Selection of Nanomaterials for Energy Harvesting and Storage Application
Prof. Kaushik Pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture - 19
Hydrogen Storage

Hello my friends, now we are going to discuss our new sub chapter on Hydrogen Storage. So, basically from the name itself you can understand in this particular chapter we are going to discuss about that how we can capture the hydrogen and how we can store it for the future purpose.

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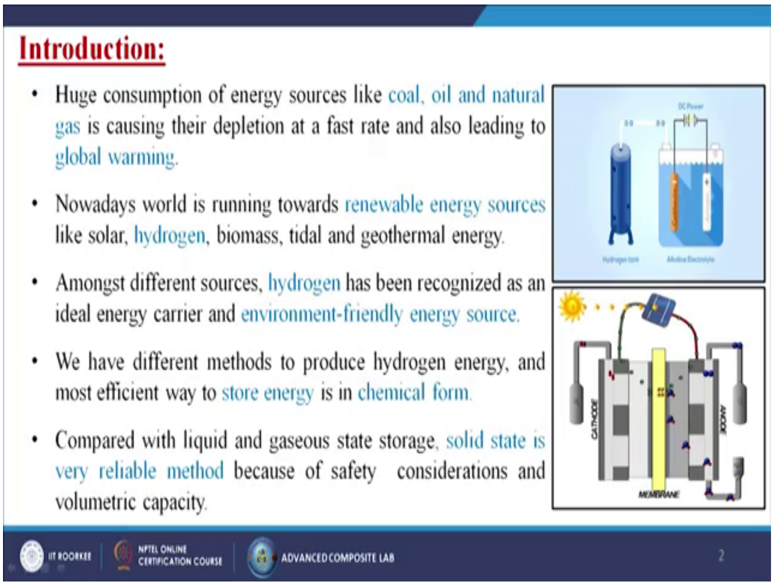

So, basically the huge consumption of energy sources like coal, oil and natural gas is causing their depletions at a fast rate and also leading to global warming, yes of course, because that is a fixed source. So, everyday just we are extracting those from the mines and automatically after some years automatically they are going to be finished and also when we are burning this particular coal or maybe the oils they are creating the huge toxic gases.

So, basically they are going into the environment and which causes the problem to the human health or maybe that pollutions to the mankind or maybe the human beings. Nowadays world is running towards the renewable energy sources, last couple of lectures we have discussed about different types of renewable energy sources that basically from the sunlight or maybe that water. So, we are able to take those particular energy and we are trying to convert those energy into the electricity. So, basically like solar, like hydrogen, like biomass, like tidal, like geothermal energy.

So, in this particular lecture we are going to discuss about briefly on the hydrogen storage or maybe the hydrogen energy. Amongst different sources hydrogen has been recognized as an ideal energy carrier and environmental friendly energy source, because the hydrogen generation is plenty. So, and also in near future it is not going to be stopped rather we can increase it.

So, basically if we are able to capture that hydrogen then it will be may be in future fuel for us. Compared with liquid and gaseous state storage solid state is very reliable method because of safety considerations and volumetric capacity. Yes, of course, because for that capturing the hydrogen as a liquid or maybe into the gaseous state, the biggest problem is that we have to make such kind of container not only that it should be leak proof, the material whatever we are using for making that container that should have the long life otherwise it cannot sustain, it should sustain the high pressure or maybe sometimes the temperature.

But now the question is that if we are able to capture that hydrogen in a solid form, so what will happen? We can keep it for a longer time and as and when it requires simple we are we can give or provide certain kind of temperature or may some kind of pressure.

So, that, that solid state will directly convert into the gas and that gas we can utilize for the future. So, scientist are thinking like that, that capturing of the hydrogen in a solid state format, so basically how the hydrogen can be stored or maybe the measured. So, basically the hydrogen storage is measured by two parameters: one is called the gravimetric density another one is called the volumetric density. What is that gravimetric density?

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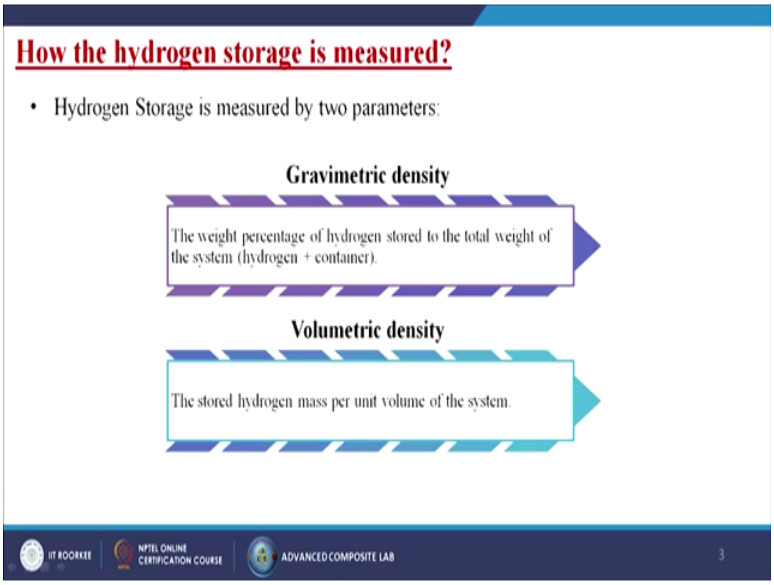

The weight percent of hydrogen stored to the total weight of the system like hydrogen plus container, if we talk about the volumetric density the stored hydrogen mass per unit volume of the system. So, either one is by the weight another is by the volume, so that is only the basic two differences. Now, what are the characterization techniques of hydrogen storage? Now the condition is that we are going to capture the hydrogen, what the characterization we need to do on may be performed by which we can prove yes, this is the storage hydrogen.

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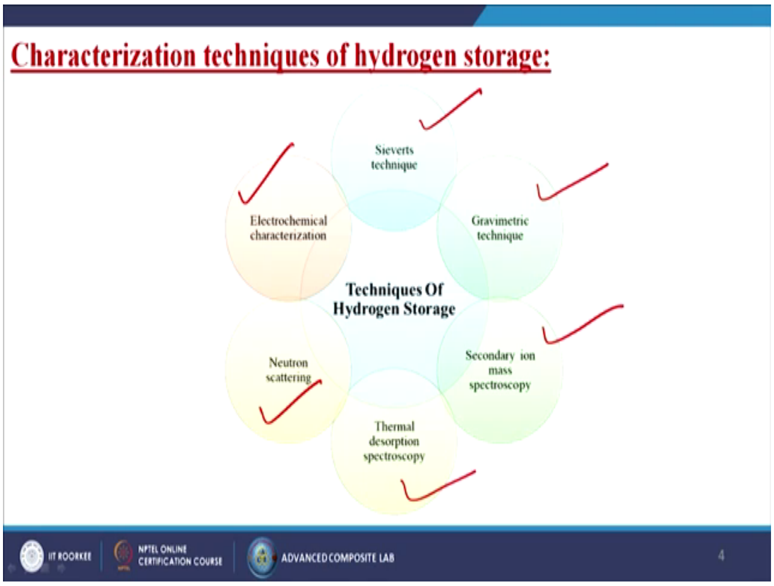

So, there are several methods like Sieverts technique, gravimetric technique, secondary ion mass spectroscopy, thermal desorption spectroscopy, neutron scattering and the last one is called the electrochemical characterizations. So, there are total six number of techniques are available till today, so first we are going to discuss one by one.

