Cryogenic Hydrogen Technology
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Week - 04
Lecture 19
Overview on Hydrogen Storage

Welcome to this lecture on cryogenic hydrogen technology. We are talking about hydrogen storage in that connection. In the last class, we have talked about the compressed hydrogen storage. Now, we will look into another storage possibility that is in the solid ah matrix and mostly it is called the I mean popularly known as metal hydride. So, let us look what is the metal hydride. First of all, we have talked about the different as I was telling that we have talked about different storage options that is the compressed hydrogen, liquid hydrogen, then cryosorption and the metal hydride.

So, first of all we will be talking all to be we have talked about the compressed hydrogen. Now, we will be talking about the metal hydride. Later on we will move to the cryosorption storage and finally, we will look in details about the liquid hydrogen part. So, in that connection ah when we were talking about these 4 possibilities, we looked into a particular application that is the on-board storage of hydrogen for vehicular application.

So, here we have shown you this particular figure where we have told you that you know our final intention is to go for a you know compete with the gasoline, IC internal combustion engine and we have to store something like 5 to 6 kg for a particular distance and where we need ah an storage tank or weight of the tank which has to be similar to I mean we wish to do that ah and it should have less weight and it should be of smaller volume and compatible to you know our gasoline ah based gasoline based car. But in that connection, we have seen that if you look at this figure, you will find that ah this compressed hydrogen comes somewhere here ah you know this tank takes a slightly ah bigger volume somewhere here is the liquid in a hydrogen. But we have also talked about this ah you know metal hydride or hydrogen absorbing alloys that is basically the metal hydride and here if you look at they have a very you know small tank volume required and sometime it is less than the liquid hydrogen volume, but weight wise something that is you know ah very ah quite ah large ok or we need a large ah tank or ah I mean large capacity tank or it is weight will be higher or heavier. So, in that respect if we ah now look at ah if we see the storage conditions ah for particularly with respect to this compressed hydrogen at 35 MPa and 70 MPa, we find the volumetric density in terms of atoms per centimeter cube. You will find it is 1.3 for compressed hydrogen at 35 MPa and ah for 70 MPa it is 2.3 into 10 to the power 22 atoms per centimeter cube. While for you know typical metal hydride it is about ah 6 to 11 into 10 to the power 11 and 22 atoms per centimeter cube even higher than the ah liquid hydrogen. So, it can hold large number of molecules in a very small volume. So, that is the essence of it.

So, let us also look into the equilibrium separation distance between the molecules in ah what is called compressed hydrogen we find that it is about 0.45 nanometer which will reduce to 0.36 nanometer when it is in the form of liquid hydrogen, but what happens then in the metal hydride that it is able to you know stored so many molecules ah in a very small or compact volume. So, we will later on see how this hydrogen is getting dissociated and it is getting inside the interstitials of the ah I mean metal to make a metal hydride and thereby you know giving an opportunity to store very large number of atoms in a very small volume a small volume. So, now let us have a look into the possible ah hydride formation there are two possible hydride formation one is in the form of gaseous state of hydrogen we can directly ah mix it with the metal and there will be direct dissociation or ah dissociative chemisorption.

And there is another way of hydrating it that is ah the electrochemical water splitting, but we will not look into this particular ah aspect in this class mostly we will be looking into the first one. And ah let us have a look into this metal hydride classification at the beginning then we will slowly move into it is ah thermodynamics and the different type of metal hydrides that is you know those are available. So, first of all this ah it is a there is a statement from ah this ah that ah almost every element of the periodic table forms one on ah you know more stable hydrides. So, it is true except there are certain hydride gaps between you know ah what is called group 6 to group 11 except some are there with respect to this like palladium hydrogen is there nickel hydride is there chromium and ah copper hydrides. So, these are the exceptions other than that mostly it forms ah certain amount of hydrides and ah they have a very you know active ah they are very active with the lanthanides and actinides, but particularly with ah you know platinum and ruthenium they I mean they though adsorbed ah or absorbed ah hydrogen, but they are not ah you know they do not form a metal hydride.

Actually, ah they are basically ah very good catalyst for the hydrogenation part ok. So, probably you remember that when we have talked about the solid polymer electrolyzer the kind of ah you know platinum and palladium these are the or nickel ah those are the kind of material we have used for ah the electrodes. So, ah basically that is what is ah I mean their role is not for ah adsorbing the hydrogen, but they are basically they are very good catalyzers. So, now let us look into ah this metal hydride classification. So, this is from this ah paper and according to this paper I mean there are several ah kind of ah classification that is possible.

