Electrochemical Energy Storage
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Module - 10
Li - Sulfur batteries
Lecture - 46
The Element Sulfur, Principles of Operation

Welcome to my course Electrochemical Energy Storage and this is module number 10, where I will be talking about lithium sulfur batteries. In the last module, you have learnt lithium air batteries.

So, here also lithium as a metallic anode, we have used and sulfur is being used as the positive electrode material. So, in this lecture which is lecture number 46, we will initially talk about the element sulfur and what is the principle of operation of this kind of battery, this we will introduce.

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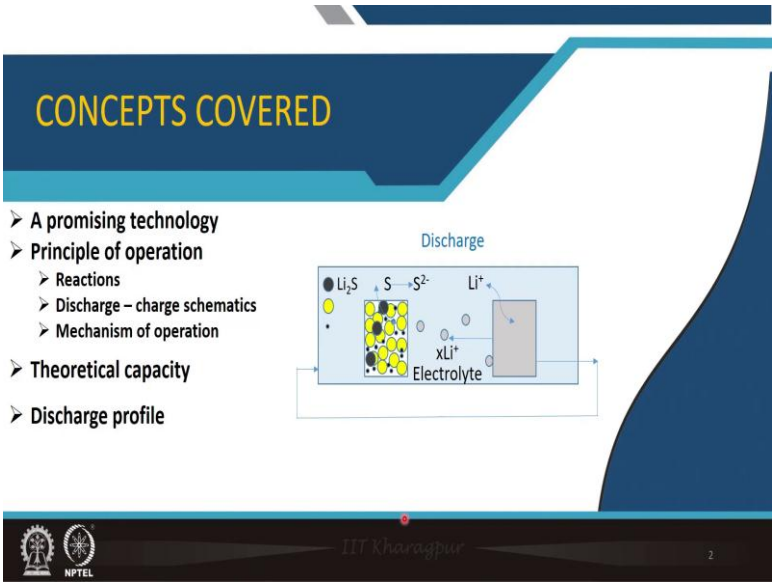

So, it is a promising technology and futuristic in nature. So, whatever data that I will be showing, that is mostly from the research laboratories, people have acquired and at the end, we will also talk about our own results on lithium sulfur batteries. And this will be the last two lectures of this module. So, first and foremost, it is a promising technology and it has lot of potential because of the simplicity of the battery.

But we will talk about the principle of their operation; what are the reaction sequences in the positive and negative electrode materials. Then, charge discharge schematic, what actually happens while discharging and as you can understand first it will start with discharge.

Because, the composite electrode, which is positive electrode they do not have any lithium in it. So, initially, it will get discharged. So, it will get lithium from the anode material. So, this charge discharge schematics, you can see and we will explain it and what are the mechanisms of operation that I will shed light on it.

And now, you will calculate, you will have to calculate the theoretical capacity of this kind of battery and you will be able to understand that huge capacity, you can get out of this batteries, although the voltage is a bit low. So, you can estimate the voltage and also, the capacity from the tricks that already I have covered part of earlier lectures and in particularly, the discharge profile what exactly happens will shed light on that.

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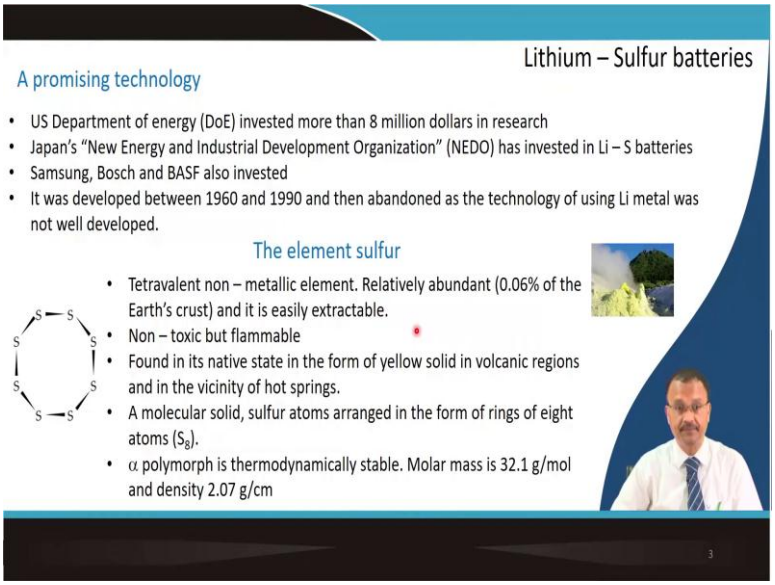