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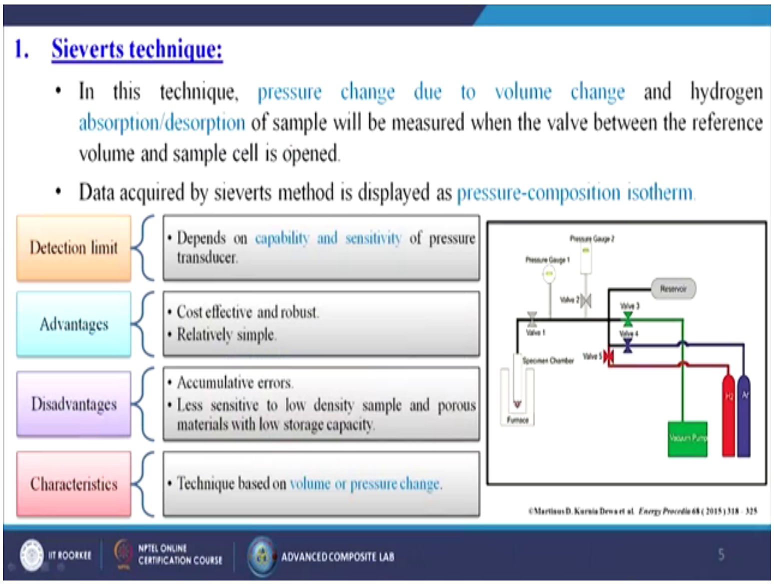

So first one is called the sieverts techniques, what is that? In this technique pressure change due to the volume change and hydrogen absorption and desorption of sample will be measured when the valve between the reference volume and the sample cell is open. Data acquired by sievers method is displayed as pressure composition isotherm. Simple, we are having one standard, so based on the standard basically we are going to characterize the storage hydrogen over there.

So, now you see we are having that hydrogen gas and we are having the argon, argon is nothing but here the reference material. So, in this particular case how we are going to capture and what is the detection limit depends on capability and sensitivity of pressure transducer. Advantages: cost effective and robust, relatively simple process; disadvantages: accumulative errors, less sensitive to low density sample and porous material with low storage capacity. Why we are using the porous materials? Because the porous material is having that ability that it can capture the hydrogen inside it or maybe inside the pores.

What is the characteristics? Technique based on volume or maybe the pressure change. So, simple, I am having that porous materials, so I am just creating some kind of pressure change in between that, so that it can capture the hydrogen. So, in this manner we can store the hydrogen inside it.

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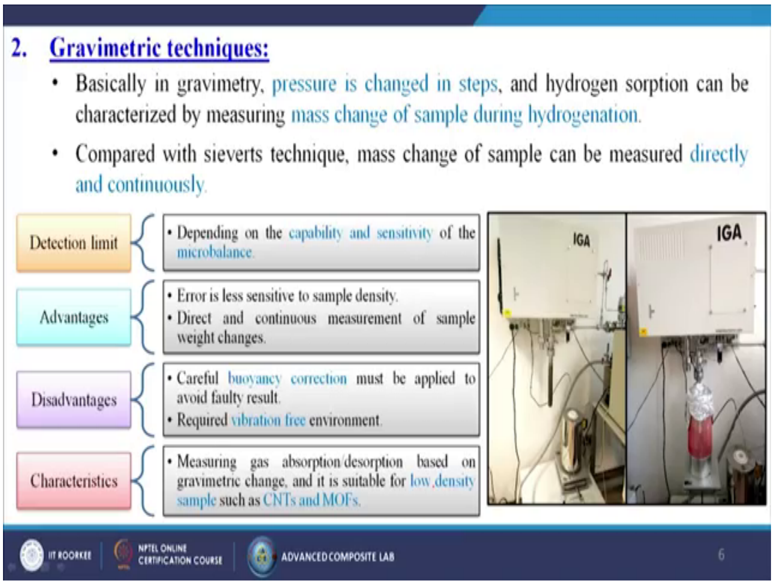

Next one is called the gravimetric technique. So, basically gravimetry pressure is changed in steps and hydrogen sorption can be characterized by measuring mass change of sample during hydrogenation. Hydrogenation is nothing but the incorporation of the hydrogen inside the system. Compared with sieverts techniques mass change of sample can be measured directly and continuously.

So, what is the detection limit? Depending on the capability and sensitivity of the microbalance, advantages: error is less sensitive to sample density, direct and continuous measurement of sample weight changes. Disadvantages: careful buoyancy corrections must be applied to avoid the faulty results, required vibration free environment.

Characteristics: measuring gas adsorption and desorption based on gravimetric change and it is suitable for low density sample such as carbon nanotubes or may be the MOFs that is nothing but the Metal Organic Frameworks which will come later.

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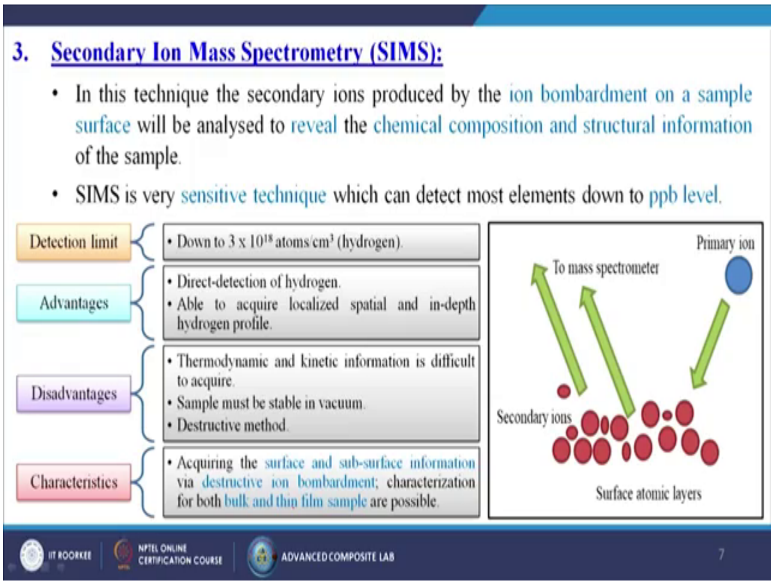

Next third one is called the secondary ion mass spectrometry, in this technique the secondary ions produced ion bombardment on a sample surface will be analysed to reveal and chemical composition and structural informations of the sample itself. SIMS is very sensitive technique which can detect most elements down to ppb means parts per billion. So, any less amount of materials also it can be detected by this particular techniques, so in the ppb level.

So, what is the detection limit? Down to 3 into 10 to the power 18 atoms per centimeter cube means of hydrogen of course. Advantages: direct detection of hydrogen can be possible, able to acquire localized spatial and in depth hydrogen profile. Disadvantages: thermodynamic and kinetic information is difficult to acquire, sample must stable in vacuum, destructive methods; of course, because you are hitting porous materials which is fully absorbed by the hydrogen by the ion bombardment. Characteristics: acquiring the surface and subsurface information via destructive ion bombardment; characterization for both bulk and thin film samples are possible. So, this is the whole about the secondary ion mass spectrometry.

