Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 31
Introduction to Hydrogen Storage

Till now we have done Hydrogen production. From this section we will start Hydrogen Storage whether hydrogen is produced in a centralized plant on an industrial scale or whether it is produced on a small scale in a decentralized plant, it is not essential that the requirement can be in pace with the amount of hydrogen being produced. Except for some of the applications where whatever hydrogen is being produced is being utilized most of the time in order to bridge the supply demand gap hydrogen storage is essential.

Now, hydrogen storage is the important part of the hydrogen value chain and it is the biggest bottleneck as well. Let us understand what are the challenges associated with the hydrogen storage.

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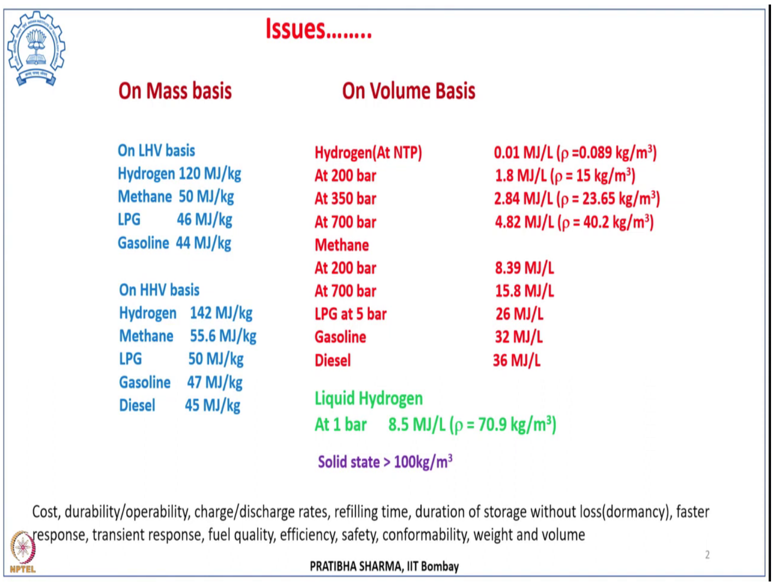

On a mass basis hydrogen has advantage its energy density on a mass basis is high like in 1 kg it is 120 mega joule of energy which is stored in hydrogen, which is more than double that of methane.

For methane, it is 50 mega joules per kg, for LPG it is 46 mega joules per kg, for gasoline it is 44 mega joule per kg these are on the lower heating value on higher heating terms hydrogen energy density is 142 mega joule per kg, for methane it is 55.6 mega joule per kg, LPG 50 mega joule per kg, gasoline 47 and diesel 45 mega joule per kg.

So, we can clearly see that hydrogen has a much higher energy density almost 3 times that of the gasoline more than double that of the methane, but the entire picture changes when we consider on the volume basis. Now hydrogen it is the smallest molecule, it is the lightest molecule, it has a very high diffusivity all that poses a lot of problem when it comes to storage.

Now, under normal temperature pressure conditions the density of hydrogen is 0.089 kg per meter cube so; that means, in order to store 1 kg of hydrogen we will require 11-meter cube of volume and that is an enormous volume the energy that will be stored in 1 litre is only 0.01 mega joule, which is very less as compared to that of gasoline. For gasoline on a volume basis the energy density is 32 mega joules per litre.

So, this is roughly 3200 times higher than the energy stored per litre in hydrogen under normal temperature pressure condition while it is 3600 times higher for diesel it is 36 mega joule per litre of diesel. Now that means, in order to store substantial amount of hydrogen in a given volume, we need to either compress it to a higher pressure or make it denser by liquefying it or we have to see some other ways in which it can be stored in the solid form.

Now, in order to increase the volumetric energy density, we can compress it to higher pressure like if hydrogen is compressed to say 200 bar the energy density becomes 1.8 mega joule per litre and the density of hydrogen 15 kg per meter cube. If it is compressed to 350 bar then it is 2.84 mega joule per litre and the density of hydrogen becomes on compression 350 bar 23.65 kg per meter cube to very high pressure like 700 bar, then the density further improves to 4.82 mega joule per litre. So, it is 40.2 kg per meter cube.

This is still half of even at such high pressures of 700 bar this is half of that of methane when it is stored at 200 bar which is 8.39 mega joule per litre. However, if we further compress methane at 700 bar it is 15.8 mega joule per litre and which we can see that this is 4 times that of the hydrogen being stored at the similar pressure. Now the other way could be we could further increase the density by liquefying it. So, the liquid hydrogen when considered at

1 bar pressure its density is 8.5 mega joule per litre and its 70.9 kg per meter cube of hydrogen being stored.

