Cryogenic Hydrogen Technology

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Lecture 13

Electrolytic Hydrogen

Welcome to this lecture on cryogenic hydrogen technology. We were talking about the production of hydrogen through electrolytic ah method or electrolysis of water. In that connection we have learned the minimum voltage, thermodynamic voltage and then thermo ah thermo neutral voltage. Then ah in terms of the practical ah ah limits ah we have talked about the ah over potential or the over voltages that is necessary. And finally, we have talked about the ah tank type and filter press type configuration or the of the electrolyzer. Now, in this lecture ah it will be a continuation to that and as we have said earlier that we will be talking about two type of electrolytic production of hydrogen one is the alkaline electrolyzer another is the solid polymer electrolyzer.

So, in this lecture we are going to talk about ah the electrolytic hydrogen and particularly we will be talking today about the alkaline electrolyzer. So, ah let us just have a look ah into the ah basically this is a recapitulation of what we have learned earlier. So, we have finite resistances ah and we have categorized them into the electrical resistance and then we have this important R3 and R5 that is the reaction resistance that is taking place at the anode and the cathode. Finally, we have the ah all are basically the lead resistances other than that.

So, this decides the ah you know over potential that will be ah necessary and we have talked about it in the last class. But what we understood is that you know this two resistances R3 and R5 ah they are again very important not only that we try to you know ah minimize all this R3 in R1, R2, R4 or R7 or the electrolyte resistance all these resistances we try to minimize and basically so that you know this R 3 and R 5 that will give us the dissociation of water into hydrogen and oxygen. So, ah if we have to do that we need to have you know a very good ah I mean minimization of this overpotentials ok or over voltages ah you know will be necessary if we want to be very close to the you know thermodynamic voltage that we have calculated fine. So, in order to do that ah, we seldom use of water in its pure form because it will have a very large resistance. So, what we need to do is that in order to increase the you know the conductivity of this water either we need to add ah you know some amount of acid in it or alkali alkali or you know the salt.

So, the commonly ah you know adopted method is to add the alkali both though you know this acid addition will also in a I mean this acid will also generate H+ ion in the solution and alkali will of course, you know induce this OH- ion in the solution. So, though they are you know producing H+ and OH- both this acid and alkali of course, salt will also increase the ah you know thermal conductivity of the it is the electrical conductivity of the solution, but this alkaline solution is preferred one because it gives a less corrosive in a resistance I mean it is less corrosive to the electrodes. So, because of that it is preferred that you know over the acidic ah solution or addition of acid in the water. So, we have the KOH and NOH both are possible, but mostly we go for the KOH one. So, the historically it has started with the KOH and because of it is corrosion resistance ah I mean less corrosive resistance with the electrodes.

So, the maximum conductivity ah is attended nearly around 28 percent weight percentage of KOH and generally we go for 25 to 35 of ah weight percentage of KOH solution ah in the water. So, that is what is the solution I mean the electrolytic solution would be having a solution with 28 weight percent of KOH in it and then what we need is the electrode and we understand that there should be high electro catalytic material. What is that electro catalytic material? As we have learned that there has to you know we will talk about the detailed reaction in the ah that is taking place in the cathode and the anode, but what we understood is that this this dissociation of this ah I mean hydroxyl ion or this hydrogen ions in the anode or the cathode will have certain activities like it will come to the anode or the cathode it will transfer the charge then it will you know form the gas bubble and that gas bubble or nucleation of that gas bubble has to you know start on the surface and then finally, it has to be separated from the surface and it should come out. So, that ah this all these activities have to occurred it in ah quite fast. So, that the electrolyte and the electrode should never be you know ah covered all the time with the bubbles of the hydrogen or the oxygen.

