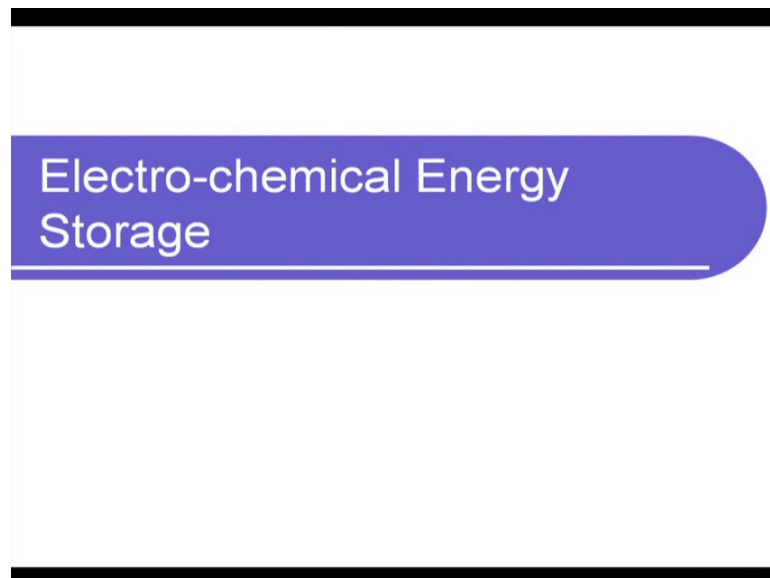


Energy Conservation and Waste Heat Recovery
Prof. Anandaroop Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 58
Energy Storage Systems – VIII

Welcome back, good morning and we will start the next lecture of Energy Conservation and Waste Heat Recovery, where we will continue our discussion again on Energy Storage. And this time we will go to a new means of energy storage which is Electrochemical Energy Storage.

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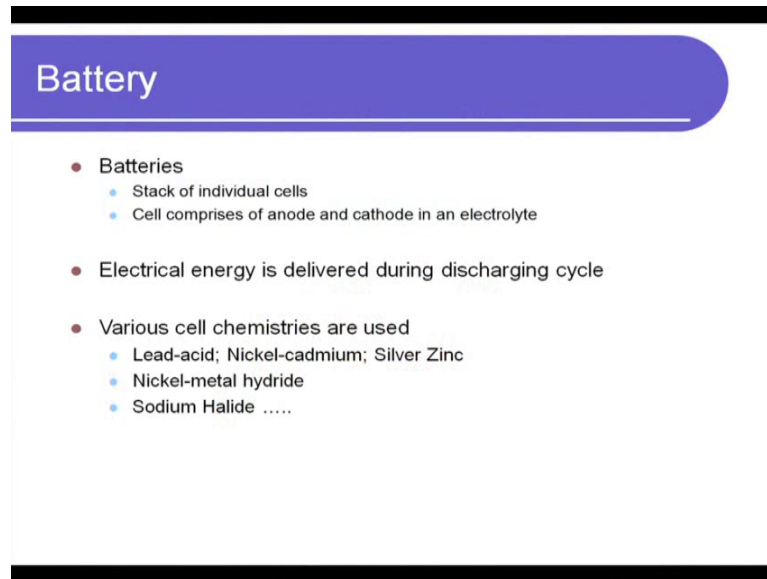
What do we mean by that? So in the first class when we talk or first class on energy storage when we started talking about it, we mentioned that the first thing that comes to our mind when we talk about storing energy and using it elsewhere whenever required the first thing that comes to our mind is battery right. We use batteries, we use to charge a battery by using electricity, and we do it in our cell phones every day.

We charge our cell phone and then use it right. We could have used our cell phone directly by always plugging in into the wall outlet, but we do not do that that is what gives makes it mobile. Laptops another example: we are able to take or work anywhere I can meet you somewhere on the street, just go to a coffee shop open my laptop and discuss and have a nice official meeting over a cup of coffee. Why? Because I have a

battery in the laptop which any which power cell machine and enables me to do work while I am on the move, right.

So, that is the electrochemical energy storage. So, finally we come to batteries as an energy storage medium.

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So batteries as we know it are a stack of individual cells. When we talk about battery we go to a shop and say let us buy a battery we typically buy one cell. Some applications just one cell is good enough, but in most applications it is not. I mean even in your TV remotes most of the times we need two such batteries, many other appliances in a torch probably we need three of them if it is a powerful one.

So a battery consists of a stack of individual cells. The cell comprises of anode and cathode in an electrolyte. We know that in a battery we have 2 electrodes: one is an anode, one is a cathode and then there is an electrolyte. The electrolyte can be liquid can be solid can be powder and so on. So we will look at that.

So what happens is again you have a charging and discharging cycle. In the discharging cycle what we do is we actually remove the heat or sorry remove the energy not heat anymore so we remove the energy. And this is when we are actually using the gadget which is powered by the battery, right. And during the charging cycle what happens is? We actually recharge those batteries so that we can where the energy is again stored.

Many a times in the regular batteries that we have they are not rechargeable; I mean they just one time use they come you to you as charged over a certain period of time they will discharge depending on the load and then we have to throw them away right. Well, I should use the word carefully they throw them away no; we have to dispose them correctly because these are hazardous materials. Sorry, this is not a course on environmental engineering, but still please keep in mind that batteries whenever you are done and you want to dispose them off do it properly, do it to the proper recycling channels a little deviation from the topic but still a good message to remind ourselves.

So, various cell chemistries are used lead acid is something that we use it. For example, most of the cars use Lead-acid battery, Nickel-cadmium, Silver Zinc, Nickel-metal hydride, Sodium halide. So different kinds of batteries are there Sodium Halide for example, when I was working for GE, G had a battery business which was making Sodium Halide batteries alright.

So, what we will do next is we will look into the functioning of the lead-acid battery ok

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Lead Acid battery

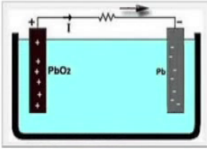
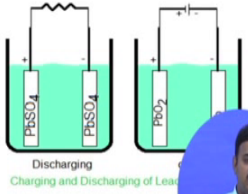
- **Materials**
 - Lead peroxide (positive electrode)
 - Spongy Lead (negative electrode)
 - Dil H_2SO_4 (electrolyte)

Overall reaction:

$$Pb + PbO_2 + 2H_2SO_4 \xrightleftharpoons[\text{Charge}]{\text{Discharge}} 2 PbSO_4 + 2H_2O$$

- During discharge, concentration of electrolyte is reduced due to removal of sulphate ions and formation of water

- **Features**
 - Used in cars (series of 6 cells)
 - Flexibility in current, high reversibility
 - Self-discharge and sulfation occur with time

Discharging
Charging and Discharging of Lead

<https://www.youtube.com/watch?v=H>

So what is the lead acid battery? It has 2 electrodes, one is Lead it is actually not solid leads what we call spongy lead which is a negative electrode. And lead peroxide which is a positive electrode the electrolyte is dilute sulfuric acid.