This density can be further increased if it is stored in the solid state form then it goes to like higher than 100 kg per meter cube. So, this is the biggest challenge that on energy basis hydrogen has a very high gravimetric energy density, but on a volume basis it is very low. So, there are challenges associated with the confirmable storage of hydrogen in a given volume.

So, the weight as well as volume required for storing hydrogen becomes a challenge when specially it is up to vehicular application. Other than that the other challenges that need to be considered when storing hydrogen include its cost of both the material as well as the tank durability, operability. So, it should have very high life at the same time the operating conditions should be optimum, it should have a high charge and discharge rate.

So, rate at which hydrogen can be put inside the tank and the rate at which the hydrogen can be taken out of the tank either system or materials as well. So, at which it gets charged in a solid state material or it gets discharged. Refilling time is another consideration when it is to be compared with IC engine based vehicles it should be of the similar order as that of a IC engine vehicle.

Duration of storage, now this becomes important when it is liquid state storage there should not be loss of hydrogen when it is being stored. So, the dormancy becomes a major parameter there it should be very fast in response like, when the hydrogen storage system is connected to fuel cell or a load whatever, are the changes taking place in the load then it should respond faster. So, the delay should be as low as possible as well as the transient response need to be considered the fuel quality.

So, there should not be any contaminants or impurities present that should come from the either the compression or from the tank which could be detrimental towards its integration to the fuel cell. Efficiency is important whether it is we have to compress it whether we have to liquefy it so, as to make it more energy compact, safety of the storage devices is important, the conformability weight and volume these are other parameters that needs to be considered when we have to store hydrogen.

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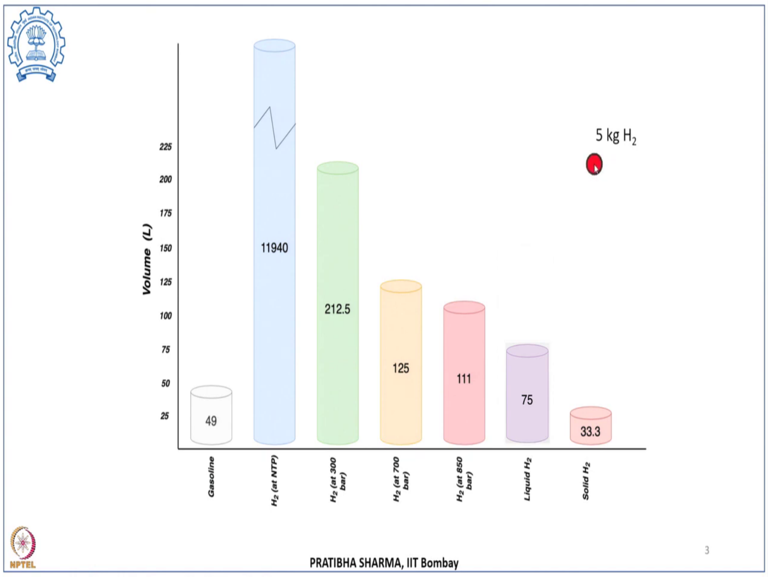

Now, just taking an example roughly 1 kg of hydrogen in a light motor vehicle we can drive about 100 kilo meters. So, in order to have a range of 500 kilo meters, 5 kg of hydrogen need to be stored in a hydrogen container vessel or tank. Now if equivalent amount of energy which is stored in 5 kg of hydrogen could have come from gasoline, the volume of the tank would have been 49 liters.

The similar energy if to be stored in the form of hydrogen under normal temperature and pressure condition would require 11940 litres of volume and that is very high as against that of the gasoline tank. Now if this is further compressed hydrogen is compressed to say 300 bar then the volume of the tank would reduce to 212 litres if further compressed to 700 bars this tank volume would reduce to 125 litres.

When it is stored at an even further higher pressure say 850 bar then the tank volume required would be 111 litres. When hydrogen is in the liquefied form in a cryogenic tank the volume required to store the same amount of hydrogen 5 kg of hydrogen would be required will be 75 litres, but if it is stored in the solid state form, the volume required will be 33.3 litres. So, this is how the different ways of storing hydrogen are related as against the gasoline tank.