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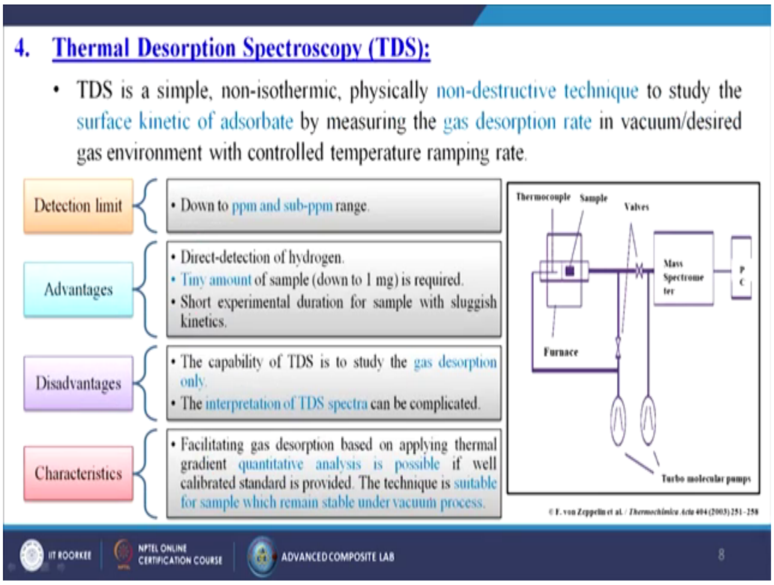

Next is Thermal Desorption Spectroscopy. So, TDS in short is a simple non isothermic, physically non destructive technique to study the surface kinetic of adsorbate by measuring the gas desorption rate in vacuum or may be the desired gas environment with control temperature ramping rate. So, simple we are hitting that particular materials and slowly it is releasing the gas itself.

So, either we can do it into the atmosphere or may be with some which gas; the gas volume should be known to us prior to the experiment. And then what is the increase or maybe increment in the volume that easily we can measure that should be due to the hydrogen when we are hitting that particular materials with a constant ram temperature. So, what is the detection limit? Down to ppm parts per million and sap ppm range, last case it was ppb parts per billion here it is little bit goes down and it is into ppm. Advantages: direct detection of hydrogen, tiny amount of sample down to 1 milligram is required, short experimental duration for sample with sluggish kinetics.

Disadvantages, the capability of TDS is to study the gas desorption only, the interpretation of TDS spectra can be complicated. Characteristics, facilitating gas desorption based on applying thermal gradient, quantitative analysis is possible if well calibrated standard is provided. The technique is suitable for sample which remains stable under the vacuum process. That means, when we are doing the vacuum, so the material itself should not decompose. So, it should remain same then only we can get the better results. Neutron scattering is little bit the advanced techniques.

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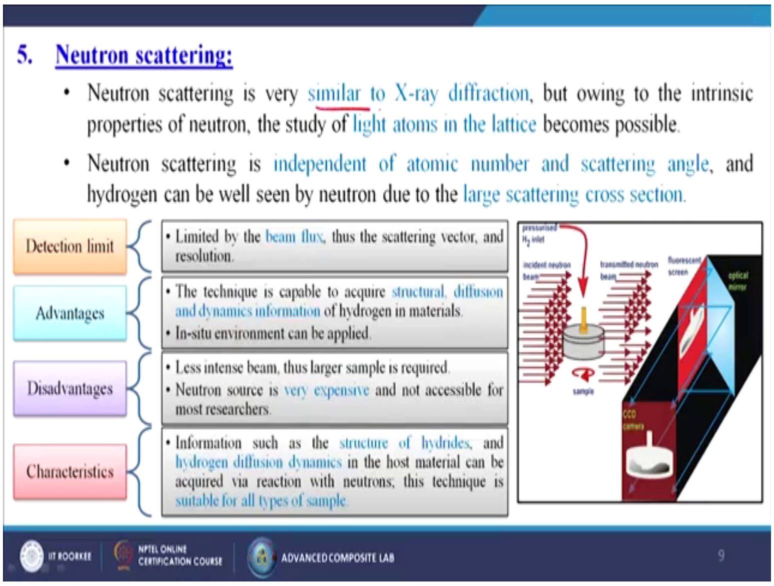

So, neutron scattering is very similar to X ray diffraction like XRD, but owing to the intrinsic properties of neutron, the study of light atoms in the lattice become possible. Neutron scattering is independent of atomic number and scattering angle, and hydrogen can be well seen by neutron due to the large scattering cross sections. So, simple what we are doing.

So, basically in this particular case you can see that the pressurized hydrogen inlet over here. So, by which we are injecting the hydrogen inside the system, and this is basically known as the sample, it is rotating and then we are simply doing the incident neutron beam over there. So, this is the incident beam and this is the through or may be transmittance or may be the transmitted neutron beam.

And now I am having that fluorescent screen over there and simple we are catching the image that what quantity of material means here of course, the hydrogen is stored inside the system. So, simple it is a one kind of X ray kind of things. So, suppose we are having any problem in our bone and joint and doctors are doing the X ray, so basically through that we are seeing inside the materials that how much quantity of the materials has been absorbed or maybe dissolved inside the system.

Detection limit: limited by the beam flux, thus the scattering vector and resolution. Advantages, the technique is capable to acquire structural, diffusion and dynamics information of hydrogen in materials, in situ environment can be applied. Disadvantages, less intense beam, thus larger sample is required, neutron source is very expensive; as I told already it is the latest technology that is why it is very expensive in nature, not accessible for most researchers, because this equipment is not available everywhere.

Characteristics: information such as the structure of hydrides and hydrogen diffusion dynamics in the host material can be acquired via reaction with neutrons, because the neutron is passing through the sample itself; this technique is suitable for all types of samples.

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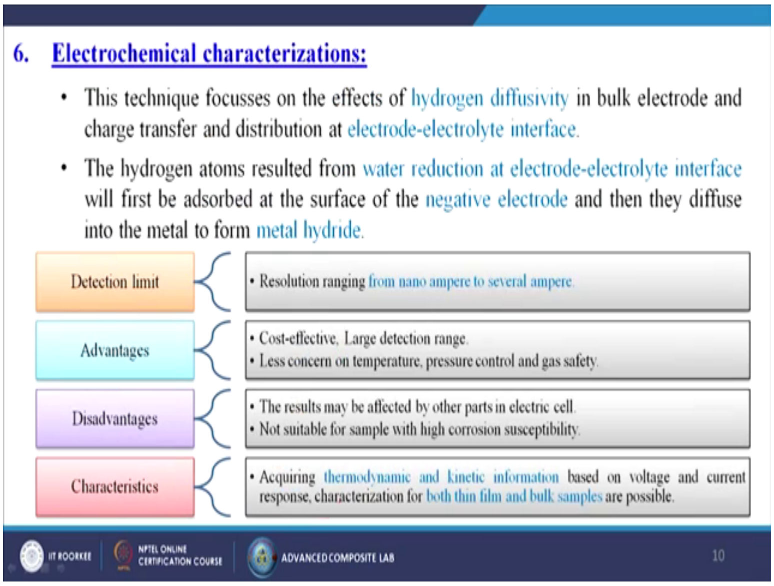

Next one is called electrochemical characterizations. The techniques focuses on the effects of hydrogen diffusivity in bulk electrode and charge transfer and distribution at electrode electrolyte interface. The hydrogen atoms resulted from water reduction at electrode electrolyte interface will first be adsorbed at the surface of the negative electrode and then they diffuse into the metal to form the metal hydride.

Detection limit: resolution ranging from nano ampere to several ampere that is a input current basically to the electrodes. Advantages: cost effective, large detection range, less concern on temperature pressure control and the gas safety. Disadvantages, the results may be affected by other parts in electric cell, not suitable for sample with high corrosion susceptibility. Characteristics, acquiring the thermodynamic and kinetic information based on voltage and current response, characterization for both thin film and bulk samples are possible by this particular method.

