrodes they are connected to an external load a flow of electron will take place and that is known as triboelectric effect and the device is known as triboelectric generator. Now, there the materials like could be used are as per the literature studies like the pyramids of polydimethylsiloxane. So, PDMS has been used and that is between the palladium decorated zinc oxide nanorods. Now, the palladium has a lower work function.

So, there is a surface charge transfer from zinc oxide to palladium that will take place. And what will happen is the adsorbed oxygen in the absence of hydrogen that takes up the electrons and as such there is less number of electrons. However, when there is hydrogen also present if the environment has certain amount of hydrogen, that adsorbed hydrogen reacts with the adsorbed oxygen producing water and so thus the electrons are available in this process.

So, the oxide reacts with the hydrogen and then there are electrons which are not taken up by the oxide ions and that causes the availability of free electrons which increases the surface charge density and that screens the triboelectric field which will result into a voltage drop and that can be considered as a measure of the hydrogen gas concentration. Now, there are other materials also which has been used for such sensors like the palladium coated ITO and polyethylene terephthalate, PET films.

Now, these types of sensors they have advantage that they are self-powered devices, they have fast response, but the major challenge is that they have a complex fabrication process or a complex design.

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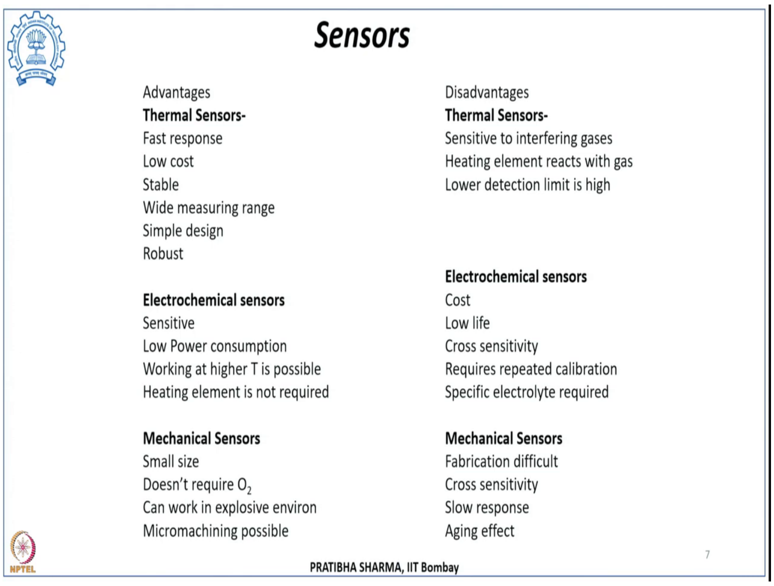

Now, in the previous class we have seen other sensors, let us quickly recollect their advantages and disadvantages, like we have seen the thermal sensors. Thermal sensors they have fast response, low cost, they are stable and they have a wide measuring range; they have a simple design and they are robust.

But at the same time they have disadvantages like there is a cross sensitivity from the other gases, the heating element that could react with the gas, there is a lower detection limit which is even higher. So, that lower detection limit itself is quite high and that makes its use little limited in the lower range detection.

The other class of sensors we have seen was electrochemical sensors. They are sensitive, they require lower power, higher working temperature is possible with these type of sensors and we are not using any heating element in these types of sensors.

But the cost is the major challenge with these, the cost is higher, there are specific electrolyte requirements which increases the cost, they have a low life then there is a cross sensitivity from the interfering gases and calibration is frequently required in electrochemical sensors, so these are the disadvantages associated.

For the mechanical sensors that we studied their size is small, they do not require oxygen, they can even work in the explosive environment and for them micromachining is possible.

But that makes it difficult to fabricate that is the disadvantage of mechanical sensor, then there could be cross sensitivity, slow response and aging effect is seen in mechanical sensors.