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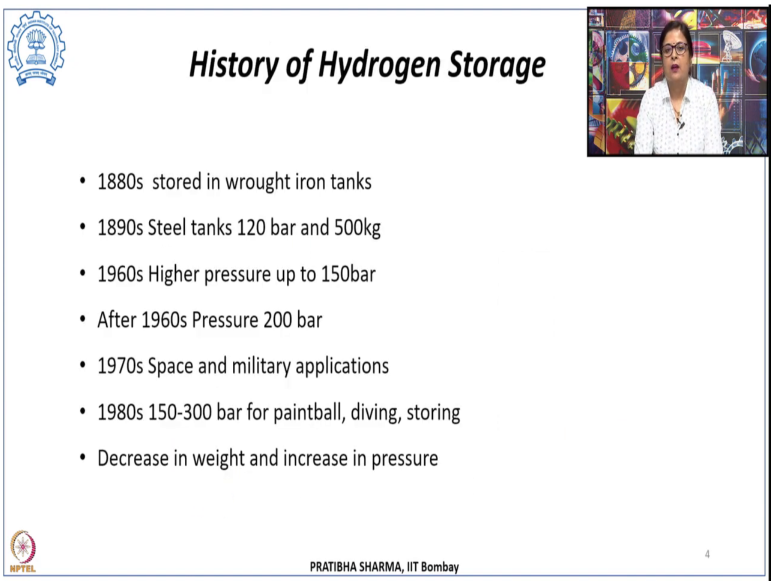

Looking back into the history of hydrogen storage, it was used for various applications and was stored as early as 1880s in wrought iron tanks; however, the pressure was lower at that time after that steel tanks were introduced wherein the pressure was increased to 120 bar, but these tanks were very heavy and the weight of the tanks was about 500 kg.

Thereafter, there was increment in the pressure in 1960s, the pressure which was increased was to 150 bar and after 1960s it was further raised to 200 bar and primarily these was used for space and military application. It was in 1980s that the pressure was increased to about 300 bar.

But at that time like these were used for laser applications like paintball for diving for storing various gases. Thereafter, it has seen a great improvement in terms of increase in the pressure and decrease in weight. So, we will see the different types of tank and we will see how the type 4 tank they have a lower weight and an increased pressure.

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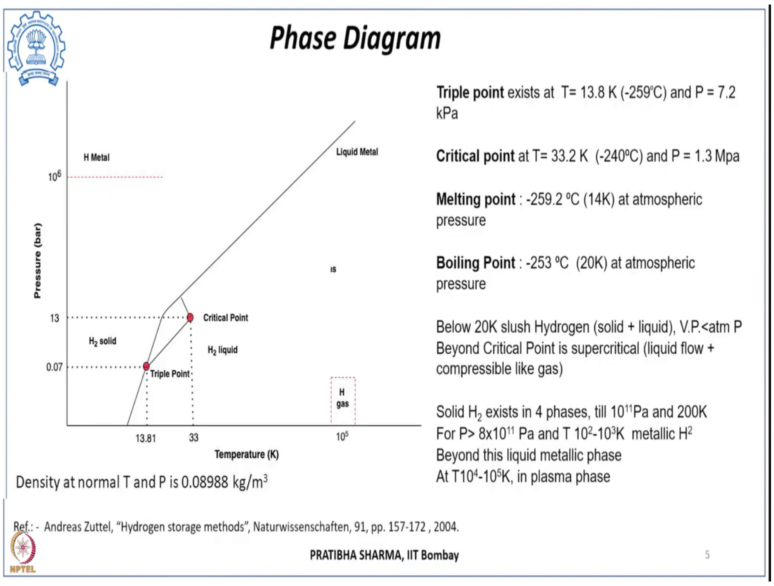

Before coming to the hydrogen storage techniques, we will first quickly look at what are the important properties which we need to revise before we go on to a particular method of storage. Let us start with the phase diagram we know that, under normal temperature pressure condition hydrogen is a gas with a very low density, now there are different lines in the phase diagram which separates the different regions, which separate solid from gas which separate gas from liquid from gas from solid. So, these are the equilibrium lines which separate the different regions in the phase diagram.

Now, as we lower down the temperature at a temperature of minus 253 degree centigrade i.e. 20K liquid hydrogen is obtained. So, this region is that of liquid hydrogen a very small region now the all the three phases solid liquid and gas phase they exist at this point which is known as the triple point. It has a temperature of 13.96 kelvin and a pressure of 7.36 kelvin.

At a critical point which has a temperature of 33.15 kelvin and pressure of 1.3 mega Pascal here the gas and the liquid phases are indistinguishable and beyond that even if we further increase the pressure we cannot liquefy hydrogen. So, this is where we can get liquid hydrogen this is corresponding to the critical point now if temperature is further reduced.