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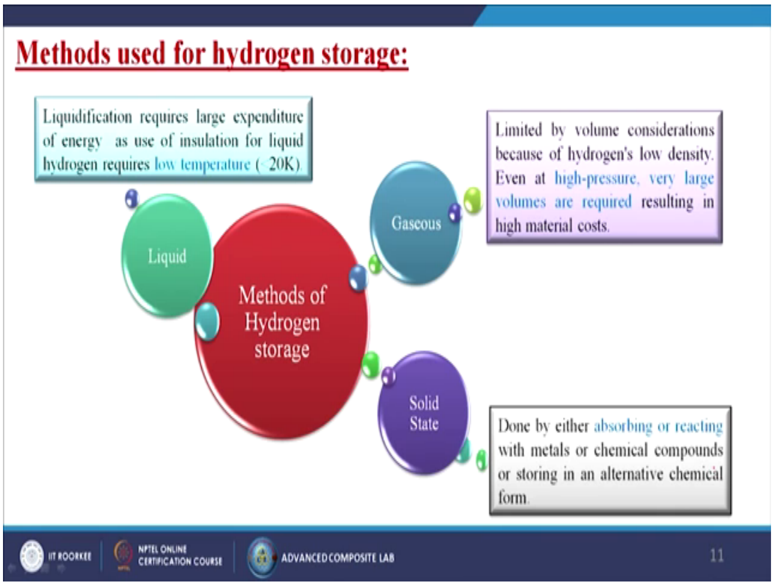

Now, basically what are the methods used for hydrogen storage. First is called the in the liquid formations. So, liquidification requires large expenditure of energy as use of insulation for liquid hydrogen requires low temperature that is less than 20 Kelvin.

As I told already and not only that we have to made that container also which can sustain in that particular temperature for a longer time, so liquid. Then come to the gaseous. Limited by volume considerations because of hydrogen's low density, even at high pressure very large volumes are required resulting in high material cost. Here we need a bigger container basically, and not only that temperature is also the another prime considerations in this particular case, so that is why the people are trying to do it by the solid state.

So, done by either absorbing or reacting with metals or chemical compounds or storing in an alternative chemical form. So, simple, suppose I am having that particular materials, now I am adding the hydrogen with hydrogen it is reacting and as a composite I am storing that particular materials as and when I require maybe I can give heat or may be the changing the pressure. So, simple from that particular composite materials hydrogen gas evolving will be taking place. So, that is the basically concept over here.

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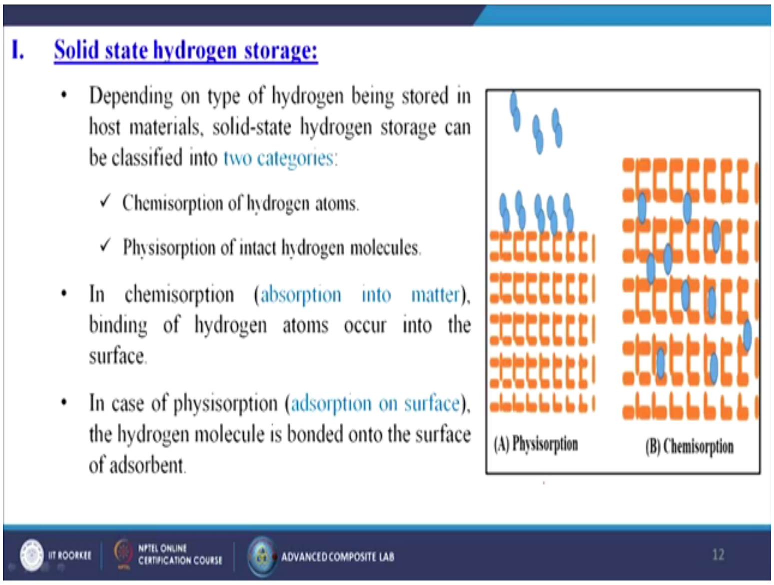

Next first one is called the solid state hydrogen storage. Depending on type of hydrogen being stored in host materials solid state hydrogen storage can be classified into two categories, what are those? First one is the chemisorption of hydrogen atoms; that means, some kind of chemical reaction will be taking place.

Second one is the physisorption of intact hydrogen molecules, so physically the hydrogen molecules will be present into the system. In chemisorption, absorption into matter binding of hydrogen atoms occur into the surface itself. In case of physisorption, absorption on surface the hydrogen molecules is bonded onto the surface or maybe of the adsorbent. So, one is that it will stay on to the surface another case it will go inside the materials into the molecular level, so that is the difference in between the physisorption and the chemisorption case.

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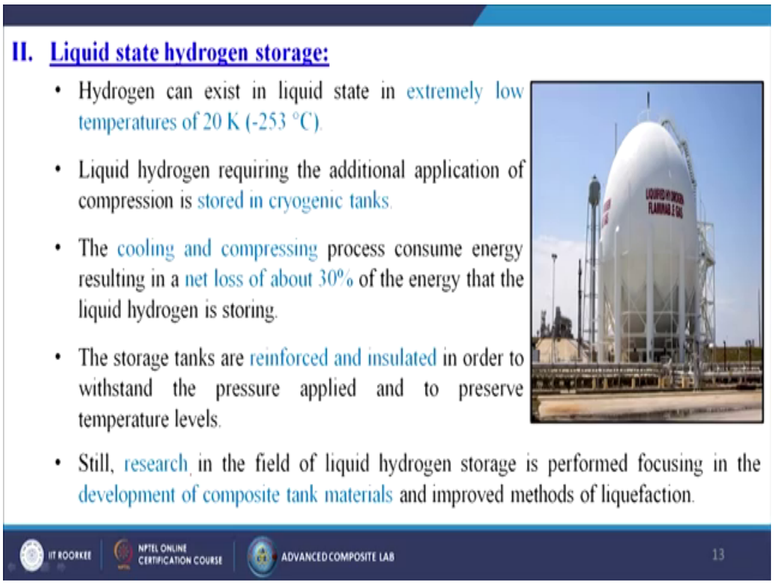

Next one is called the liquid state hydrogen storage. Hydrogen can exist in liquid state in extremely low temperatures of 20 K or may be less than that that is nothing but the minus 253 degree centigrade. Liquid hydrogen requiring the additional applications of compression is stored in cryogenic tanks, because minus 250 degree centigrade without using the liquid nitrogen it is not possible.

So, that is why in this particular case we can see the image and how we are maintaining that temperature constantly. The cooling and compressing process consume energy resulting in a net loss about 30 percent of the energy that the liquid hydrogen is storing. The storage tanks are reinforced and insulated in order to withstand the pressure applied and to preserve the temperature level constantly for longer time. Still research in the field of liquid hydrogen storage is performed focusing in the development of composite tank materials and improved methods of the liquefaction.