So, as I said, it is a promising technology and lot of investments people are doing, starting US department of energy. They invested more than 8 millions of dollars and the data is a bit old around 2014. So, must be a lot of money has been invested to understand this technology better. Japan is also aggressively working on it under this "New Energy and Industrial Development Organization", abbreviated as NEDO, they have invested quite lot of money for this lithium sulfur batteries and the companies like Samsung,

Bosch and BASF. The last two are from Germany and Samsung is a Korean company, they have also invested.

In fact, Samsung, they have a unit in India as well. They were particularly interested for this kind of battery. We did some work with them not related to lithium sulfur battery, but with some other batteries. And historically, if you see that this lithium sulfur batteries, they were developed in 1960s. So, earliest paper, I can find in around 1960 and till 1990, you will see couple of papers have been published and then eventually, this technology was abundant.

So, beyond 1990 when lithium ion cell technology was commercialized by Sony, so around that time, this lithium sulfur technology was abundant mostly due to the use of lithium metal. Because you know lithium metal, it is having some intrinsic problem of dendrite formation and also, it is very reactive and with sulfur also, it is quite reactive it forms ACI layer. So, due to those kind of problem, it was really abundant.

But if you look into the raw materials, it is tetravalent and non metallic element and in earth crust, it is relatively abundant because you can see about 0.06 percent of the earth crust that sulfur is there and you can extract it quite well. Suddenly, it is nontoxic; but it is flammable in nature and as you can see mostly it is yellow colored and wherever hot spring or volcanic regions are there, lot of sulfur you can get in the vicinity of those regions.

So, plenty of availability is there. Some kind of industry for example, steel industry, they produce lot of sulfur as a waste material, very high purity sulfur, so I will talk about it. We have used some of their waste sulfur and prepared in coin cell fabrication and in coin cell configuration, lithium sulfur battery and quite effective we found. So, we will talk about it.

And eventually, it is a molecular solid, where you can see that the sulfur atoms are arranged in the form of a ring, where 8 atoms are involved. And usually, they have several polymorphs and alpha polymorph, they are considered thermodynamically stable and its molar mass is about 32 gram per mol and it is light weight. So, if you use it in conjunction of lithium metal, then for sure you will get a very high energy density out of this batteries.

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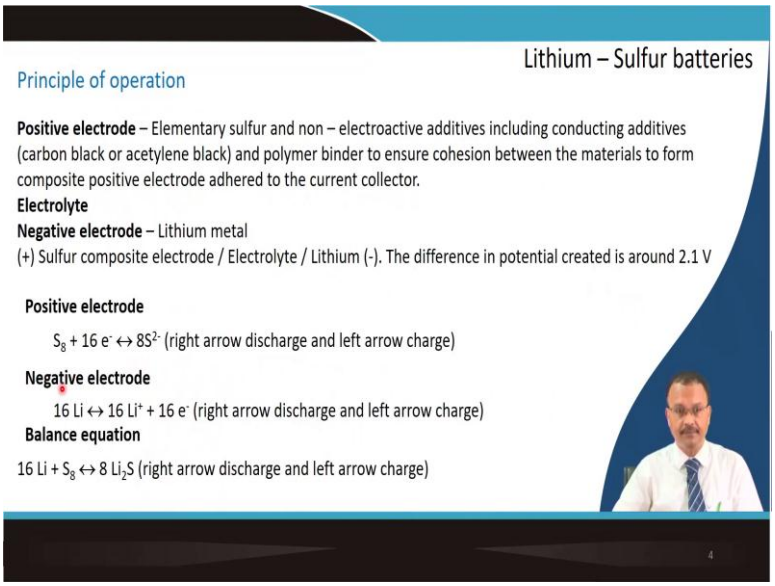

So, principle of operation is quite straight forward. Just something similar to lithium air batteries, where this elementary sulfur, they are basically used which is a non-conducting kind of material. So, some other additives are required which are not electro active in nature. For example, here also we use conducting additives like carbon black or acetylene black that is used.