One possible classification could be in terms of the bond that they form and say here this is the internal I mean interstitial ah metal hydride where the prevalent I mean mostly it is the ah dominantly it is a covalent bond and there is non-stoichiometry. So, non stoichiometry means we can have ah I mean ah non integer value for the hydrogen at with the metal and like ah we say ah A B ah or A B2 this B2 if it is ah A B ah H2 ah it may not be H 2 ah it may be 0.7 of H or like that. So, it may not be a whole number. Then we also have the ionic or saline hydride this is mostly ionic in nature and they follow of course, the stoichiometry.

Then this saline or ionic hydrides are again ah divided into 2 parts ah mostly simple hydride and complex hydride we will try to look example for each of them. But to start with let us have a ah look into the hydride formation steps ah which are like this that when this molecules ah hydrogen molecules they are coming near to the metal surface and this is still in the molecular form. So, when they are coming to this surface ah they will be slightly dissociating as you can see that this ah you know hydrogen molecule is getting dissociated there would be slight polarization and I am not going into that detail at this moment. There would be basically this you know attraction is ah chemisorption in nature and because of that this dissociation takes place on the surface of it. So, now, it was ah earlier it was a molecule now it has become ah an atom and to be ah basically speaking you know ah this is ah only a proton and this proton will now try to get inside this ah bulk of the material.

So, this diffusion of hydrogen atom into the bulk of the material and this hydrogen when it is getting dissolved into the interstitial host metal it forms a solid solution which we call it as alpha phase and we will come into the further details when it is the solid solution alpha phase when it is ah beta phase. So, as it happens you know this will ah they they will ah I mean come inside this bulk material and there would be ah I mean formation of beta phase when it exceeds the particular certain limits depending on the metal ah or the host material. So, what happens ah they are coming as molecule they are getting dissociated into atoms and that atom is going inside the interstitials. So, after sometime what will happen ah this alpha phase will you know after sometime as we increase the concentration they will form more and more number of such you know ah layers or the bulk you know interstitials will be gradually filled up. So, at that time what happens this ah earlier this ah this atomic form or this ah this hydrogen atom was coming inside or proton was going inside and almost freely it was able to choose the interstitials position, but as time passes you will find or this this this atom will find or the proton will find that there is a layer of a hydride or beta phase.

So, they have to get inside or overcoming this hydride layer ah and then only you will be able to or it will be able to choose a particular interstitial. So, you can understand that what is the rate limiting process that means, initially when it was coming getting dissociated it is finding an empty space or interstitial. So, they are occupying all this you know empty space wherever they find position, but the you know the ah proton which is coming or the hydrogen atom that is coming late they will find that the all the sheets are occupied. So, they have to overcome that barrier or hydride layer barrier and then get inside that interstitials. So, that will be ah I mean the rate limiting process and it is you know in terms of several seconds.

So, it is not like that you know it will immediately come in. So, they have I mean they will be able to get inside or the reversible process I mean when we want the hydrogen to come out exactly opposite thing will happen. And so, this you can understand that when it was on the surface it was a kind of physisorption and when it goes inside it is a kind of chemisorption though there is no ah reaction that is going to take place inside this one except that they are going inside I mean breaking that hydride layer and or overcoming the hydride layer they will have certain barriers to overcome and there is some finite amount of ah you know enthalpy of reaction. So, but overall ah this dynamics of this molecules or molecular movement will be restricted by this processes. So, now let us look into ah the thermodynamics part as we were talking ah that you know when the pressure is this is about the concentration that is the number of hydrogen molecules per the metal and this is pressure equilibrium.

So, here ah this is the low pressure and high temperature. So, here you can see that T1 is the lower one and T3 is the highest one these are the three temperatures lines. And when this concentration is ah relatively lower about less than h by m ah less than 0.1 there would be some phase called the alpha phase. So, that is you know when this hydrogen molecules are getting inside they are forming a solid solution and it is called the alpha phase.

So, here you can understand that there is ah ah I mean pressure ah it is varying with the the concentration ah there is some relation with which it will be varying ah this concentration. And ah this alpha phase ah you can understand that there is ah basically a dependency between this two whereas, inside this when we are increasing the concentration level ah up to a a part you know greater than 1. So, this hydride precipitation part will start or the solid ah sorry the beta phase will start precipitating. So, when we come to this part this is the other limit and finally, you will find that again it is ah you know changing with the concentration limit in between at a particular temperature this will be almost a constant inside this. So, like you know we have seen it in the case of ah I mean ah phase change ah or say we have the gas ah I mean ah pressure it was changing inside this ah vapour liquid dome.