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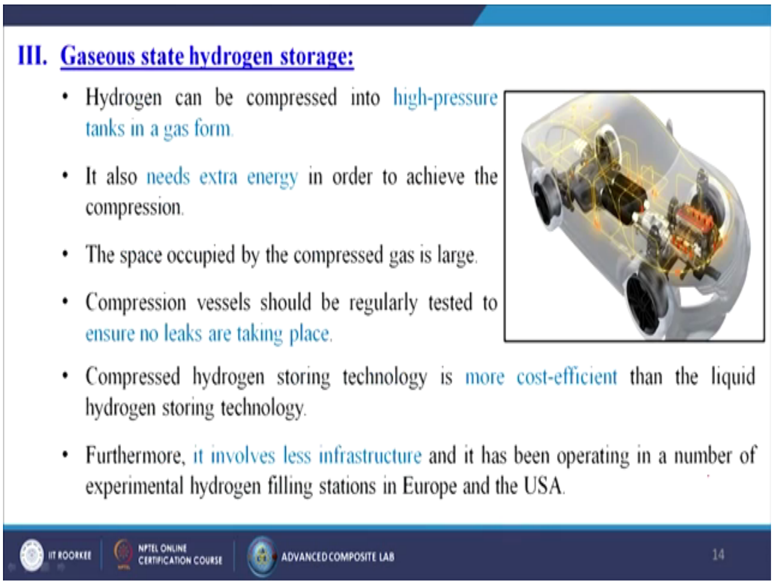

Next gaseous state hydrogen storage: so it is simple like the our gas cylinder in our home. So, basically the hydrogen can be compressed into high pressure tanks in a gas form, it also needs extra energy in order to achieve the competition, the space occupied by the compressed gas is large, compression vessels should be regularly tested to ensure no leaks are taking place otherwise it can be blasted.

Compressed hydrogen storing technology is more cost efficient than the liquid hydrogen storing technology. Furthermore, it involves less infrastructure and it has been operating in a number of experimental hydrogen filling stations in Europe and the USA. So, basically nowadays people are tending that we can run the automobiles, or may be the cars, or may be the buses by the hydrogen gas itself.

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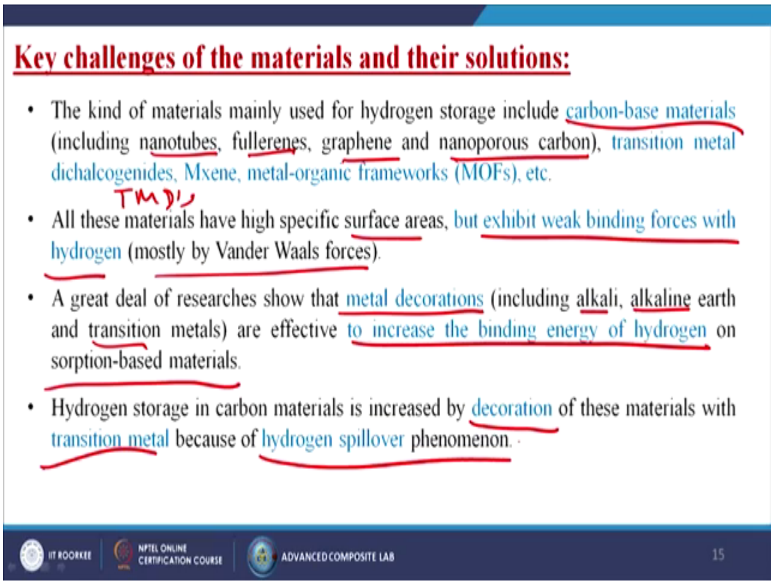

Next what are the key challenges for the materials and their solutions, means what kind of materials I can use, so that I can capture the hydrogen? So, basically the kind of materials mainly used for hydrogen storage include carbon based material including the nanotubes, fullerenes, grapheme, and the nanoporous carbon, transition metal dichalcogenides. In short basically we are calling it as a TMDs then Mxene it is the new class of materials then the metal organic framework or maybe the MOFs, sometimes we are using the COF also.

So, all these materials have high specific surface areas, but exhibit weak binding forces with hydrogen mostly by the weak Vander Waals forces. A great deal of researches show that the metal decorations including alkali metals, alkaline earth and transition metals are effective to increase the binding energy of hydrogen on sorption based materials.

So, that the material hydrogen can stick with the surface or maybe (Refer Time: 19:22) absorption it can go inside. Hydrogen storage in carbon materials is increased by decoration of these materials with transition metal because of hydrogen spillover phenomenon. What is the hydrant spillover I will come in subsequent slides. So, basically what is hydrogen spillover?

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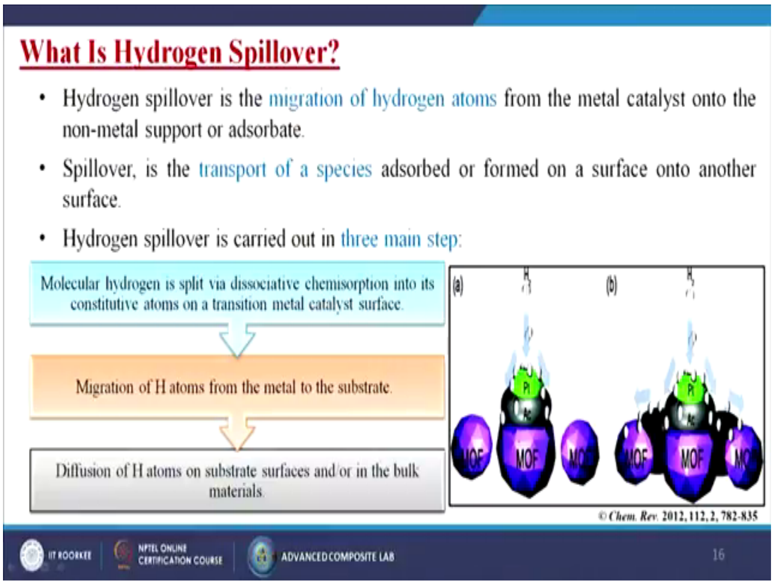

Hydrogen spillover is the migration of hydrogen atoms from the metal catalyst onto the non metals support or may be the adsorbate, simple the transferring of the hydrogen ion. Spillover, is the transport of a species absorbed or formed on a surface onto another surface, so simple from this surface the hydrogen atom is going into the this surface, so that is called as spillover.

Hydrogen spillover is carried out in three main step; what are those? That is number one: molecular hydrogen is split by dissociative chemisorptions into its constitutive atoms on a transition metal catalyst surface, migration of H atoms from the metal to the substrate, diffusion of H atoms on substrate surface or in the bulk materials.

So, simple I am having one materials where I am giving some temperature or heat it is generating the H plus ion then the H plus ion is going from metal surface to the substrate. And then on the substrate other either it is sitting on the surface or maybe it is going inside the substrate itself. So, that is why it is called the hydrogen spillover.

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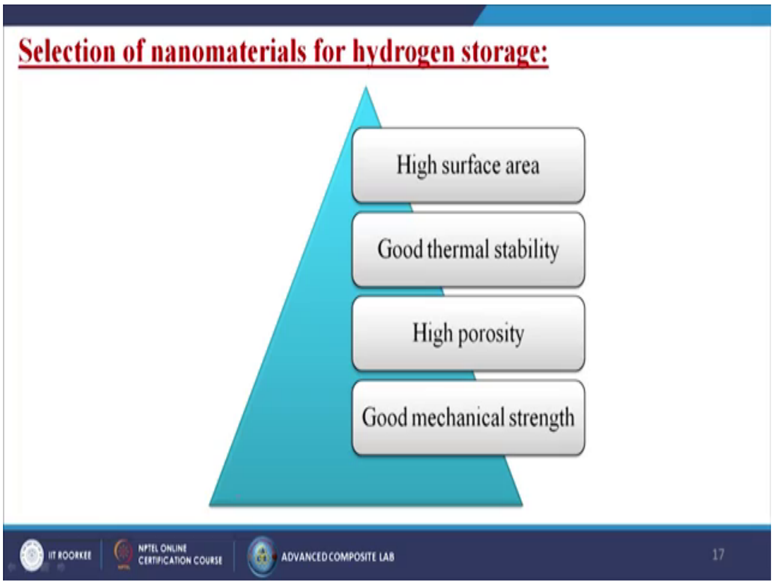

Now, what should be the criteria by which we can choose the nano materials for hydrogen storage? First and foremost is that it should have the high surface area, second one is that it should have good thermal stability, it should have the high porosity, and it should have the very good mechanical strength. So, these all four are my input parameters by which I have to choose the right materials for storing the hydrogen.