A binder is required and by this time, you must be knowing that what are the purpose of this binder, it is needed to adhere the composite electrode materials and also, a good adhesion between this composite electrode with the underlying current collector.

So, that they are properly adhered. We will talk about the electrolyte which are specifically used for this kind of battery. So, usually, organic solvent based electrolytes are used along with lithium salts; but not Li Pf 6, something else is used and also not carbonate based solvents are used.

So, ether based solvents because particularly of its lower voltage limit; therefore, it is quite it is advisable to use ether based solvent, we will talk about it. And negative electrode is lithium metal. So, if you see the electrochemical shell chain, then you can see the positive electrode consists of sulfur composite electrode. So, sulfur will be there, electronically conducting agent as carbon that will be there and then, binder as PVDF etcetera that will be there.

Then, we will have an organic electrolyte and then, lithium metal. If you can calculate the potential that you will get out of this battery and you can calculate that this will be around 2.1 volt from the standard reduction potential table, which I discussed earlier in the course. So, 2.1 volt that you will get out of this battery; it is not as high as lithium ion battery. But you are getting lot of capacity, you can calculate the capacity of this battery. So, energy density, I am considering it is lightweight battery. So, energy density will be quite high.

So, first, we will talk about the negative electrode. Reaction is quite straight forward as you can see that lithium is oxidized. So, it gives electron to the outside circuit and sulfur takes this electron get reduced. And then, eventually, this sulfur which is negatively charged and lithium which is positively charged, they react and it forms eventually Li 2 S.

$S_8 + 16\ e^- \leftrightarrow 8S^{2-}$

$16\ Li \leftrightarrow 16\ Li^+ + 16\ e^-$

Balance equation

$16\ Li + S_8 \leftrightarrow 8\ Li_2S$

So, the right arrow here, this is the discharge reaction and exactly the reverse reaction takes place along with the left arrow, where this solid product that will eventually break to lithium and sulfur. So, we are getting back the same original configuration and you can recharge this battery to get capacity out of it. The principle is quite straight forward. It is easy for you to write this kind of equation, which is quite straight forward; but there are lot of problems associated in it.

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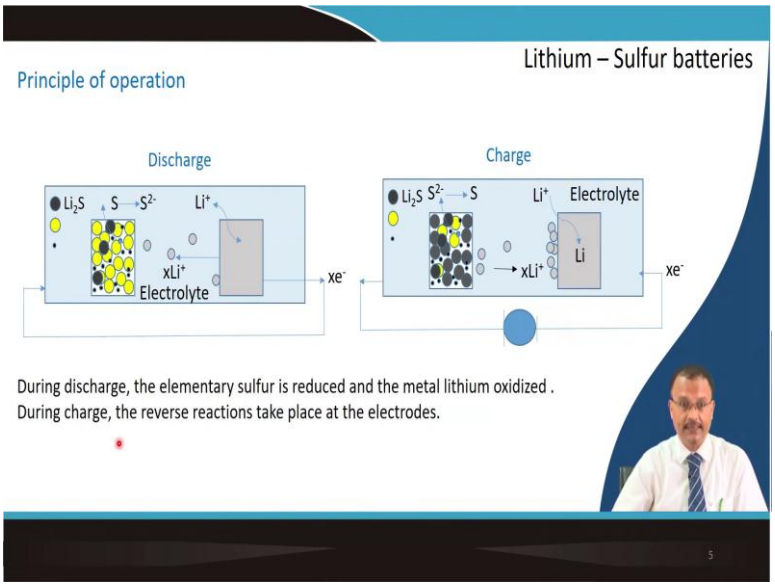

See if you schematically see the discharge operation, you can see this small sphere that is the conducting agent which is carbon; then, you have this yellow sphere which is sulfur. And then, the reaction product finally, you will get Li 2 S during discharge because this and this will get react reacted. So, in case of the oxidation, the lithium is getting oxidized from this metallic lithium and the, this electron travels outside the battery because of course, it will not go through electrolyte, then it will be short circuit.