So, it remains the constant here the pressure remains constant and the concentration you know is here in this case of course, this is variation between the pressure and the concentration. So, here ah for ah if we plot it with respect to say 1 by T here we have seen this is 1 T1 this is T2 and this is T3 we find that if we plot it with respect to 1 by T and there are 3 points corresponding to ah say T1, T2 and T3 we will have ah 3 points. So, T1 is the ah ah lowest temperature and T2, T3 is the highest one. So, 1 by T 1 will be the highest one here sorry the lowest one here this this is ah 1 by T1. So, T 1 is the sorry this is T1 is the smallest value.

$$ln\frac{P_{eq}}{P^0{}_{eq}} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

$$y = mx$$

So, 1 by T1 will be the highest value. So, this is 1 by T this is wrong and ah if we are plotting this we will find that they are following ah ah constant line and here the slope would be ah ΔH by R whereas, this intercept is minus ΔS by R that is that is ΔS is the change in the entropy and this ΔH is the change in the enthalpy and R is the gas constant. So, if we put it ah with respect to this equilibrium pressure and this is the reference pressure of course, then then you can understand that this will this is since this is with respect to 1 by T and since the slope is ΔH by R we will have ΔH by R into 1 by T that is y equals to m x ah that is the van't Hoff equation. So, for each material this will be ah different graph like this. So, every time ah you know during ah say ah when it is getting charged.

$$F = C - P + 2$$

So, ah initially when the concentration is low it will be in the alpha phase gradually the beta phase will come in picture in between they will be having alpha plus beta phase and ah of course, this Gibbs phase rule will also be you know applicable over here. So, here we have ah then this ah we have 2 ah component that is metal and hydrogen. So, C minus P plus 2 that is what is the ah number of independent parameters. So, here inside this we have you know 2 components 2 phase and so, the number of variables would be say ah here 2, but ah when it is inside this we have another phase alpha plus beta phase. So, we have 3 phases and ah then you have 2 component 3 phase and 2 so that means, we have only 1 parameter that means, you know the pressure will remain constant independent of this concentrate I mean concentration part.

So, that is how it goes, but ah whenever you know there is a ah I mean pressurization or charging of this metal hydride we find that there is a kind of expansion that is this by this value 2 to 3 angstrom cube per hydrogen atom. So, it looks a very ah small though, but when we have very large number of you know hydrogen atoms you will find that they are getting absorbed and they are causing some kind of expansion collectively that may be slightly higher. So, again when there is the desorption or this is getting discharged so, there would be you know lessening or expansion I mean then there would be reduction in the volume by the similar amount per atom. So, what does it mean that every time we are charging the metal hydride we will find that there is expansion and then there is contraction. So, this expansion and contraction because of you know repetitive ah what is called ah charging and discharging we will find that there is a large the kind of what is called decay ah in the ah or dissociation sometimes this metal hydride will be dissociated into powders. So, that is a ah I mean problem of metal hydride and this is the basic reason for causing this kind of degradation in the metal hydride. So, now let us look into ah the charging and discharging part. So, as I was telling that this is during the charging part. So, now, if you have to take out this ah hydrogen ah from this metal hydride whenever it is needed. So, we need something you know some ah energy to allow the exactly the reverse process will be followed this hydrogen has to come out from the I mean interstitial positions then they will be coming to the surface they will reunite and finally, they will leave the surface as molecule.

So, if you look at discharging process if we you know see this is a you know the molecule then it is getting dissociated then it is coming ah then finally, this alpha phase will finally, get into a complex I mean beta phase completely beta phase. So, that is what is charging part. Now, when it is discharged I mean again we have the you know alpha phase will exactly the reverse thing will happen this will come out and from the beta phase you know finally, they are moving out of this surface or the bulk material they are coming out they are coming to the surface and from the surface they are going as you know they are getting discharged. So, everything is coming back to a solid solution where very small amount of hydrogen atom will be present in the system and you have to keep it in mind that there may be sometime hysteresis loss. So, that means, some of the hydrogen atoms will not be leaving that interstitial they will remain inside this metal.

So, every time we charge and discharge they will get inside this and that is what is the hysteresis. So, you would not be able to take them out of the system. Now, let us look into the ah I mean actual some of the promising ah metal hydrides which are being taught or thought of you know using it for vehicular application, but what are the advantages and what are the disadvantages we will try to look at. So, first of all it is the magnesium hydride it is just like ah A and ah I mean it is a kind of ah MgH_2. So, there are a metal A and that is you know associating with H_2 to form ah H_2 something like this and magnesium hydride being you know the light element.

So, it is having very high ah energy density. So, 9 mega joule per kg of this ah magnesium ok. So, this is the highest energy density ah hydride and it is having a very high ah capacity that is the gravimetric capacity is 7.7 weight percentage. So, it is basically as we were talking initially that ah this metal hydride ah are very bulky in ah nature or they are heavy in nature, but that is not really true that this gravimetric ah weight density or gravimetric ah this part of the ah hydrogen capacity is very good with this magnesium hydride.