So, if we go further down from 20 kelvin say to 14 kelvin or minus 259.2 degree centigrade at atmospheric pressure we can get solid hydrogen. Now prior to that when we reduce the temperature below 20 kelvin we get a state, which is slush hydrogen this is a phase where in solid and liquid phases are indistinguishable, but this is obtained at a lower vapour pressure.

So, while storing this hydrogen any air in gas need to be avoided because the vapour pressure is below the atmospheric pressure. Now what happens is beyond the critical point is the supercritical hydrogen. Now this supercritical hydrogen it is like both the characteristic it has a characteristic like liquid as well as gas. So, it can have a flow like a liquid flows while it can be compressed like a gas.

So, this is the beyond this 20K it has a solid region. Now this solid hydrogen it was found that even if we keep on increasing the pressure this solid hydrogen will exist and it is till a pressure of 10^{11} pascal or 200 kelvin the solid hydrogen was identified to have four different phases. And these four different phases are like HCP-hexagonal close packing or FCC or orthorhombic and monoclinic.

But if we further increase the pressure to beyond 8×10^{11} Pascal at a temperature of 10^2 to 10^3 kelvin we can even get metallic hydrogen and if we go further beyond this in that case we can get a liquid metal. This liquid metallic phase was identified way back in 1935, but it was observed in 1996 and this is the phase which is found in various planets like Saturn and Jupiter.

At further higher temperatures 10^4 to 10^5 kelvin, it can be found in plasma phase now this phase is found in stars this phase is found in sun. So, this is the overall like which region hydrogen can be found in which phase.

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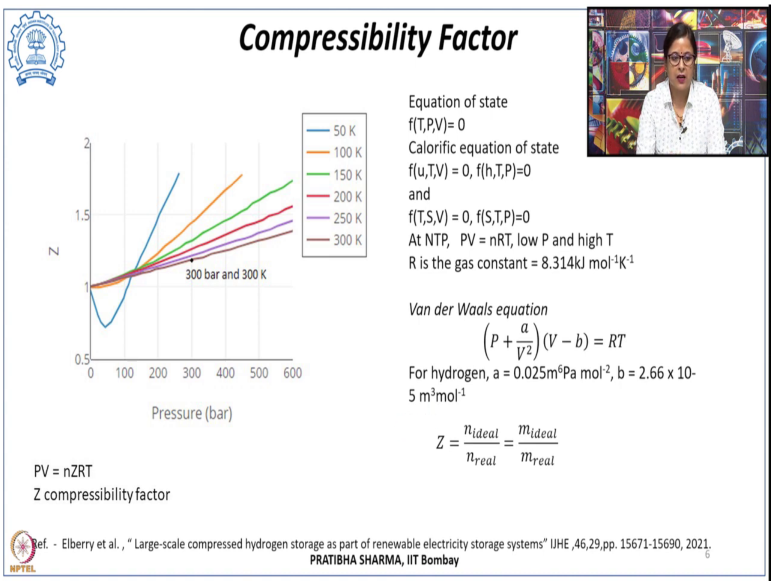

Now like any pure substance the state of a hydrogen can be described using two intensive state variables and rest of the variables we can find using the different relationship which are the like the equation of state which relates the temperature, pressure, volume.

The calorific equation of state which relates the internal energy, temperature, volume and the enthalpy, temperature, volume or there can be entropy relations like temperature, entropy, volume and temperature, entropy, pressure relationships. Now other state variables we can found using these three relations. Now at and normal temperature and pressure conditions we know that hydrogen behaves like an ideal gas and it follows the ideal gas law PV = nRT.

And this is for low pressures and high temperature, temperatures beyond the critical point and we know that the ideal gas assumptions are like the forces between the molecules should be negligible, molecules are considered as a solid, hard, spheres incompressible spheres, but then at high pressures and low temperatures deviations from the ideal gas behavior is observed and that can be accounted by various models.

Like the Van der Waals equation where in the intermolecular forces and the molecular volume is accounted for by addition of two more terms like to the pressure term plus a/V^2 and $(V - b) = RT$, where a and b values for hydrogen are like 0.025 m^6Pa/mol^2 and same for b value we can obtain. Another way to represent this deviation of hydrogen from its ideal gas behaviour at a higher pressure and lower temperature is by including a dimensionless quantity which is the compressibility factor. So we can write the modify the ideal gas equation as PV = nZRT. So, Z is here the compressibility factor and this accounts for the deviation from the ideal gas behaviour.