So, it travels outside and you get the energy out of it, you can light a bulb out of that and finally, sulfur will get reduced and then, this fellow will react with this fellow to form lithium Li 2 S which is a solid product and discharge is exactly the reverse.

So, it will get dissociated to S 2 minus and lithium and then, eventually, this lithium will form lithium ion will form metallic lithium. So, you know that this formation, it is not a layer by layer kind of deposition. So, you have still the risk of having a dendrite formation and of course, during charge you know that we will have to connect it through a battery.

So, that this positive end is connected to the positive electrode and negative end is connected to the negative electrode that is lithium. So, it has a tendency to go to the negative electrode. So, during discharge as we have learnt that elementary sulfur is reduced and the metallic lithium is oxidized and during charge, exactly the reverse

reaction takes place. So, very straightforward reaction that usually takes place for this kind of battery.

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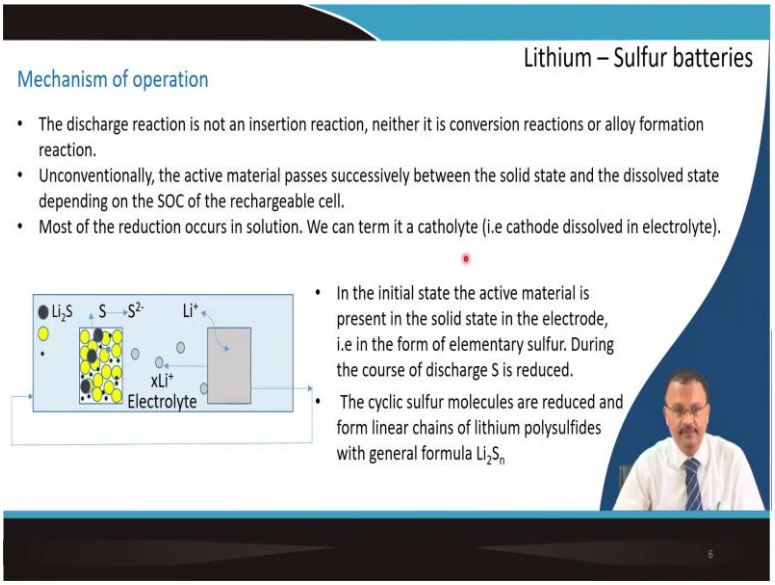

But there are problems associated with it. So, if you consider the mechanism of the operation as you can understand, this discharge reaction whatever we have learnt so far, it is not a insertion reaction like in graphite, you have inter planar spacing. So, lithium is going into the inter planar spacing; it is not like that.

It is not a conversion reaction like the oxide material, lithium goes into it, break the structure, form lithium oxide, form metallic particle and then, alloy form with the metallic particles, it is not like that. So, it is a different reaction, formation of compounds and this is also not a final stage, final compound Li 2 S is forming. There are lot of intermediate compounds that form in between.

Active material passes successively between the solid state and the dissolved state depending on the state of charge of the receiver rechargeable cell. So, this active material which is sulfur, so initially sulfur is solid and finally Li 2 S is also solid. But as I said it is not a one step reaction, there are several steps involved.

So, the several intermediate step whatever is forming that is not confined to the positive electrode. So, there is a strong tendency for those phase to get dissolved into the

electrolyte. So, you have something, some active material, it is getting dissolved into the electrolyte.

So, this reduction, that means, reaction with the active material of sulfur that is reacting with lithium to form this reaction product and in the process, it is getting reduced because lithium is reacting with sulfur. So, that comes into the electrolyte solution. So, we can term this is a catholyte; that means, the cathode material, a compound of lithium that is dissolved into the electrolyte. So, in the initial state, the active material is present in the solid state inside the electrode.