Now, let us start with the materials, so first we are going to discuss about the metal organic frameworks or maybe the MOFs. This is also the latest kind of materials, the scientists are working on that particular materials to capturing or maybe the storing the hydrogen inside it. So, in short metal organic frameworks is known as MOFs.

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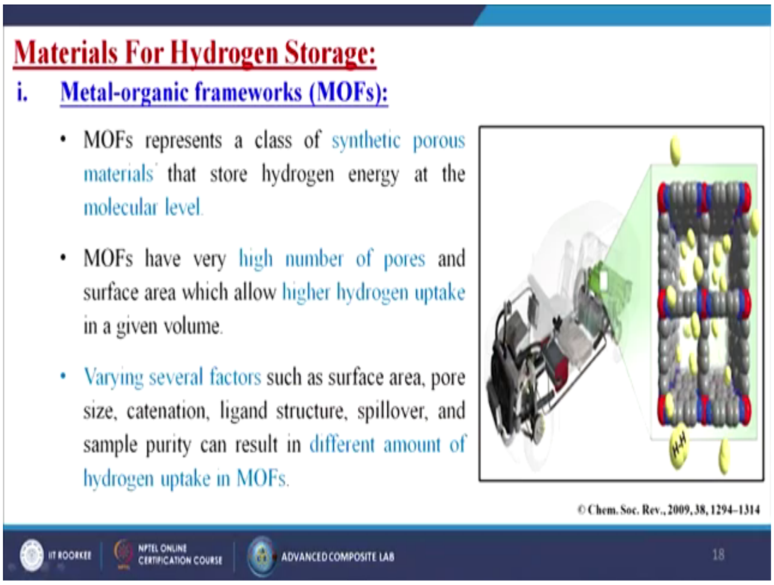

So, basically MOFs represents a class of synthetic porous materials, as I told already it is like a sponge. So, sponge if you see that when we are putting that particular sponge into the water, so what will happen? While taking out no water will come out unless and until you are going to squeeze that particular sponge. So, when you are going to squeeze the sponge the water molecule will come out. The same principle applied over here also we are making the porous materials and then we are passing the hydrogen gas inside it.

So, the hydrogen gas will be trapped inside the porous structure and as and when required either by giving the temperature or may be the pressure we are going to extract the hydrogen gas for the direct applications. So, MOF have very high number of pores and surface area which allow the higher hydrogen uptake in a given volume.

Varying several factors such as surface area, pore size, catenations, ligand structure, spillover, and sample purity can result in different amount of hydrogen uptake in MOFs. So, that is research are going on that how to increase the porosity, how it can withstand with the high temperature or maybe that mechanical strength it can remain same or maybe what kind of material I can be used, so that more hydrogen can be captured so these type of research is going on. Next is called the carbon nanotubes in short it is basically the CNT that is also the two type especially we are using in our research, one is called the multi wall carbon nanotubes another one is called a single wall carbon nanotubes.

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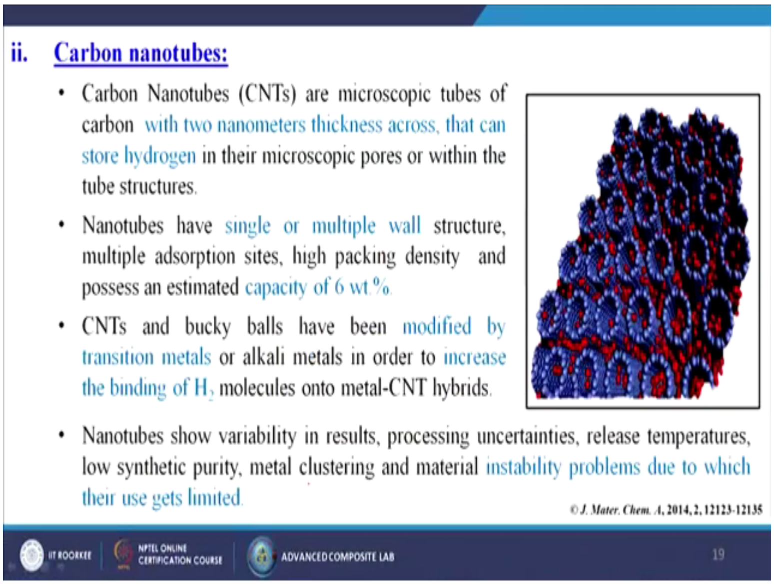

So, basically the carbon nanotubes are the microscopic tubes of carbon with two nanometers thickness across that can store hydrogen in their microscopic pores or within the tube structure, either it is inside or maybe that gap in between the two cubes. Nanotubes have single or multiple wall structure as a told multiple absorption sites, high packing density and possess an estimated capacity of 6 weight percent, CNTs and bucky balls.

So, it is the formation of the same carbon structure and the shape is like a ball, so that is why it is called the bucky balls have been modified by transition metals or alkali metals in order to increase the binding of hydrogen molecules on to metal carbon nanotube hybrids. Nanotube show variability in results, processing uncertainties, release temperatures, low synthetic purity, metal clustering and material instability problems due to which their use gets limited means it is having disadvantages. So, that is why people are using it with some transition metals or maybe as a hybrid composites.

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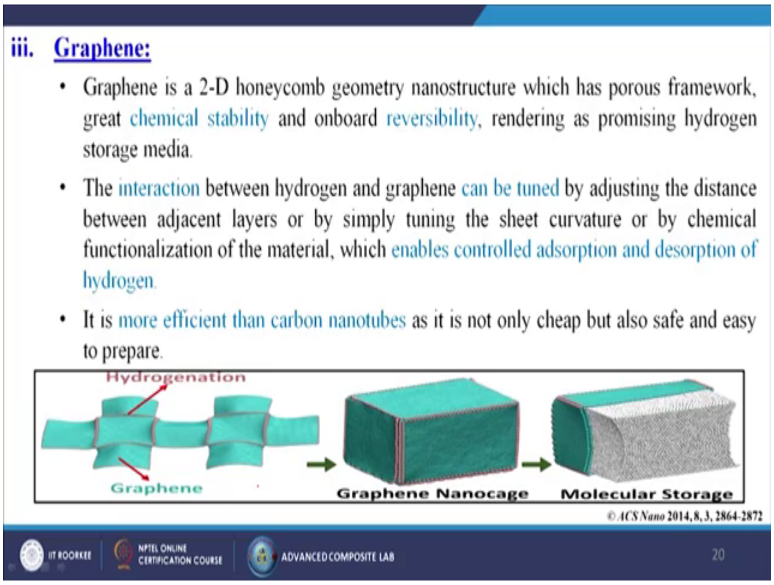

Next one is called the graphene, so it is also comes from the graphite. So, graphene is a 2 D honeycomb geometry nanostructure which has porous framework, great chemical stability and onboard reversibility, rendering as promising hydrogen storage media. The interaction between hydrogen and graphene can be tuned by adjusting the distance between adjacent layers or by simply tuning the sheet curvature or by chemical functionalization of the material, which enables controlled adsorption and desorption of hydrogen.