So what happens is during the discharging cycle the lead and lead peroxide react with the sulfuric acid when we have actually a polarity or a load attached to the batteries. Then what happens is and essentially what happens therefore is the dilute sulfuric acid becomes even more diluted. Because it loses the sulfate ions which goes to the lead and what we have is lead sulfate deposition on both the electrodes.

During the discharging cycle, what happens is or sorry during the charging cycle what happens is this lead sulfate. During the such charging cycle is when we actually attach a polarity across then what happens is the lead sulfate the sulfate ions are released and then they again recombine with the water and what we finally get is again lead and lead oxide and dilute sulfuric acid.

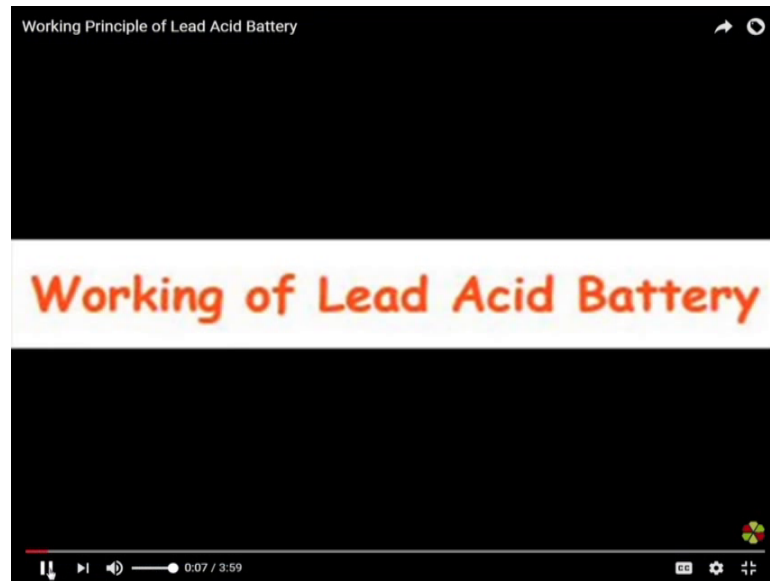
So, after a charging cycle this is what we again get back and discharging of course we have. Let us we have a further reduction in concentration of the electrolyte in this case sulfuric acid and we have sulfate, lead sulfate formation on both the electrodes. So, what I will do is I will play you a small video the link is over here and that will kind of show the sequence in which the reactions take place I think this is explained in a very nice animated way much better than what I can do using the paper etcetera that I have.

So I will just run this video.

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Let us have a discussion on working principle of Lead Acid Battery.

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This is very commonly used as storage battery or secondary battery.

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Before going through the working principle, we should know about materials used for lead acid storage battery cells. The main active materials required to construct a lead acid battery are:-

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Lead peroxide.

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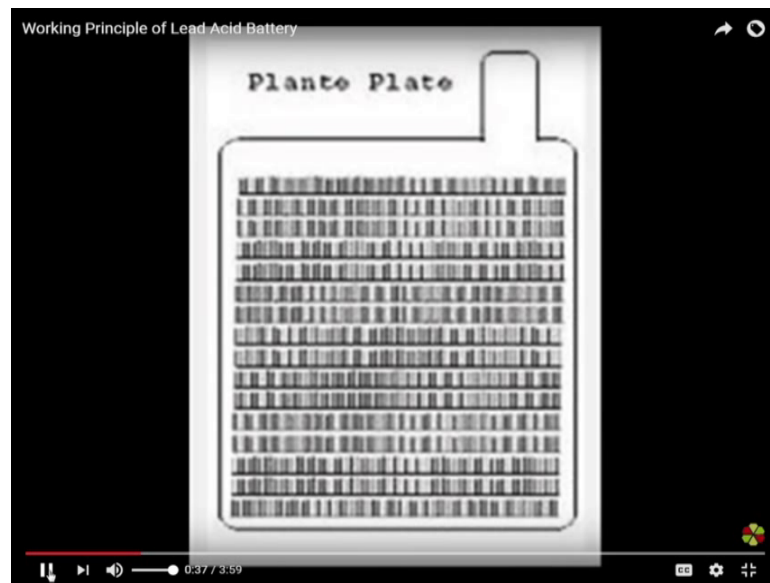
Sponge Lead.

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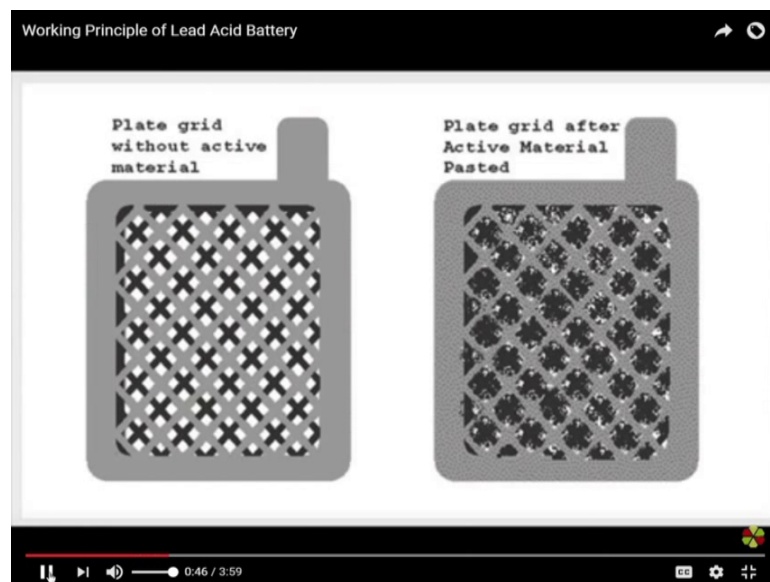
And dilute sulfuric acid.