So, that is the elementary sulfur and during the course of the discharge reaction, sulfur is reduced because it is reacting with lithium. Now, the cyclic you have seen the cyclic sulfur molecules, when they get reduced by reacting with lithium, they form linear chain. So, they are no longer cyclic; but they form a linear chain and we call this is a poly sulfides and this poly sulfides is having a general formula of Li 2 S n. So, the final product is Li 2 S, where n equal to 1.

So, several form, several formula can be generated it could be Li 2 S 8, it could be Li 2 S 6, it could be Li 2 S 4 and not everything, except Li 2 S 2 and Li 2 S, they are solid. So, the remaining intermediate reactions if you cannot control it well, what will happen? They will go to the electrolyte, form the catholyte and in the process, you will be losing lithium. So, if you loose lithium, it is a problem capacity will be suddenly gradually it will get reduced and the cyclability will be a problem; good cyclability of this kind of battery is a prominent problem.

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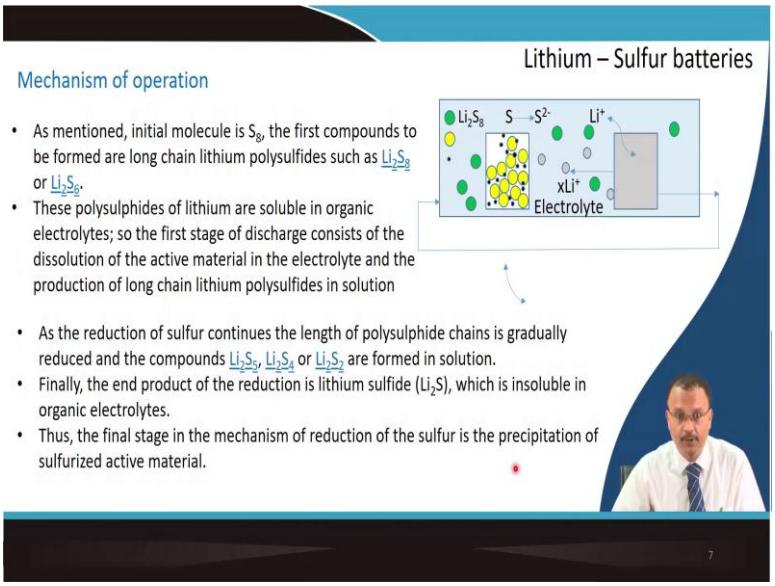

So, initial molecule as I have indicated it is a Si, S8; then the first compound that is formed, they are long chain lithium poly sulfides. So, it could be Li 2 S 8 or it could be Li 2 S 6. Now, as I have said that this polysulfides of lithium, they are actually soluble in the organic electrolyte.

So, the first stage of discharge that consists of the dissolution of the active material into the electrolyte to form the cathode lights and this product whatever is being prepared, they are having long chain molecule. So, we call this is lithium polysulfides and there is no natural way to bind those polysulfides.

Here you have seen this green ball is the polysulfides, you cannot retain it into the positive electrode; but it will get dissolute dissolve into the electrolyte. So, it will be there in the electrolyte right. So, the reduction of the sulfur as it continues, then the chain gradually reduced. Initially, they are large chain Li 2 S 8 and then, they reduced to relatively smaller compound, many compound can form; Li 2 S 5 can form Li 2 S 4 can form.

So, they are relatively reduced chain size, but all are there in the electrolyte. Finally, the end product of this kind of reduction is lithium sulfide which is a Li 2 S and fortunately, both Li 2 S and Li 2 S 2, they are insoluble in the organic electrolyte.

So, if they are insoluble, so then they will stay back into the positive electrode. So, the final stage, the mechanism of the reduction of sulfur is eventually the precipitation of the sulfurized active material into the positive electrode. So, that is the last stage that we can get.