If the anodes are covered with the bubbles of say either hydrogen and oxygen the fresh electrode or electrolyte will not be able to see the ah electrode. So, that is why this electrolytic ah you know this material the catalytic material or the electrode material is very important and there are quite a few ah materials which are ah you know is in use. So, in group 8 in the periodic table you will find that Iron, Ruthenium, Osmium group 9 we have Cobalt, Ruthenium, Iridium, and group 10 Nickel, Palladium and Platinum. So, these are ah quite some of them are quite costly ah though they are having you know high electro catalytic ah I mean potential over potential low over potential ah for the alkaline electrolyzers, but the most commonly one ah used one are Nickel, Cobalt and the Iron. So, the preferred electrodes because of the low over voltages that means, they will ah allow this formation of this charge transfer transform charge transfer then you know formation of the bubble leaving of the bubble or detachment of this bubble from the electrode will be having you know quickly occurring with this kind of materials and often ah the nickel coated stainless steel is another popular choice as electrode material.

So, because of when we are talking about ah the production of this hydrogen ah be it electrolytic production or any other means we have to also look at the cost of the ah equipment. So, though you know this platinum is highly ah corrosion resistance material or rhodium or this you know ruthenium they are ah definitely they are corrosive to this alkaline solution corrosion resistance properties are very good with this material, but they are rare materials or they are costly materials. So, we should always look for some material which are cheaply available. So, ah there is another ah material which is called Raney Nickel which are preferred material for this as electrode it is having high catalytic activity and low over potential and it is also porous in nature. So, this Raney Nickel is ah is again another commonly used electrode for this electrolytes process.

Then we have another important part this diaphragm ah which we have learned that in the cell we have this diaphragm which is separating the ah both the products hydrogen and oxygen. So, it is pore size has to be ah you know less than the ah bubble size of say the hydrogen or the oxygen. So, here compared to hydrogen and oxygen I mean comparing if we compare this two we will find that the hydrogen is a smaller molecule and obviously, ah it is of the order of 10 micron. So, what we need in the diaphragm. So, it should have diaphragm with pore size ah you know smaller than 10 microns. So, that the hydrogen molecules cannot ah pass through this you know from one end to the other end. So, that there is no addition I mean mixing of ah O2 and H2 and because that if they are mixing and ah and then there is some amount of ignition and it it can generate a kind of explosive mixture. So, that is a that will create a kind of safety hazards and ah, but at the same time it has to allow the ions or hydroxyl ions or the ah you know hydrogen ions through it and. So, diaphragm plays a very important role in separating the products, but allowing the movement of the ions and at the same time we have to also keep it in mind that this resistance of this electrolytic resistance or the ah resistance of these ions will again you know give some amount of over voltage. So, it has to allow these ions easily, but it has to restrict the ah gas or the product gases rather.

So, we have a quite a few ah commonly used ah diaphragms one of them is asbestos, then we have oxide ceramic like NIO and PTFE (polytetrafluoroethylene). So, these are the commonly used ah one, but this asbestos it is having you know some health hazards. So, in some of the countries they have you know ah I mean they have restricted use of this asbestos, but newer materials are coming in picture. So, ah this is about the details of the electrodes and the diaphragm that will be ah used and of course, there is the KOH solution as we have understood that it is maintained it is ah I mean concentration is maintained ah around 25 to 35 weight percentage of KOH in the aqueous solution. So, now, ah let us look into the ah detailed reaction that is you know taking place in the cell ah as we have understood that ah um when we are putting the KOH in water this KOH will dissociate into K^+ and ah OH^- you know ions.

So, this K^+ ion will try to move to this ah you know this is the positive and this is ah it will be attracted toward the cathode and here it will try to collect one electron. So, this K ah with the ah you know one electron it will it is K^+. So, it will pick up one electron to become neutral and it will be in the nascent condition. So, it will be said that this nascent K^+ will react with the water to form a kind of K^+ again and half of H_2 and OH^-. So, this half of H_2 will now mix this is basically the nascent hydrogen which will combine with another nascent hydrogen to give the hydrogen molecule.