So, n ideal upon n real or same the mass when we consider as ideal gas to the mass when we consider it as a real gas now, any value which is away from one shows that its deviation from the ideal gas behaviour. So, this is like as we decrease the temperature the deviation further increases. Now let us take an example where say at 300 kelvin and when it is compressed hydrogen is compressed to 300 bar that compressibility factor is 1.2 under this condition of temperature and pressure.

That means, if we have considered ideal gas equation to calculate the mass of hydrogen stored in a tank we could have overestimated the mass by 20 percent. Now these relationships like the compressibility factor relationship these are available in the literature these graphs are already there and that can be used to see, how much is the deviation from the ideal gas behaviour.

And now here if we find the reduced pressure like by dividing the pressure by critical pressure or dividing by the temperature by critical temperature, in that case we can get the generalized compressibility factor which is for different gases.

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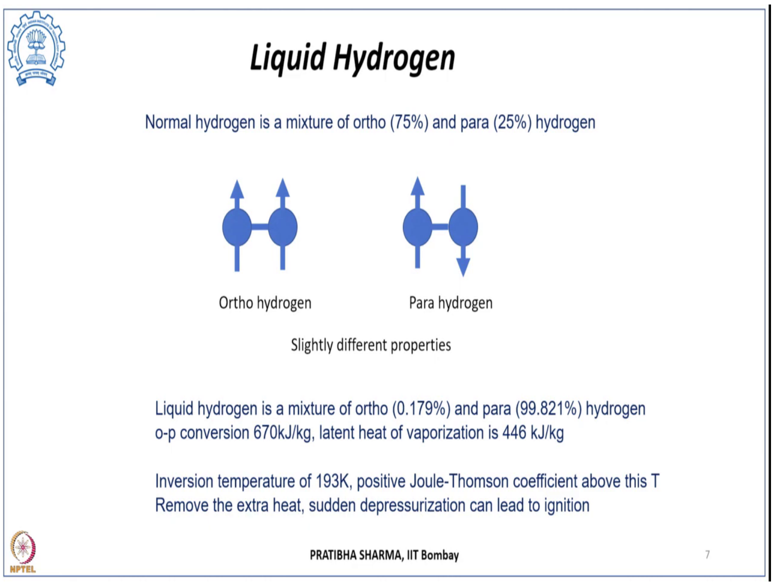

Now, when it comes to storing hydrogen in liquid form we need to understand that the hydrogen which is a diatomic molecule. So, hydrogen atom has a proton and the spins of the elementary particles, they can be either parallel or they can be anti parallel.

Now, when we consider the equilibrium concentration or under the normal conditions, the normal hydrogen is a mixture of 75 percent of ortho hydrogen and 25 percent of para hydrogen. So, this is also known as equilibrium hydrogen. Now these two states of hydrogen ortho and para hydrogen they have slightly different properties.

Now once we start cooling from the normal temperature pressure condition to liquefy hydrogen this ortho hydrogen has to be converted into para hydrogen because, in liquid hydrogen it is a mixture of ortho hydrogen as small as 0.179 percent and para hydrogen 99.821 percent. Now this conversion of this ortho hydrogen from room temperature to 20K into para hydrogen this is an exothermic process because the para hydrogen is in a lower energy state. So, when you cool it down the extra energy is released.

So, this conversion is an exothermic process releasing energy of 670 kilo joule per kg this is even higher than the energy required for liquefaction. So, the latent heat of vaporization for hydrogen is 446 kilo joule per kg. So, when we are trying to liquefy hydrogen, we have to not only remove that energy we have to provide the required conditions to liquefy it at the same time we will have to remove this energy or the heat which is coming out because of this ortho para conversion.

Also for hydrogen the inversion temperature is 193 kelvin; that means, it has a positive Joule Thomson coefficient above this temperature. So, we have to cool it down and we have to remove that much amount of extra heat which is being produced for a positive Joule Thomson coefficient when we are trying to expand hydrogen it will infect heat.

So, that extra heat needs to be removed. So, there are two major disadvantages because of that we have to not only remove that extra heat, but if there is a sudden depressurization release of pressure then a large amount of heat can be produced and that can even lead to ignition actually it is not ignition, but it can lead to explosion as well. Now these are some of the important things we need to know before we look at the different hydrogen storage methods when we see how we can categorize these methods.