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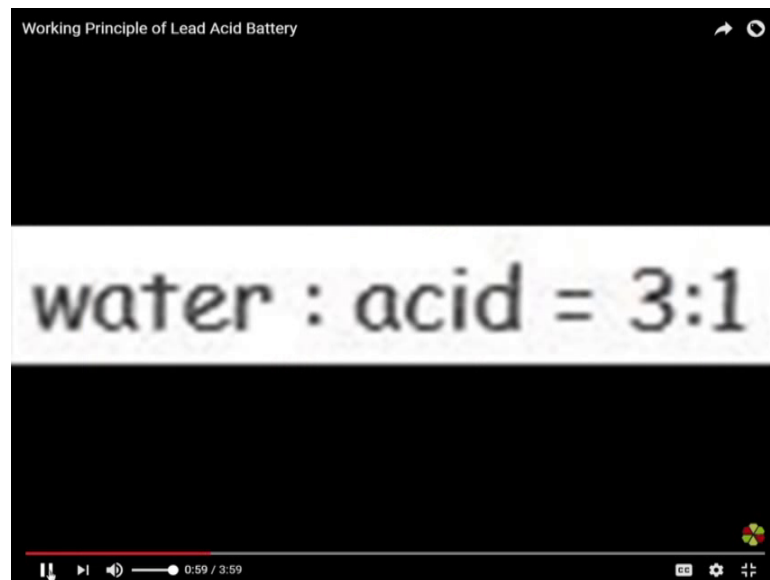
The positive Plate of lead acid battery is made of lead peroxide this is dark brown, hard and brittle substance.

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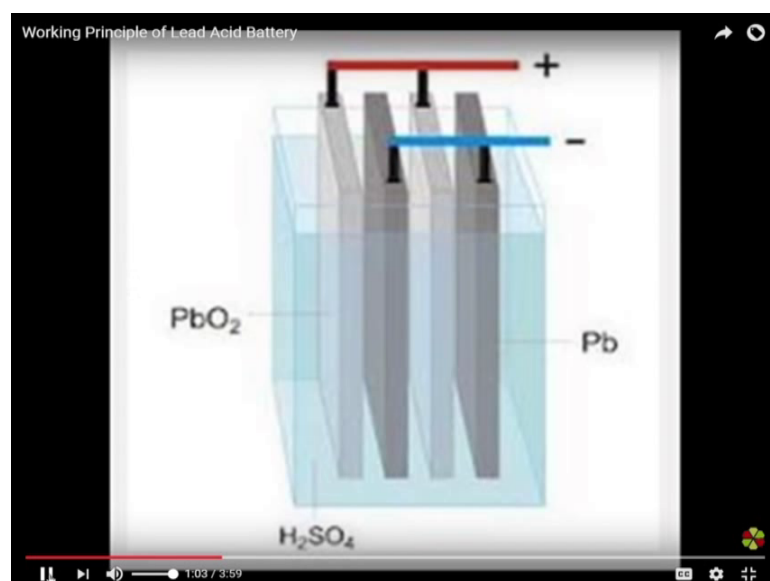


The negative Plate of lead acid battery is made of pure lead in soft sponge condition, dilute sulphuric acid used for lead acid battery as ratio of water is to acid equal to 3 is to 1.

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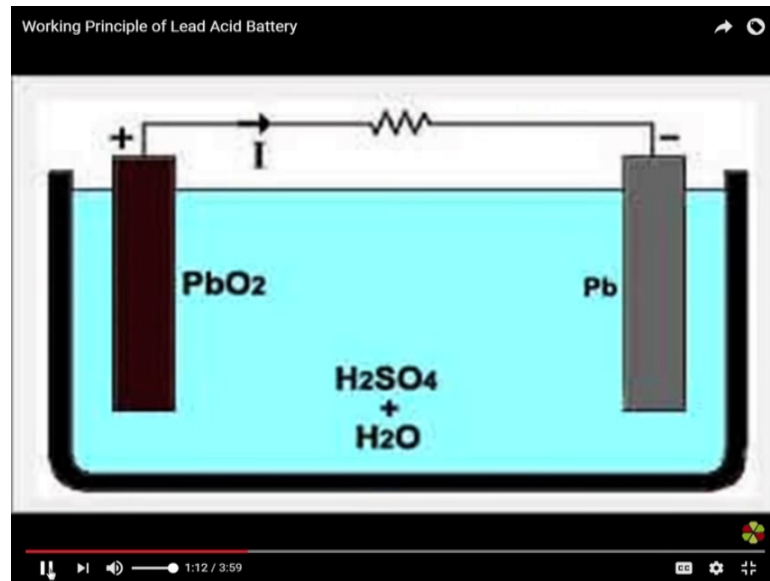


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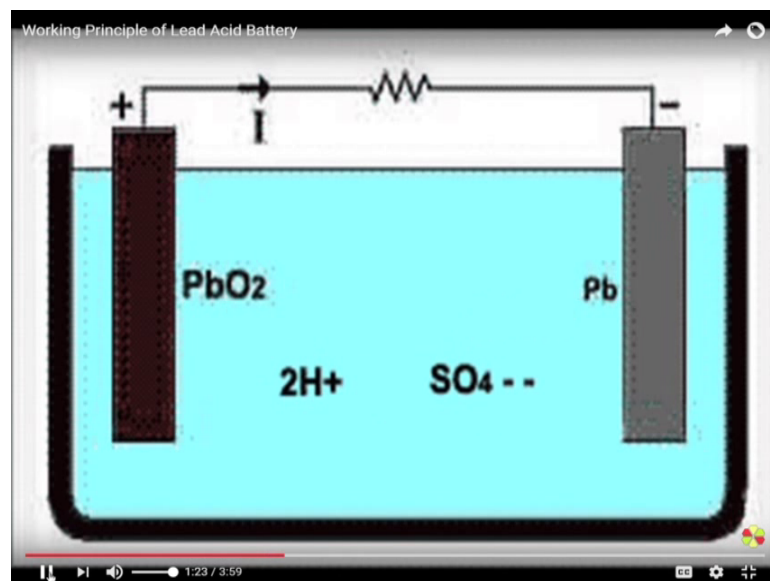
The lead acid storage battery is formed by dipping lead peroxide plate and sponge lead plate in dilute sulfuric acid.

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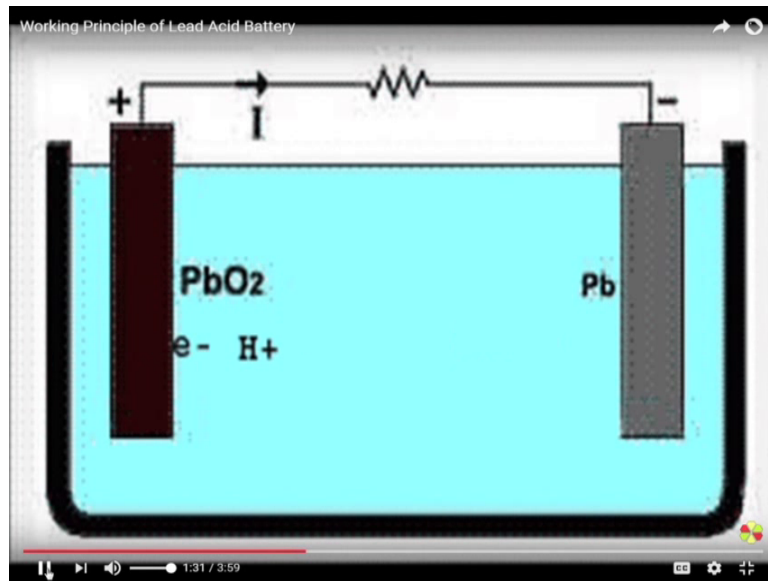
A load is connected externally between these plates in diluted sulfuric acid.