So, that will be formed on this surface this nucleation has to take place and then it has to detach from this surface and then it has to come out of this surface. So, what happens to the other ah you know molecule like ah we have the hydroxyl ion from here we have also seen this hydroxyl ion from here. So, they will move towards the this you know this surface on this anode here this hydroxyl ion they will give this electron and they will you know become this electron will be given to the circuit and so, ah what is what we have is the hydroxyl, but this is ah you know the in the nascent condition. So, this is neutral and from here what we have is half of O_2 will be generated and then we will have H_2O. So, we have this hydroxyl ion will produce half of O_2 or that is basically the nascent ah oxygen.

So, this half O_2 will be combined with another half of O_2 to give us the oxygen molecule. So, this oxygen molecules are formed on this anodic surface and they has to depart from this anodic surface and then finally, it has to come out. So, as we were telling earlier that this formation of the charge transfer then you know formation nucleation of this bubble on the surface of this ah electrode then detachment of it and finally, moving out of this electrolytic cell. So, that this electrolyte is finding or this electrolyte is finding a fresh electrode ah you know free from the bubble. So, this all this ah you know movement of this bubble dynamics or say the charge transfer ah it depends on the type of electrode that we are using in practice.

So, based on this ah information so, let us just have a consolidated value of this. So, on this cathode as we have said this is the reaction that is taking place ah and, on this side, we have the anode where this oxygen will be generated and here we have you know on this side hydrogen will be generated. So, this is the consolidated part of the detailed reaction.

So, here ah based on this information let us try to look at ah a practical or a commercial electrolyte that how it what it does ah it is ah. So, far you know we have said that we are putting ah cell voltage and connected with the 2 electrodes that is what is giving rise to the oxygen and hydrogen at the cathode and the anode and so, but is it ah just like that ah and here of course, now we have learned that we should have a k o h solution and ah the oxygen for example, that is coming out or the hydrogen that is coming out you know it is ah finding in passing through the KOH solution.

So, that means, it is not pure hydrogen that will be obtained. So, we have to get rid of those elements and let us see in a commercial ah electrolyzer ah what is done. So, but before that we just need to look at if it is a commercial electrolyzer we have understood ah from our previous lecture depending on the type of ah electrolysis cell electrolytic cell that is in use either we use a tank type or filter press type. So, that will give us a requirement of the ah voltage and current. So, that is very important and it is ah I think ah it is needless to say that what we will be ah looking for is a DC voltage at this point, but we may start with an alternating current ok which is available in the ah I mean in the grid.

So, here comes ah this power system. So, this alternating current which will be available in the grid ah will be you know taken into a transformer this is called the isolation transformer it will be ah in a put in and then it will come to a full wave rectifier and the filter capacitor it will pass through. So, that we have you know the the ripples are not there in this ah voltage and this rectified and filtered DC voltage that will come to the anode and cathode and we have to look at the particular voltage that is necessary and the current that is that we are looking for. So, ah this is about the power system that will be used in the ah in the electrolyzer. So, based on this electrolytic you know this voltage requirement then you know this all these cells will be connected either as we have said that in a tank type all the you know cells are ah in parallel connection and in the filter press type all of them are in ah you know series connection.

So, the voltage requirement is different for both of them ok. So, we will be talking about the filter press type in the ah next ah I mean when we talk about the solid polymer electrolyzer, but in this ah mostly we will be talking about the tank type electrolysis process. So, let us try to look ah into the ah electrolysis electrolytic process which are commercially ah available what are the kind of ah components which are available with it. So, we have the electrolytic module where it may be ah as we said the tank type or the filter press type I mean that will decide what is the kind of ah electrical requirement we have for the voltage and the current. So, what we get from here is the O_2 after separation and what we have also on this other side is the hydrogen gas, but as we said that it will be ah KOH solution and KOH solution nearly around you know ah 25 to 35 percent concentration we are supposed to maintain.

So, this aqueous solution of KOH ah will give rise to hydrogen and oxygen. So, when they are coming out of this ah cell this hydrogen gas will carry certain amount of KOH, but we are looking for you know the hydrogen in the pure condition and we also do not want this KOH solution you know to deplete in this electrolytic module because we have you know understood that the KOH solution conductivity electrical conductivity will be reaching a maximum around 28 weight percent. So, if it is continuously you know losing the KOH solution from this ah you know aqueous solution. So, it is going to ah deteriorate the performance or replenishment of KOH will be necessary from time to time. So, we want to get rid of the KOH from both oxygen and hydrogen product.