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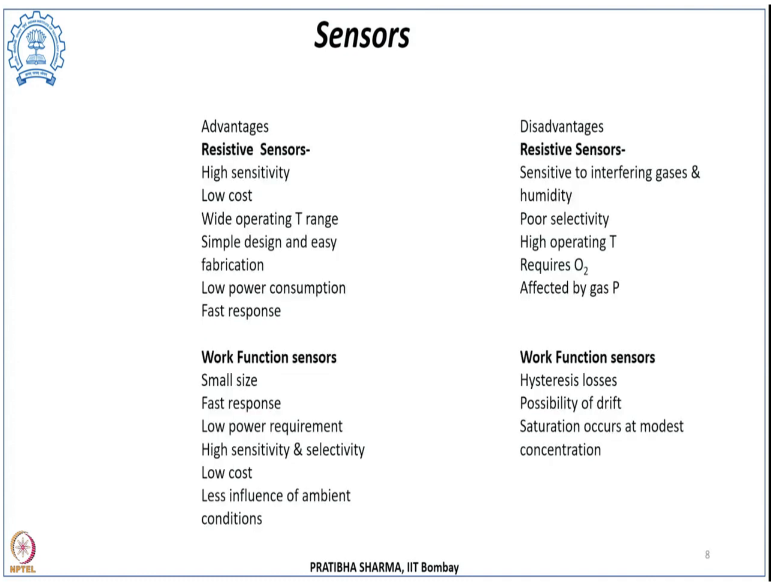

In the resistive sensors that we have seen in the previous class they have a high sensitivity, low cost, they have wide operating temperature range, simple design and they are easy to fabricate, they require less of power consumption, they have a faster response. But the disadvantage is they can have sensitivity towards other gases and humidity. So, there is a poor selectivity towards hydrogen, they can have higher operating temperature, require oxygen and they are affected by the gas pressure.

The work function sensors they are smaller in size, they have a faster response, they require less of power, they have high sensitivity and selectivity, low cost and they have less of influence of the ambient condition. But the major disadvantages are there is a hysteresis loss involved, possibility of drift and the saturation occurs at modest concentration.

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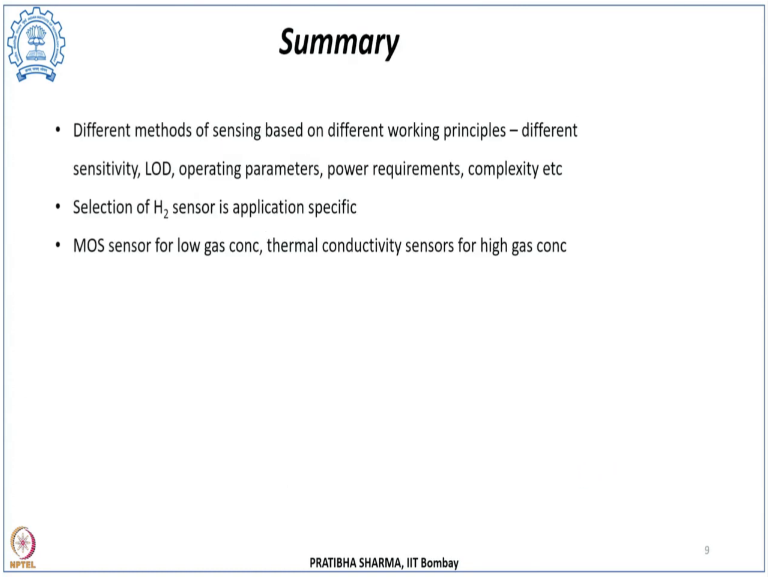

To summarize these sections onto the on the hydrogen sensing, we have seen the different methods of hydrogen sensing which are based on different working principles and based on the working principle the sensitivity, the level of detection, operating parameters, power requirements and the complexity may vary from sensor to sensor. Now, which sensor will be used for a particular application that depends on the application itself.

So, the selection of hydrogen sensor is highly application specific. For example, metal oxide sensors, they will be they can be used for low gas concentration while the thermal conductivity sensors could be used for higher gas concentration. So, these are all application specific.

In the next class we will see the hydrogen safety and its safety related challenges, what are the major considerations when it comes to hydrogen safety at the point of production, storage utilization and transport.

Thank you.