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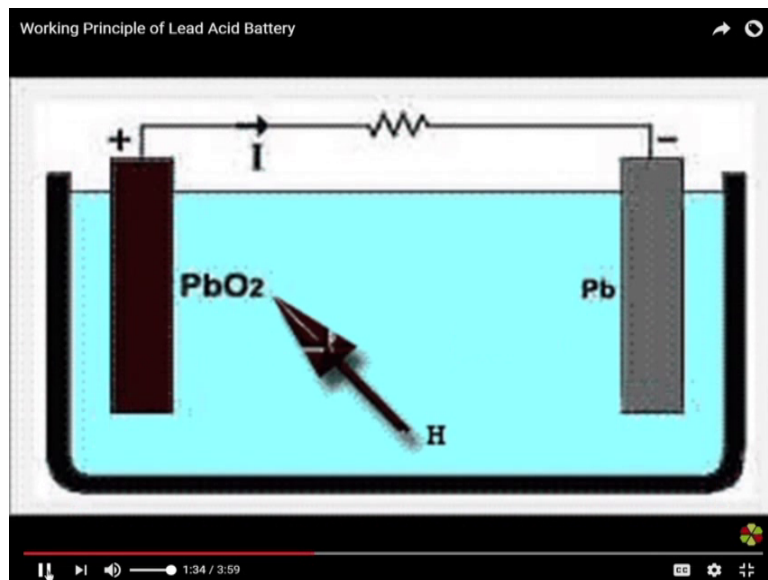
The molecules of acids split into positive hydrogen ions and negative sulfate ions.

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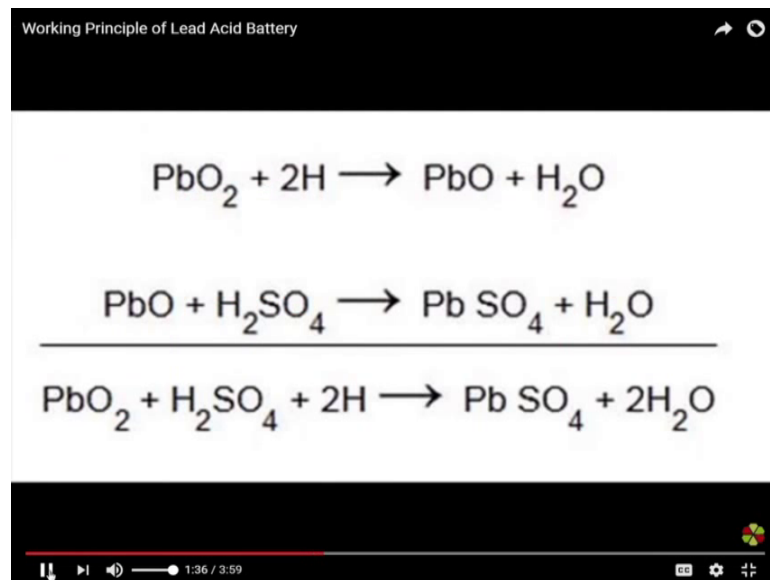


The hydrogen ions when reach at lead peroxide plate they receive electrons from it and become hydrogen atom which again attacked lead peroxide.

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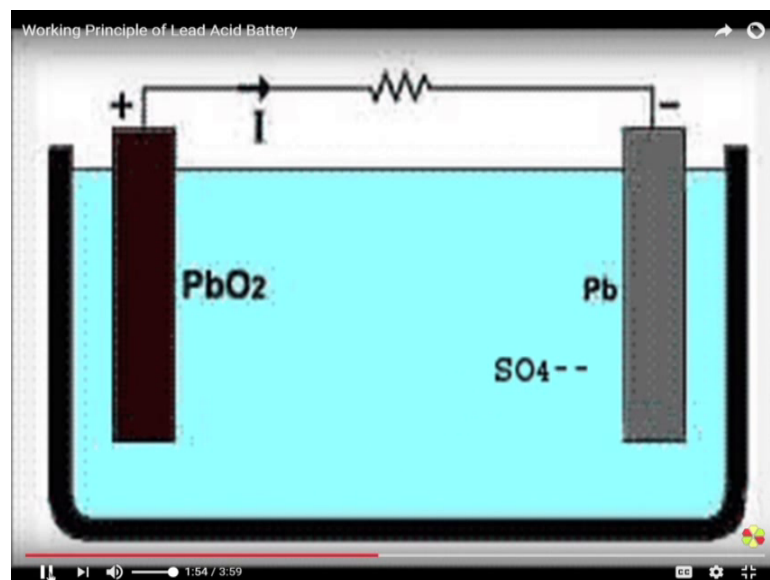


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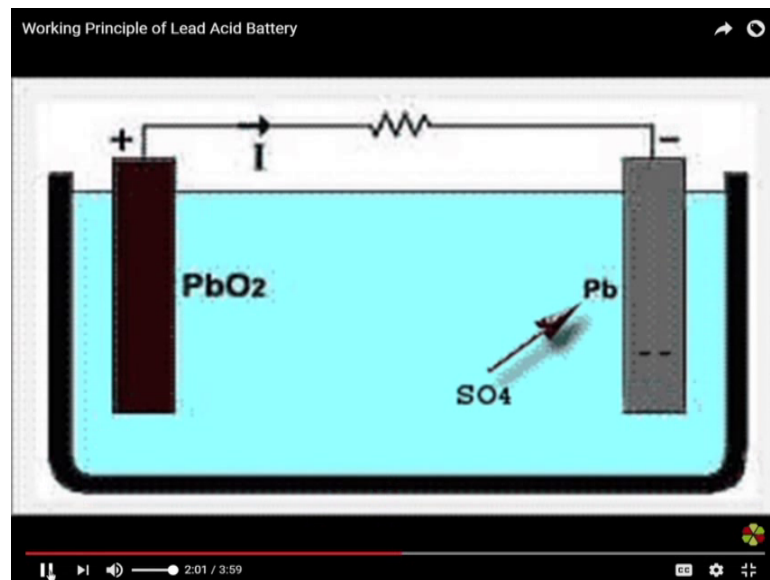
And formed lead oxide and water this lead oxide reacts with sulfuric acid and forms lead sulfate and water.