It is more efficient than carbon nanotubes as it is not only cheap but also safe and easy to prepare. So, basically the graphene, so we are doing the hydrogenations or maybe we can use a graphene nanocage kind of things, so now inside it is like a storage tank. So, basically the hydrogen gas can be stored inside it like a box.

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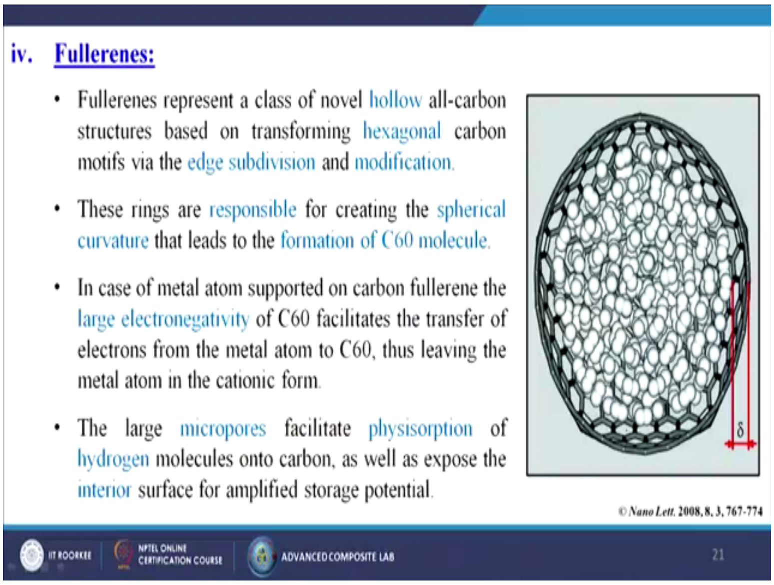

Next one is called the fullerene: fullerenes represent a class of novel hollow all carbon structures based on transforming hexagonal carbon motifs via the edge subdivisions and modifications. These rings are responsible for creating the spherical curvature that leads to the formation of the C60 molecule, so sometimes the fullerene is known as the C60 molecules.

In case of metal atom supported on carbon fullerene the large electronegativity of C60 facilitates the transfer of electrons from the metal atom C60, thus leaving the metal atom in the cationic form. The large micropores facilitate the physisorption of the hydrogen molecules onto the carbon, as well as expose the interior surface for amplified storage potential. So, basically you can see what is the gap. So, in between that gap simple the hydrogen atom is storing basically or rather I can say capturing.

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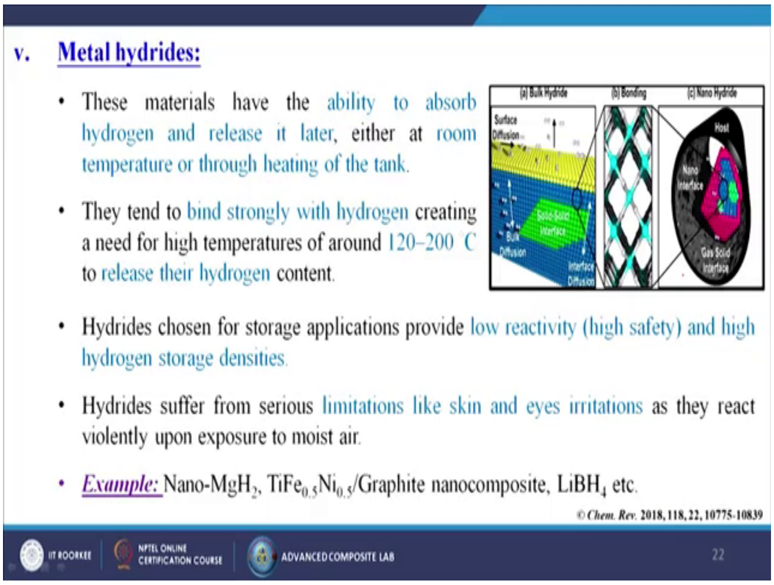

Next one is called the metal hydrides, so this material have the ability to absorb hydrogen and release it later, either at room temperature or through heating of the tank itself. They tend to bind strongly with hydrogen creating a need for high temperature of about 120 to 200 degree centigrade to release the hydrogen consent inside it. So that means, what about the hydrogen I am putting inside it, so at the time of release I have to heat that materials, so that whatever the hydrogen has been captured inside it that will come out.

Hydrides chosen for storage application provide low reactivity; that means high safety and hydrogen storage densities. Hydrides suffer from serious limitations like skin and eye irritations, so that is not good for the workers as they react violently upon exposure to moist air. What is the example? Like nano magnesium hydrides, TiFe Ni, graphite nanocomposites, Li BH4, so these all are the materials.

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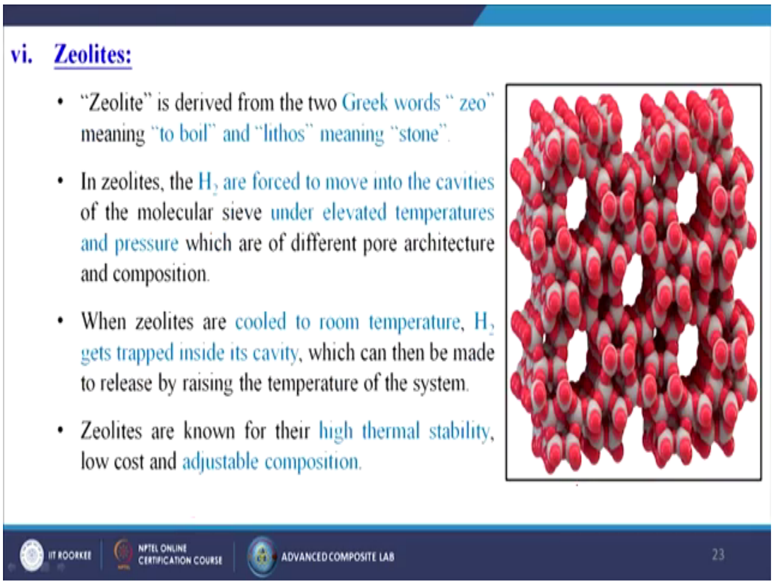

Next one is called the zeolites, so zeolites is derived from the two Greek words that is zeo meaning to boil and lethos meaning the stone, so; that means, we are capturing and at the time of getting that we have to heat that particular materials. In zeolite the hydrogen are forced to move into the cavities, you can see there are lots of cavities over there.

So, of the molecular sieve under elevated temperatures and pressure which are of different pore architecture and the composition. When zeolites are cooled to room temperature, hydrogen gets trapped inside its cavity, which can then be made to release by raising the temperature of the system itself. Zeolites are known for their high thermal stability, low cost and adjustable compositions.

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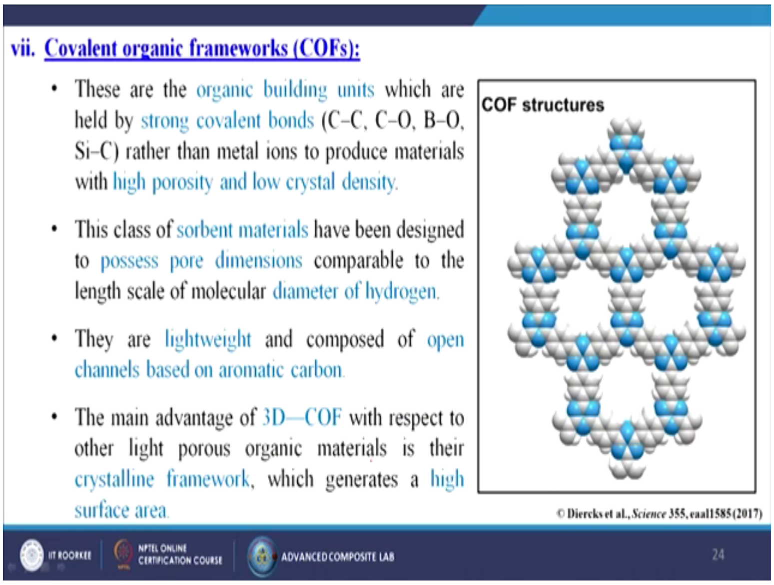

Next is called the covalent organic frameworks in short its COFs. So, these are the organic building units which are held by strong covalent bonds either C bond C, C bond O, or maybe B bond O or may be Si bond C rather than metal ions to produce materials with high porosity and low crystal density.