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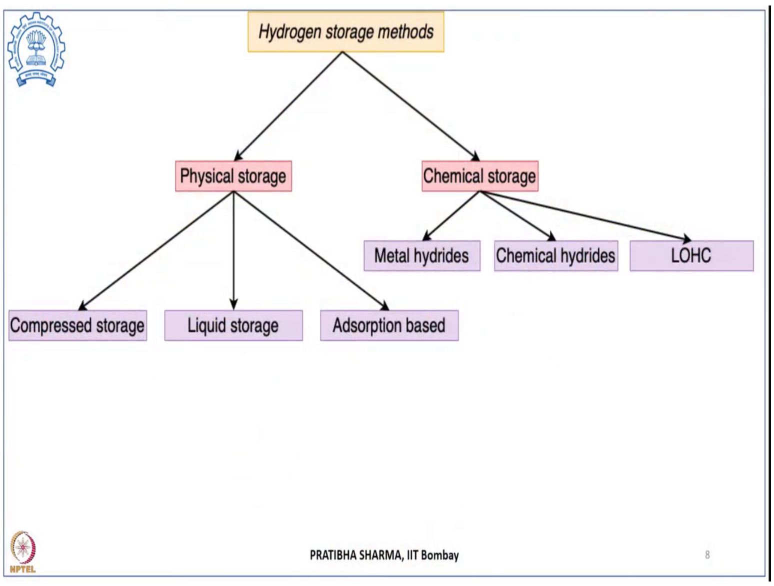

So, the different hydrogen storage methods can be categorized into the way like physical storage wherein we are storing it in the molecular form, it can be either in the form of gas being compressed to higher pressure. So, compressed state storage or hydrogen can be liquefied and stored in the liquid form or it can be stored in the molecular form using the adsorption based methods on high surface area materials.

Hydrogen can be stored using chemical storage method this can be on various materials using like solid state storage these can be either metal hydrides, complex hydrides or in some of the chemical hydrides or in liquid organic hydrogen carriers. So, all these methods we are going to learn in more detail.

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Onboard Hydrogen Storage Targets

Storage Parameter	Units	2025	Ultimate
System Gravimetric Capacity: Usable, specific energy from H_2 (net useful energy /max system mass)	kWh/kg (kg H_2/kg system)	1.8 (0.055)	2.2 (0.065)
System volumetric capacity: Usable energy density form H_2 (net useful energy / max system volume)	kWh/L (kg H_2/L system)	1.3 (0.040)	1.7 (0.050)
Storage system cost: • Fuel cost	$/kWh net ($/kg H_2) $/gge at pump	9 300 4	8 266 4
Durability / Operability:			
• Operating ambient temperature	°C	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85
• Operational cycle life (1/4 tank to full)	Cycles	1500	1500
• Min delivery pressure from storage system	bar (abs)	5	5
• Max delivery pressure from storage system	bar (abs)	12	12
• Onboard efficiency	%	90	90
• "Well" to Powerplant efficiency	%	60	60

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Now, these systems which are developed for hydrogen storage or these materials which are going to be developed for hydrogen storage, they need to satisfy certain requirements in terms of mass basis, in terms of volume basis cost under what conditions we need to operate what should be the refuelling time, what should be the dormancy all these parameters for that USDOE has laid down certain targets in association with US drive.

So, these targets are system level targets, which are considered not only for the storage stored mass the fuel in that tank, but also considering all the associated auxiliary components whether these are the tank weight or volume whether the walls piping, fittings, manifolds, balance of plant cooling system, the storage media it could be even the integration where it is it has to be connected to the refuelling unit.

So, all those auxiliary components are also considered when considering these storage target. So, these are considering that for the onboard on a vehicle considering that a vehicle light duty vehicle has to be driven for 500 kilometres and this should be at par with the IC engine vehicles.

Now, these targets which are offered these are revised after every 5 years considering the improvements in the technology. So, these are not this based on the state of art the technologies, but rather these are based on what is the customer demand and what are the requirements in terms of a particular vehicle when it is being considered. So, these targets are for different storage parameters like the system gravimetric capacity.

So, this always is gravimetric when it comes then it is per unit mass which is being considered. So, this is the amount of usable energy, which the system will have. So, this is a specific energy from hydrogen which can be provided to the fuel cell system. So, it is the net useful energy divided by the maximum system mass.

Now, the system mass includes, the mass of the hydrogen being stored as well as the mass of the tank storage media, the valves, fittings, tubings, any cooling devices compression related unit filters, safety units, monitoring, sensing, all these devices are to be considered when it is being considered as a storage system its units are in kilowatt hour per kg. So, by 2025 it has to be 1.8 kilowatt hour per kg and ultimate it should be 2.2 kilowatt hour per kg.