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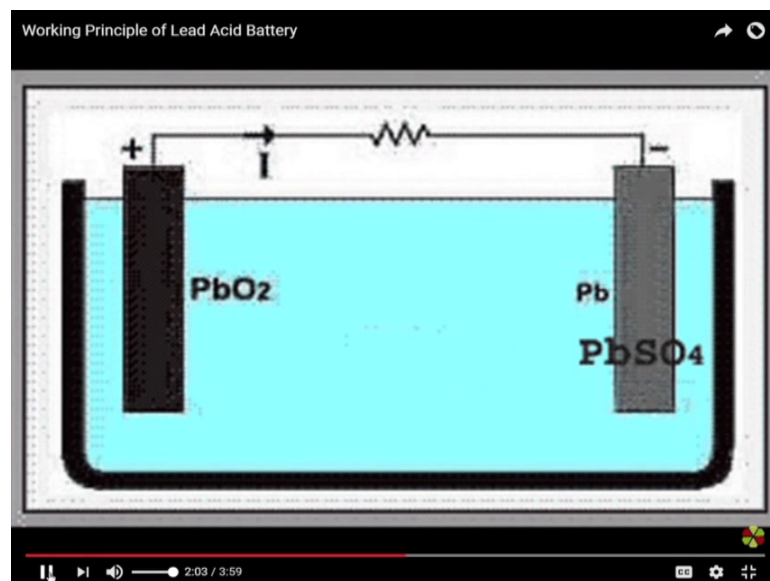
Negative sulfate ions are moving freely in the solution so some of them will reach to pure lead plate where they give their extra electrons and become radical sulfate.

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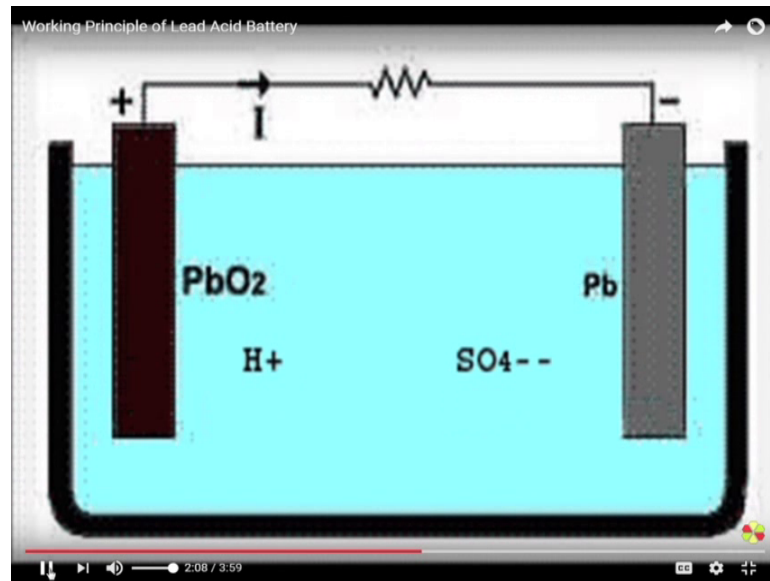
As the radical sulfate cannot exist alone it will attack pure lead,

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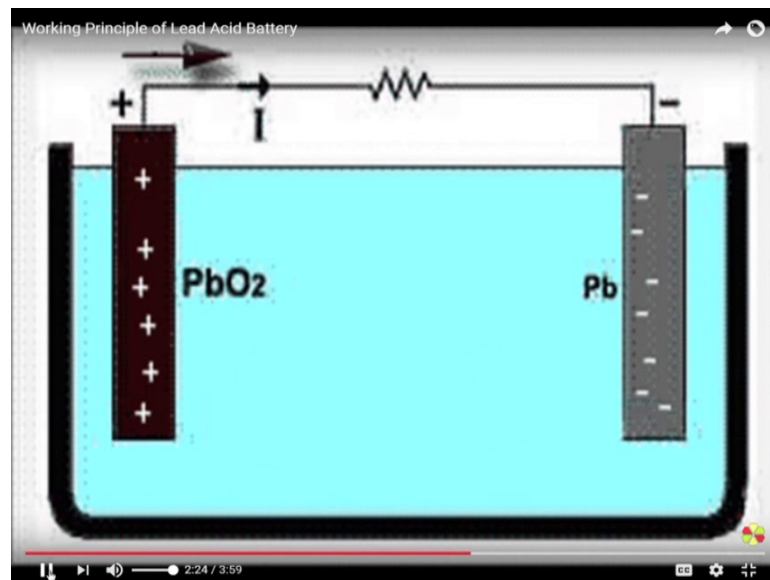
And will form lead sulfate.

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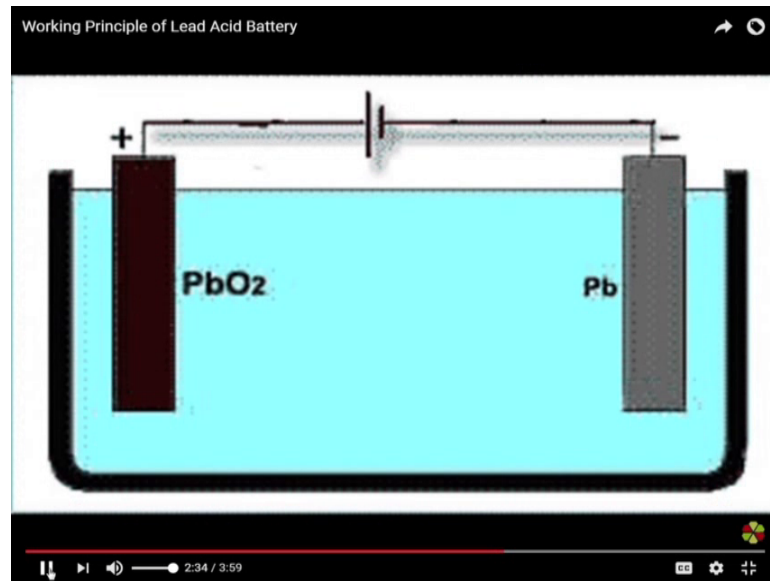
As positive hydrogen ions take electrons from lead peroxide plate and negative sulfate ions give electrons to lead plate.