So, ah, but this ah I have forgotten to mention that ah this ah cell voltage is also you know operated at a relatively higher temperature between 80 ℃ to 150 ℃ depending on the ah temperature and pressure of the product that you are looking for ah. Here there is ah ah it has not been mentioned maybe we will talk about it later on sometime. What is the ah pressure effect ah all the time we have talked about the temperature and I mean if we enhance the electrolytic temperature ah of the solution temperature and we said that you know there is a lessening of the ah over potential ah with a dependency of that over potential or the voltage with temperature we have seen ah, but we have not talked about the pressure effect sometime maybe we will be talking about that later on, but assume that it is having ah a temperature of 80 ℃ to 150 ℃. So, if it is coming out this along with this vapor of ah say hydrogen gas and ah oxygen gas it is not only carrying the KOH solution, but they are carrying it at a particular temperature. So, what we need to do is that we need to get rid of this KOH and put it back into the solution.

So, for that what we have to do is that we will ah you know ah put it in a heat exchanger and the KOH electrolyte will be pumped back after filtering it if there is any kind of ah what is called if there is any kind of ah you know ah accumulation of dots and etcetera. So, that has to be filtered out and then ah it will be ah you know put back into the system. Similarly this oxygen will also be you know get rid of this KOH and from the you know this heat exchanger is necessary why because we will find that while removing the KOH solution we are trying to you know use some kind of water through it and then you know this will be ah put back and with the ah temperature control ah because this cell will be maintained at a particular temperature. So, after filtration now this is this electrolyte is going back. So, this hydrogen gas first of all as we have understood that it was ah this KOH solution it was mixed with it and we have getting rid of that ah electrolyte.

So, that is put back and again as we have understood that we are taking help of some ah aqueous or water the demineralized water to you know separate this hydrogen gas from this KOH solution. So, what we have to do is that again we will you know put it in a heat exchanger and through that heat exchanger it will be taken ah to ah basically ah you know the condenser part are demystered. So, this when it is passing through the condenser they will remove the water part and this water will be this demineralized water will be coming back to this ah hydrogen gas separation or say the O2 gas separation part. And of course, what is not shown here is that if we are steadily getting this hydrogen gas as the product we need ah this H2O supply into this electrolytic module. But again, we it has to come with a particular temperature.

So, there has to be a temperature controller to put it before it is administered into the ah electrolytic cell and it has to maintain a particular concentration in the electrolytic cell. So, that is also to be monitored continuously. Finally, this hydrogen gas which you know is ah having some little bit ah you know moisture or ah you know as it is getting rid of it though it is condensed the moisture. So, if it is a little bit of it is present. So, that is to be you know passing through the PSA with the ah adequate ah I mean relevant adsorbent.

So, that they will be adsorbed and we will have the dry hydrogen ah available with us. So, this is an electrolytic schematic electrolyzes schematic mostly the practical system which ah you make use of not only the electrolytic module, but ah it is having the ah couple of exchangers, filters, rounds, etcetera. So, finally, ah typical alkaline cell ah you know in a commercial ah I mean conventional cell typically we use 1.8 to 2.2 voltage and the current density is about 0.4 $\mathrm{A/cm^2}$. The advanced cell this is you know they have typically 1.6 volt and current density nearly 2 $\mathrm{A/cm^2}$, but ah with an efficiency of the ah conventional cell between 60 to 80 percent and with the modern one ah particularly the filter press type which are compact in nature they give rise to nearly about 90 percent efficient ah cell efficiency. So, these are the references ah you can you know go through and finally, ah let us look at the conclusions say we have ah you know ah seen that the alkaline solutions are preferred one over the acidic solutions, then we have the detailed ah anode cathode reaction we have learned in this lecture and finally, we have said that between 35 25 to 35 percent KOH solution is ah typically used for alkaline electrolyzer. And thank you for your attention.