In terms of kg of hydrogen stored per kg of the system weight it is 0.055. So, that is about 5.5 weight percent of the hydrogen should be stored per kg of the system weight. Similarly, the ultimate it is 0.065. So, 6.5 percent of the hydrogen to be stored to the system mass. Same is expressed in terms of the volumetric capacity that is the amount of energy which is available in the form of hydrogen to the maximum system volume.

So, the net useful energy divided by the system volume and this is expressed in kilowatt hour per litre of the system or kg of hydrogen per litre of the system. So, if we consider in unit of kilowatt hour per litre, it is 1.3 kilo watt hour per litre by 2025 and an ultimate of 1.7-liter kilowatt hour per litre.

Similarly, 40 grams of hydrogen to be stored per litre of the system by 2025 and 50 grams of hydrogen to be stored per litre of the system as an ultimate target storage system cost it is in dollars per kilowatt hour net; so, 9 dollars per kilowatt hour and 8 dollars per kilowatt hour as ultimate. Hydrogen, dollars per kg of hydrogen and at the pump so, this is 300 and 266 and 4 dollars per gasoline equivalent gallon of gasoline equivalent at pump.

Now, when whatever is the method of storage being used whether it is compressed state or liquid state or solid state storage, the conditions of operations are important like it should be able to operate under ambient condition temperature conditions in degree centigrade from minus 40 degree to 60 degree; that means, it should we should be able to operate at in countries where it is extreme winters.

So, it should we can still use it at a temperature of minus 40 degree or extreme summers, where even the temperature is considered inside the vehicle the temperature may go as high as even 60 degree, then also we should be able to operate such systems minimum or maximum delivery temperature that is when hydrogen has to be delivered to the fuel cell system usually PEM fuel cell is used which operate at close to 80 degree centigrade but we should be able to operate it in a range of minus 40 degree to 85 degree centigrade.

Life cycle of the storage system from one fourth tank to full tank the number of cycles it should be we should be able to get is 1500 cycle. Nowthese targets are considering a wide range of vehicles, wide range of amount and finally, these targets have been come across.

Now, the minimum delivery pressure from the storage system to fuel cell so, the pressure in bar this is 5 bar 2025 as well as ultimate and that maximum pressure from the storage system 12 bar. On board efficiency of the fuel cell of the hydrogen storage system 90 percent well to power plant efficiency on board off board everything it is 60 percent, which is desired the charging and discharging rate they have importance when we consider the refilling time of the tank.

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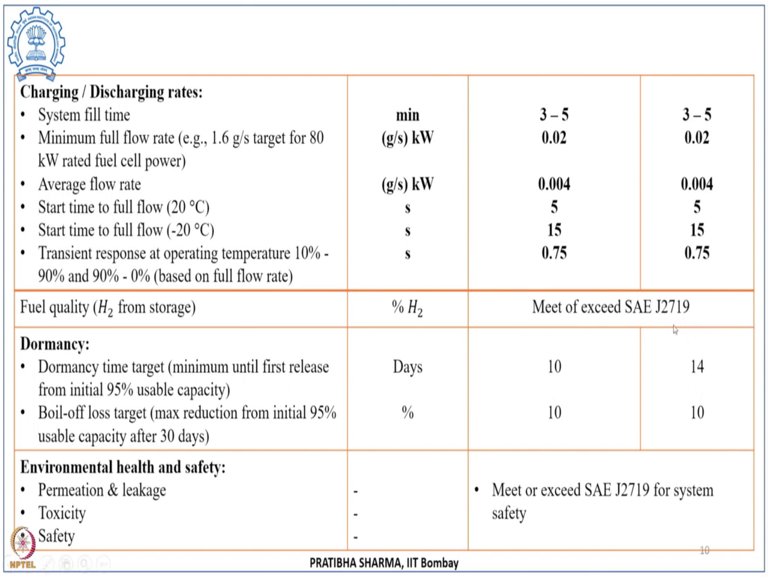

Charging / Discharging rates: • System fill time • Minimum full flow rate (e.g., 1.6 g/s target for 80 kW rated fuel cell power) • Average flow rate • Start time to full flow (20 °C) • Start time to full flow (-20 °C) • Transient response at operating temperature 10% - 90% and 90% - 0% (based on full flow rate)	**min** **(g/s) kW** **(g/s) kW** **s** **s** **s**	**3 – 5** **0.02** **0.004** **5** **15** **0.75**	**3 – 5** **0.02** **0.004** **5** **15** **0.75**
Fuel quality (H_2 from storage)	% H_2	Meet of exceed SAE J2719	
Dormancy: • Dormancy time target (minimum until first release from initial 95% usable capacity) • Boil-off loss target (max reduction from initial 95% usable capacity after 30 days)	Days %	10 10	14 10
Environmental health and safety: • Permeation & leakage • Toxicity • Safety	- - -	• Meet or exceed SAE J2719 for system safety	