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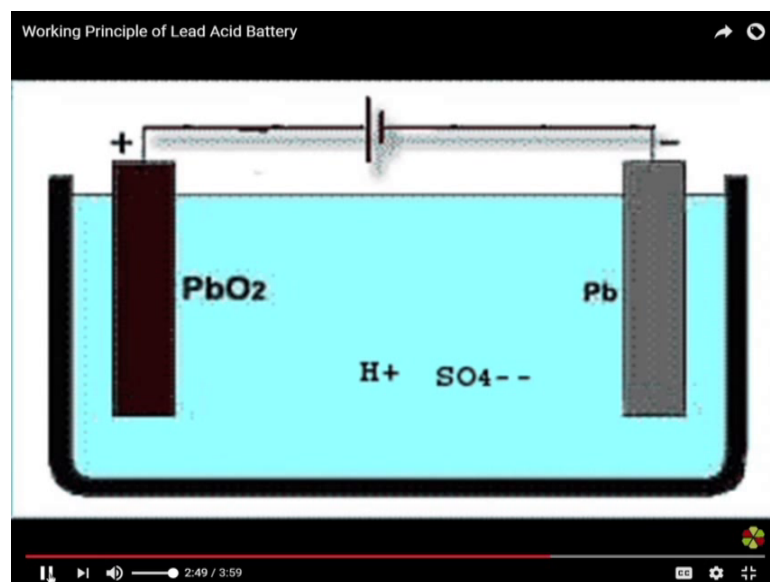
There would be an inequality of electrons between these 2 plates. Hence there would be a flow of current through the external load between these plates for balancing this inequality of electrons this process is called discharging of lead acid battery.

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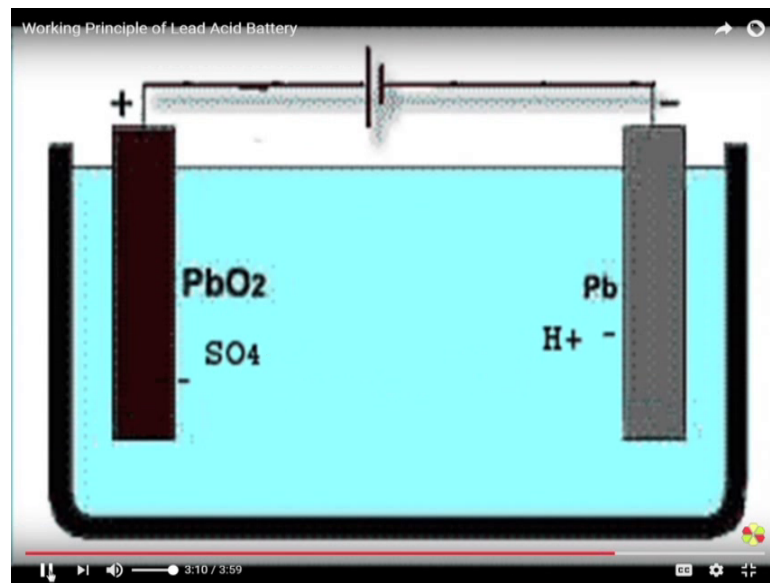
Now, we will disconnect the load and connect lead sulfate covered lead peroxide plate with positive terminal of an external dc source and lead peroxide covered lead plate with negative terminal of that dc source.

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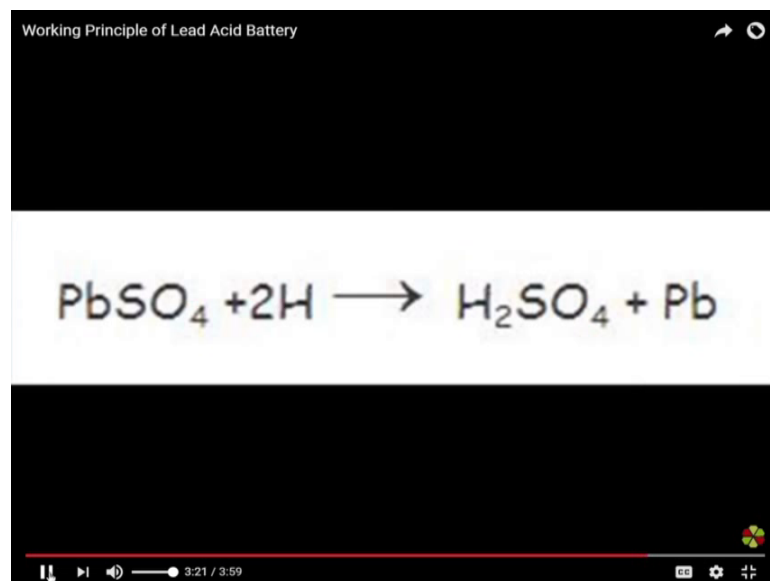
During discharging the density of sulfuric acid falls, but there still sulfuric acid exists in the solution. This sulfuric acid also remains as positive hydrogen ions and negative sulfate ions in the solution hydrogen ions being positively charged moved to the electrode connected with the negative terminal of the dc source.

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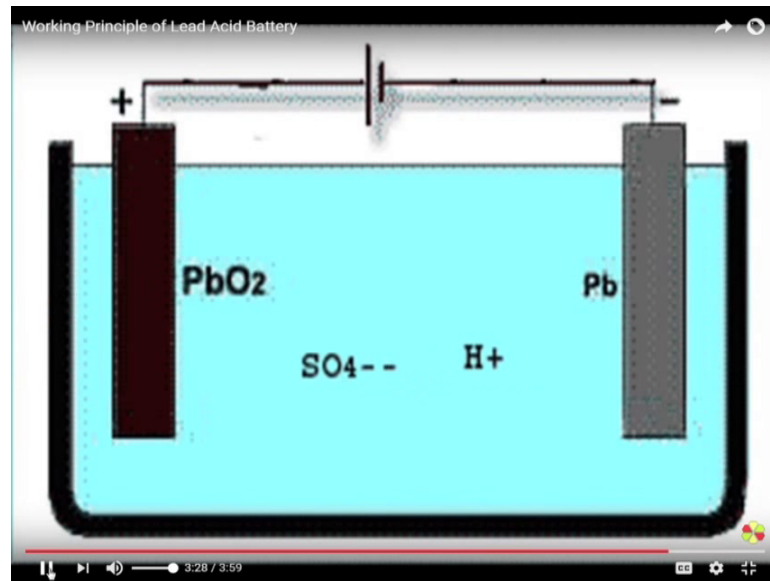
Here each hydrogen ion takes 1 electron from that and becomes hydrogen atom.

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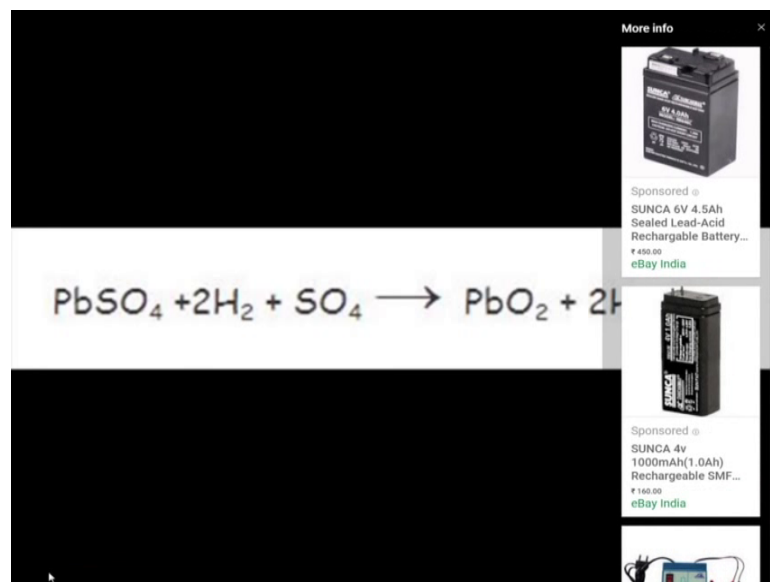
These hydrogen atoms then attack lead sulfate and form lead and sulfuric acid.