So, these all are the gaps over here. This class of sorbent materials have been designed to possess pore dimensions comparable to the length scale of molecular diameter of the hydrogen. They are lightweight and composed of open channels based on aromatic carbon itself. The main advantages of the 3 dimensional covalent organic frameworks with respect to other light porous organic materials is their crystalline framework which generates a high surface area.

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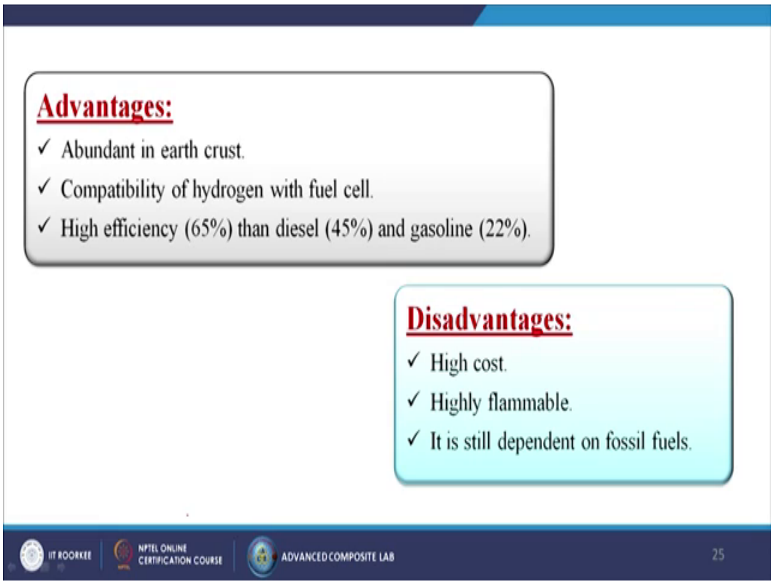

So, now what is the advantages? Abundant in earth crust because hydrogen, compatibility of hydrogen with fuel cell, because now people are working on the hydrogen fuel cell, high efficiency 65 percent then diesel 45 percent and the gasoline. So, now, we can understand that why we are giving much concentrations to store the hydrogen energy because in a less amount it can give the maximum efficiency than the diesels means petroleum products or any other coal products. Of course, there are certain disadvantages what are those? It is high cost to store the hydrogen, it is highly flammable, its needs the highest or maybe that most precautions and its still dependent on the fossil fuels itself.

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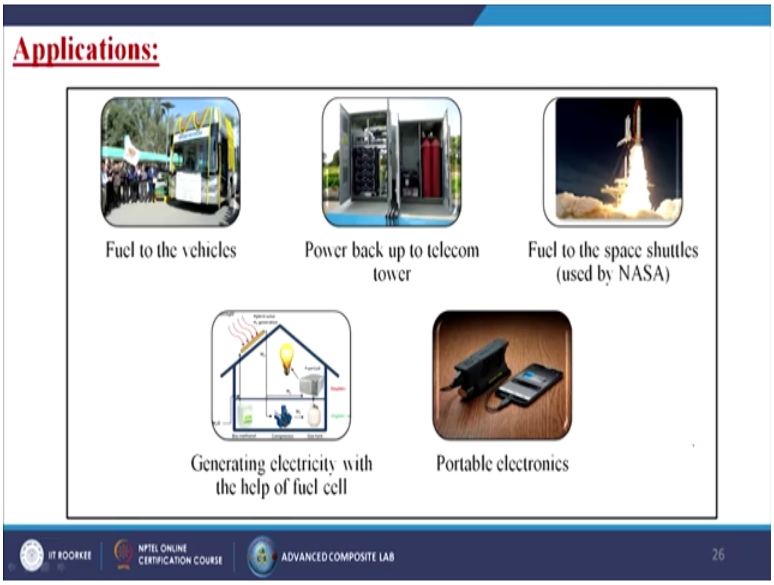

Applications: nowadays people are using for the enormous applications, but always keep in your mind that storing of the hydrogen its bit difficult still research is going on or maybe in near future we will be able to store the 100 percent hydrogen and we can use it as a fuels for the future applications. So, you can see that fuel to the vehicles, the bus is running by the hydrogen itself, power backup to telecom tower, fuel to the space shuttles that is the best examples generally NASA is using that particular technology. Generating electricity with the help of fuel cell at as I told already that is the hydrogen fuel cell, and the portable electronic case nowadays we are using.

Now, we have come to the last part of this particular lecture. So, in summary we can say that hydrogen storage technique is rapidly emerging as a first alternative to fossil fuels, but it needs for the improvements in terms of infrastructure and applications. Yes, because now we are into the developing stage we have not yet developed. So, every day we are making new materials to store the hydrogen and just to increase the efficiency.

Two mechanisms already we have discussed which is involved in the hydrogen storage, one is the physisorbtion, another is the chemisorption technology. Various methods used for hydrogen storage studies which was discussed in this particular lecture, properties like large surface area, porous nature, mechanical strength, and stability are ideal parameters means for choosing the hydrogen storage material. A wide variety of carbonaceous material, metal organic frameworks, hydrides etcetera are used for the latest research.

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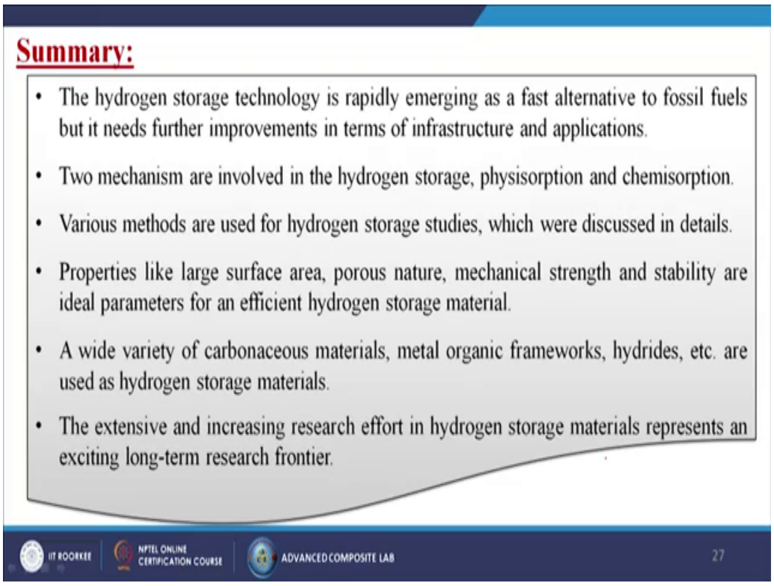

The extensive and increasing research effort in hydrogen storage materials represents an exciting long term research frontier, which we will be able to use in the near future in a versatile manner.

Thank you.