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So, how much time it has to it takes to fill the tank that should be at par with the conventional gasoline based vehicles. So, a system fill time, which is expected to be 3 to 5 minutes 2025 and ultimate minimum full flow rate example like 1.6 grams target for 80 kilowatt rated fuel cell power. So, what is desired is it should be 0.02 grams per second per kilowatt.

An average flow rate 0.004 start to full time at 20 degree centigrade it this is important when we consider the starting up of vehicle. So, from the start to the maximum flow rate that should be achieved within 5 seconds of the operation. And similarly start time to full flow rate at minus 20-degree centigrade maximum acceptable is 15 seconds.

The transient response at operating temperature from 10 percent to 90 percent, this is important when it is considered as the starting of the vehicle. So, certain amount of hydrogen will be there in the pipes and tubing's, but after that it should attain it should get the required hydrogen for to be supplied to the fuel cell. So, that it can achieve 90 percent of the required energy.

So, 10 percent to 90 percent the response should be achieved within 0.75 second this is important during the starting up and 90 percent to 0 percent; that means, during the stopping up of the vehicle it should immediately stop and that response time should be 0.75 second. The fuel quality again when it comes to integrating with fuel cell the quality should be very high like the impurities which can be allowed to be there in the hydrogen flow should be at PPMs level.

And this is as per the SAE J2719 standard dormancy this is important when we consider the liquid state storage. So, we will see in detail when we will study the liquid state storage that there are losses which are unavoidable in case of liquid hydrogen stored. So, the dormancy time, which is targeted is 10 days in 2025 and 14 days in ultimate target.

So, this is the minimum until first release from initial 95 percent usable capacity if the tank is filled to 95 percent of its usable capacity, the number of days it will require for the first release of hydrogen from the tank due to boil off. So, the boil off target maximum reduction from the initial 95 percent usable capacity after 30 days it should be still 10 percent as target of 2025 and ultimate.

Regarding the health and safety requirements whether it is permeation or leakage, toxicity or safety all the needs to be met by the associated standards, which are already there. So, these are the requirements for onboard hydrogen storage system.

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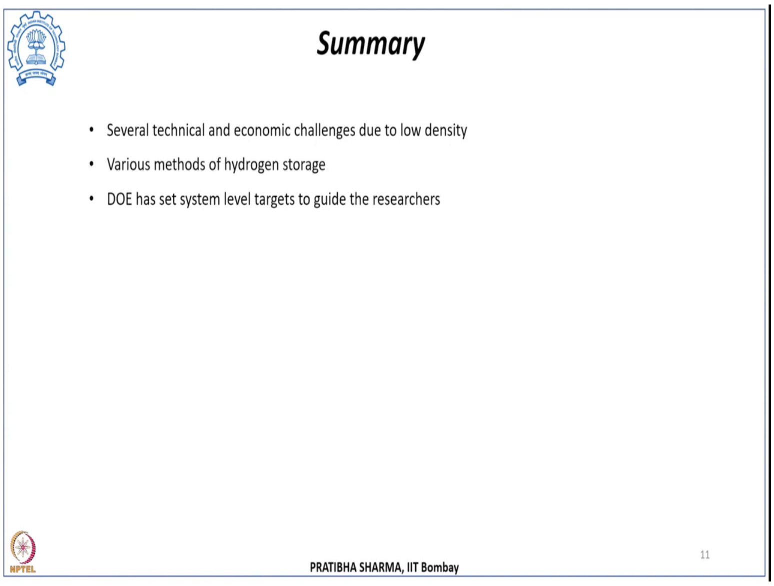

To summarize this part, we have seen that because of the low density hydrogen being the lightest molecule it also has a very high diffusivity, it is very difficult to confine hydrogen and that causes several technical challenges.

And also when we are compressing or when we are liquefying there are economic challenges associated with it. So, there are different methods which we are going to see in more detail from the next class and so, these methods can be used for hydrogen storage and then we have also seen today the doe targets, which has set in terms of system level targets, these are just to guide the researcher that these are the minimum requirement, which the system should meet in order to be these systems to be commercialized.

Thank you.