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Negative sulfate ions move towards the electrode connected with the positive terminal of dc source, where they will give up their extra electrons and become radical sulfate.

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This radical sulfate reacts with lead sulfate of anode and forms lead peroxide and sulfuric acid, hence by charging the lead acid storage battery cell becomes ready for discharging alright.

So, I think that video very nicely explained the reactions that happen inside a lead acid battery, both during the charging cycle or both first during the discharging cycle and next during the charging cycle alright.

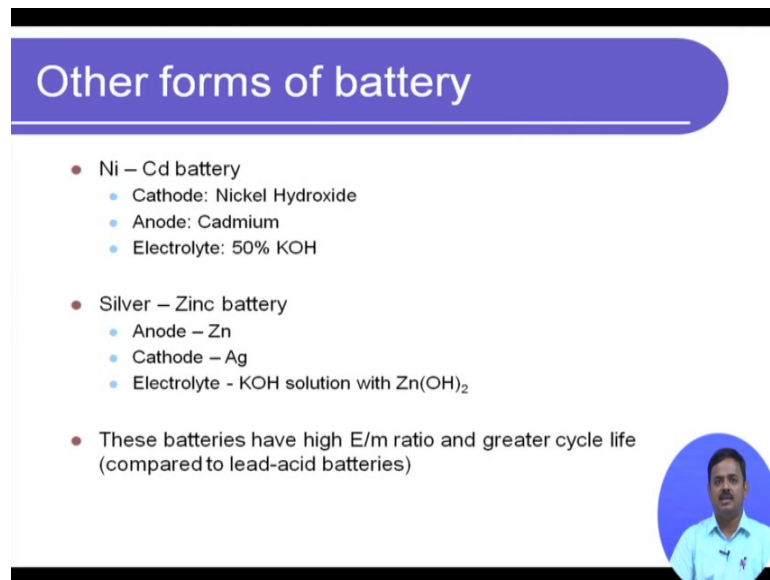
So what we will do now is look at some of the features so this as I said is used most commonly what we see is used in a car and a car battery if you look at it even from outside you will see there is 6 different cells so there were 12 electrodes there is a flexibility in current and it is high reversibility.

So the car batteries I mean they typically these batteries lasts 4, 5 years. Actually, in car whatever I have driven I think in each of the car I have driven so far which is only 2 and each of them I have driven for like 5 to 7 years I have had to change battery only once and that too in one of the cars where the battery I think they installed an old battery to start with, but typically the batteries run pretty reliably for 4 to 5 years unless actually you have done something wrong for example, if the lights on through the night and then it will get discharged all that.

So, the batteries that way is high reversibility there is a flexibility in current because depending on the what you are it I mean how much current that you want to draw and therefore, how fast is going to be discharged there is some flexibility that is available alright and the cells just the problem is if you leave the battery in itself or if you do not use it for a long time leave it even in a charged condition. There is a self discharge that happens that is true for any battery actually and the other thing that can happen is because of this repeated coating of the electrodes with sulfate this is called sulfation. So sulfation with time happens where the electrodes are not completely cleaned and again that is contamination that happens with time ok.

So, these are some of the features, but as I said they are pretty reliable, but the thing is these batteries are heavy alright so energy to mass ratio if you look at it is not as high as compared to some of the other batteries which are much lighter.

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Other forms of battery

- Ni – Cd battery
 - Cathode: Nickel Hydroxide
 - Anode: Cadmium
 - Electrolyte: 50% KOH
- Silver – Zinc battery
 - Anode – Zn
 - Cathode – Ag
 - Electrolyte - KOH solution with $Zn(OH)_2$
- These batteries have high E/m ratio and greater cycle life (compared to lead-acid batteries)

So other forms of battery nickel cadmium, silver zinc I have written the electrode materials and the electrolyte and as you can see that here they are different of course, silver zinc will be more expensive nickel cadmium is used typically in our portable electronic materials and these batteries of high energy to mass ratio. Why typically? Because the mass is lower it is a lighter than then the batteries that we use in cars the lead acid batteries and greater life cycle greater cycle life sorry so number of cycles that these batteries go through is much more compared to a lead acid battery.

So, actually there used to be a time when the lead acid batteries I remember from my father and my uncles people who had cars among the ones who had cars they would bring the they would bring the battery home and they would once a battery is discharged and they would charge it, it will take a long time and then they will put it back in the car these days that does not happen that much probably because of you know reduction in cost etcetera for consumerism.

We see most of the batteries typically of course, they go through charging and discharging cycles in the car, but I really do not see when the battery has been completely drained. The modern batteries are brought home or taken to a charging station where they are charged again recharged again and then brought back into the car so that does not happen alright ok.

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Chemical Energy storage

- Heat of reaction of **reversible chemical reactions** is used to store the thermal energy during endothermic reactions and release it during exothermic reactions
- Example : Methanation – Reformation
 - Methanation – exothermic

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

- ← reformation – endothermic

$Q = 250.3 \text{ kJ/g-mole}$

Next what we are going to look at is chemical energy storage. So, previous one was electrochemical you had a certain electrolyte and an anode and cathode immersed in it and we were using electrical energy also. Because there was movement of ions etcetera this is completely chemical energy storage and in some way you can even argue that this is thermal energy storage because the form in which the energy is stored or released is again heat.

The overall principle on which this operates is there are certain reactions chemical reactions which are reversible and which involve a heat of reaction. What is heat of reaction? So what it means is heat of reaction is when a certain chemical reaction is exothermic, it generates heat and then when the certain chemical reactions are endothermic where you have to actually supply thermal energy and which is absorbed when the reactants turn to products right.

Now imagine such a reaction which is reversible then what happens then when the reaction takes place in 1 direction from reactants to products you have an exothermic reaction and when the reversible happens and or the reaction happens in the opposite direction the products now turn back to reactants you it you actually absorb heat and it is an endothermic reaction right so one such example as i shown there is the Methanation and Reformation reaction. The Methanation is when methane is formed from carbon

monoxide and hydrogen right and this is a reaction that happens and this is an exothermic reaction.