But ah let us also look into the other advantages it is abundantly available. So, we do not have really problem with the cost of it and it is a good reversibility, but what stops it from being ah you know positive or an attractive solution for the ah what is called for the vehicular application. The disadvantages of this particular metal hydride is something like it is the slow kinetics. The slow kinetics means what that we want to absorb or we want to charge it, it processes slow and we have talked about what is that rate limiting process. That rate limiting process is that you know it has to come to the surface, it has to dissociate, then it has to go inside the bulk of the material, then it has not only that it has to you know overcome the what is called the barriers.

So, all these are the disadvantages and this discharge needs of course, high temperature. So, particularly if you look at this magnesium hydride, it needs a nearly 300 degree centigrade temperature at atmospheric pressure to you know dissolve the hydrogen. So, if I have to I mean get hydrogen from a car, we need something like 300 degree centigrade temperature and then only it will be able to you know release this hydrogen and it will be available for the use. So, that is not a very small you know ah degree or I mean temperature ah particularly with respect to ah vehicle. So, it is a you know this is not very attractive thing that we can look at though it is having you know very high ah energy mass energy density and volumetric I mean the gravimetric storage capacity.

So, ah we can you know look into it ah I mean, but this is the what is the limiting process and as I told you that slow desorption kinetics. So, it means the adsorption and desorption will take place for some time to I mean it is not very easy thing to take it out or get inside. So, high reactivity with the air and oxygen that is the for the magnesium part ah ok it will reacts ah I mean severely with the oxygen of the in the air or oxygen as such. So, that is another limiting parameter for this magnesium hydride. So, other than that we have as we have talked about that inter ah metallic compounds that is ah it is ah earlier we were talking about say ah magnesium hydride that is basically a binary system.

So, here now we have a tertiary system where the generalized formula is ABxHn and here ah if you if you have noted that they are having you know the ah quite that they follow the tertiary and it is like ah Bx can be 0.5 or 1 or 2 or 5 like that. So, the generalized formula for this you will find that A particularly is having a very high affinity for hydrogen and they form a stable hydride or basically this rare earth and alkaline earth material they are basically composing the A part whereas, the B part is basically an unstable metal hydride and there have low affinity for the hydrogen. So, mostly they are the transition in the materials. Now, if if we look at the particular I mean the interstitial compounds there AB5, AB2, AB3, AB and A2B there are some more I have not listed them up here.

So, you can look at any standard book for I will show you the references at the at the end. So, there the inter metallic compounds and the inter metallic hydrides would be something like this ok. So, here you can see that ah it is not correct ah LaNi5H6 it should be this is zirconium this should be A in I 5 and AB3 is I mean this is the compound and AB is this is titanium iron A2B is magnesium nickel hydride. So, like that we have different kind of metal hydride that is possible and they will have different heat of adsorption and heat of you know release of course, they will be different. So, then we have the complex metal hydride which are ah quite promising one of them is sodium malonate ah and they are basically the sodium ah compound of ah sodium and complex hydride of aluminium and sodium.

So, sodium tetrahydroaluminate and trisodium hexahydroaluminate these are the type of compounds and let us look into the kind of reaction that it undergoes at different temperature. So, you can understand that these temperatures are a bit high and we have nearly ah 3.7 percent and though the actual you know theoretical storage capacity is 7.4. So, it is a capacity is like 1.9 percent for this and 1.3.7 weight percentage for the sodium tetrahydroaluminate. The advantage is of course, theoretically reversible of ah and it is having the storage capacity of 5.6 you can sum it up to 5.6 weight percent and the low cost and availability in bulk is the other advantage, but the disadvantages part are again poor kinetics and slightly irreversible that ah I mean as we have talked earlier. So, that is about the metal hydride complex metal hydride part and let us now look into the references. So, these are the references we have you can have a look into it and then ah you can read and you will get there are plenty of materials on material metal hydride I have just limit ah listed some of them if you need any further assistance you can talk to the TA later on. So, now let us look into the conclusion part. So, we have many transition materials and metals and alloys which can ah I mean a reversibly ah adsorb large amount of hydrogen and then charging and discharging can be done as we have said in two ways.

The binary hydrides ah basically if you look at you will find that they are mostly having a metallic nature and that is why it is called the metal hydrides. Many of these compounds ah show large deviation in terms of the stoichiometry and the limiting composition is of course, ah MH, MH2 and etcetera. So, this lattice structure is ah of course, ah I mean in in the interstitial and that is why they are also sometimes called the interstitials metal hydride as because this hydrogen atoms or you know in the atomic form they get inside this metal interstitials. So, thank you for your attention.