So, when methane happens there is heat that is given out and that heat of reaction as I have shown is q is 250.3 kilo Joules per gram mole right. On the other hand when methane and water reacts and form carbon monoxide and hydrogen which is what is happening here in this schematic, then it is an endothermic reaction we have to supply heat clear and that is what is happening over here.

I am supplying heat and then this heat is kind of stored in these products. So, the overall principle over here is let us say I want to generate. Let us say let us again think of the power plant where during off peak hours I have additional generation of electricity or I can have additional generation of electricity based on the energy that I have at my disposal.

So what I will do therefore is instead of using that come energy, let us again talk about a steam turbine power plant instead or a fossil fuel power and which is powered by fossil fuel or let us say nuclear reaction whatever it is or natural gas, coal, natural gas whatever it is what I would do is I would use this source of thermal energy.

Partially during off peak hours partially to generate the steam and the rest of it to have a reformation reaction, where I will have methane and water as reactants and I would supply the additional thermal energy, additional heat and get carbon monoxide and hydrogen alright.

And during off peak hours what I will do is therefore, I will have these to react and have a methanation reaction so that they react with each other and the products are methane and water and during that reaction I get some additional thermal energy out of the reaction which can be used for generating additional steam and therefore electricity clear so again this is the overall principle that we are using alright.

This is chemical energy storage that is what we are calling it, but you can also think about it as or you can also argue that well this is also a form of thermal energy storage because the energy is stored in the form of thermal energy. But then the reason why this thermal energy or the heat is absorbed and released is because of a chemical reaction and

a reversible chemical reaction and the example that we have taken is methanation reformation clear alright.


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Thermo-chemical storage

- Direction of reaction reverses at Turning Temperature (T^*)
Reversible reaction: $AB \leftrightarrow A + B$
 - Temperature above T^* : reaction shift to right
 - Temperature below T^* : reaction shift to left

- Only reactions producing two distinct phases (ex: *solid and gas*) considered suitable since reactants are easy to separate and store

Reaction	ΔH° (kJ)	T^* (K)
$NH_4F(s) \rightleftharpoons NH_3(g) + HF(g)$	149.3	499
$Mg(OH)_2(s) \rightleftharpoons MgO(s) + H_2O$	81.6	531
$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$	106.6	670
$NH_4HSO_4(l) \rightleftharpoons NH_3(g) + H_2O(g) + SO_3(g)$	337	740
$Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$	109.26	752



The next one that we are going to talk about is thermo chemical storage. So, again you can argue why is the previous one not thermo chemical and this we are calling thermo chemical well it is all about nomenclature. So here again it is a reversible reaction there is a product AB and a reactant A plus B or the other way because it is a reversible reaction. So A plus B converts to AB or AB dissociates into A plus B, the way this happens is that trigger has to which direction this reaction will happen whether AB will convert to A plus B or A plus B will convert to AB is dictated by the temperature and that temperature quite appropriately is known as the turning temperature, because the direction of the reaction turns depending on whether we are above that turning temperature or below the turning temperature alright.

So temperature above the turning temperature the reaction will shift from left to right and temperature below turning temperature the reaction will shift to from right to left it is either way I mean this above and below can be different I mean if I just put A plus B and AB on the other sides, this above and below will change so that does not matter.

What I am trying to say is the reaction happens in a certain direction above temperature and in the opposite direction below that temperature. So I am showing some examples over here in this table, where the heat of reaction is shown and of course this and very

important point like, in chemical energy storage these have to be exothermic or exothermic and endothermic reactions, exothermic endothermic reversible reactions only then is that energy going to be stored in the form of heat in one case and released in the form of heat in the other case clear.

So, let us take one example over here ammonia and hydrogen fluoride. Both of these are in gaseous state and they will react to form this component maybe ammonium fluoride I do not know what it is called and it is solid the turning temperature is close to 500 Kelvin and the heat of reaction is 149.3 kilo Joules per gram mole I am sorry I should have written that per gram mole clear.

Similarly here magnesium hydroxide is magnesium oxide and water and again we have these temperatures and heat of reactions written there are a couple of reactions where I did not have the data. So I have left that blank, but I hope I am able to tell you the message or convey you the principle of using this type of energy storage system.

Now out of these reactions which are the ones that are more favorable. So, typically they say is the reactions that are producing 2 distinct phases like a solid and gas are considered to be favorable or suitable because then these 2 can be easily separated out. For example, ammonia and hydrogen fluoride both being in gaseous state it is very difficult to for them to be separated, but think about this one the third-one which is magnesium oxide and carbon dioxide one is solid one is gas.

So, let us say when this reaction has happened I can easily separate out these reactants and keep them separately alright and then later when I need them to react and give me the endothermic or exothermic reaction I will again bring them together and ensure that the temperature is above or below the turning temperature clear so that is important.

Let us say in the first case if we had both gaseous products, then it would be very difficult we have to use I mean of course separation is possible gas to gas separation is not it is not like it is impossible, but we have to use more sophisticated methods or more complicated methods.

So, for example this one ammonia water vapour and SO₃ right it will be very difficult to separate out these 3 phases and compare that to calcium oxide and water vapour. I can easily say, but 1 is a gas just by gravity itself just by due to density difference I can

separate out these 2 clear alright. So, that kind of wraps up these were the last 2 especially, I did not want to go to too much of details these are just wanted to give you the feel. So, what did we study today or in this lecture are 3 different types of energy storage.

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- ELECTRO-CHEMICAL ENERGY STORAGE
 - Batteries
- CHEMICAL ENERGY STORAGE
 - Methanation & Reformation
- THERMO-CHEMICAL ENERGY STORAGE
 - Turning Temp (T^*) based on which direction of reaction reverses

The first one was electrochemical energy storage and where we spent a little more time and we talked about batteries right. The second one was chemical energy storage and here what we said is these are reversible chemical reactions endothermic in one direction exothermic. In another direction and the example that we took was Methanation and Reformation and the last one that we talked about was thermo chemical energy storage alright.

So, this one again we were talking about reversible reactions and here we said that there is a there exists a certain temperature, the concept of turning temperature T^* based on which the direction of reaction reverses alright. So these are the 3 types of energy storage systems that we discussed in this lecture or related to chemical energy. The first is electrochemical next one is chemical energy purely through chemical reactions. But again thermal is involved because energy storage is in the form of thermal energy and thermo chemical energy storage is I would say it is very similar to that of chemical energy storage except that the reversal of the reactions happen based on depending on the temperature that the reactants are subjected to alright.

So, that kind of wraps up this section on energy storage where we learnt about 3 new techniques for energy storage I will not say battery is new because you all know about it, but I thought I hope it was a good recap of how a lead acid battery functions and to and for us to know that apart from lead acid what are the other types of batteries that are being used today alright.

So thank you very much, I hope you learn something new and we will meet in the next lecture again where we will take up some new topic.

Thank you very much. Have a great day.