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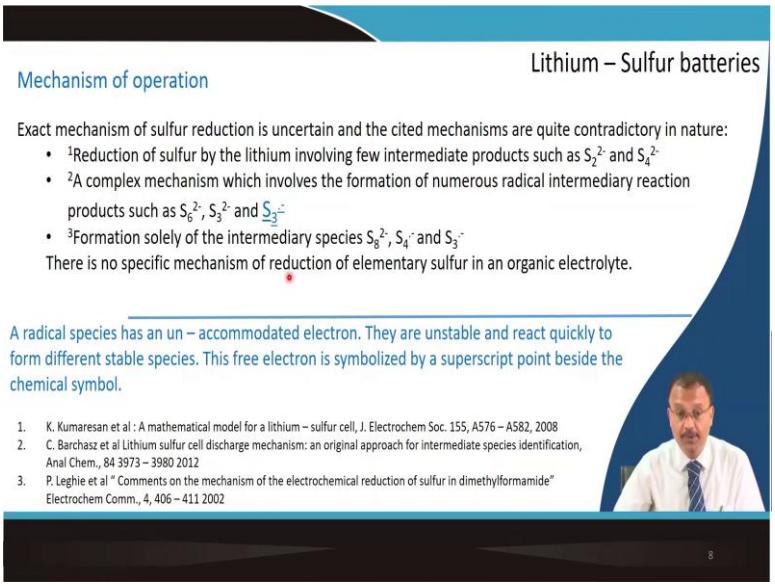

So, how this transformation takes place? It is not very well-known. So, it is quite uncertain and lot of mechanisms have been cited and sometimes, they are quite contradictory; the nature of this reaction products which are formed in between.

So, there are certain literature, I have reviewed and first of this, it says that few intermediate products that form that is S 2 minus 2 or S 4 minus 2. Likewise, it can be quite complex and as has been given by this reference. So, this complex mechanism, they form numerous radical intermediate reaction products.

So, we can see a radical species that has an unaccommodated electron, they are very unstable and very reactively, very quickly react to form different stable spaces. So, intermediate stage, identification remains a problem and this free electron whatever they are having that actually is symbolized by a small superscript as you can see. So, this can also form and it is also possible to form solely intermediate spaces which are S 8, S 4 and S 3.

So, what kind of intermediate product will form in terms of this sulfur species that depends on the system, the nature of the sulfur, the kind of electrode that you are making and that basically controls the whole discharge and charge profile of this kind of battery. So, the whole thing, whole research is to understand the intermediate product whatever is soluble just bind it inside the positive electrode so that they do not go into the organic electrolyte and how to control this intermediate species. So, people have started working on that.

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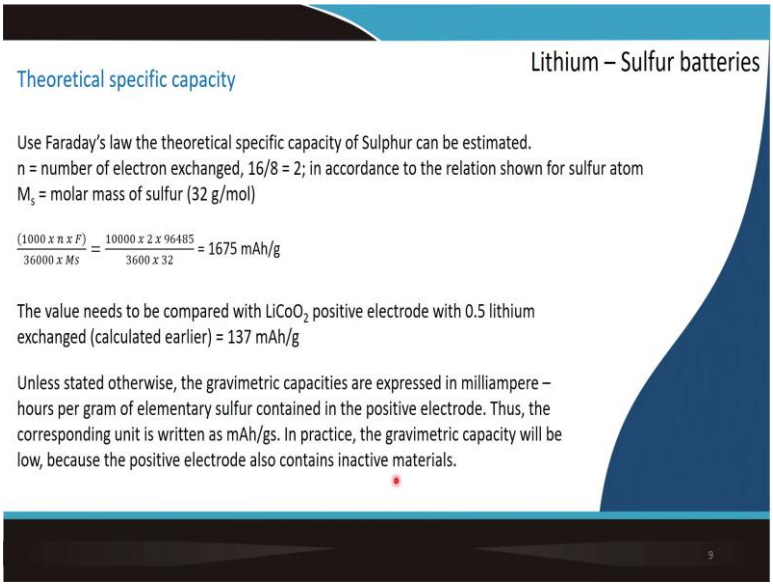

And this is the whole story because you have enormous source of lithium because you are using lithium metal as one of the electrode. So, the problem is if the lithium metal, it forms ACI layer and then, it is not accessible for electrochemical reaction, then your reaction will stop.

And continuously, if lithium poly sulfides, they get dissolves into the electrolyte, the viscosity of the electrolyte will rise and that will not let enough lithium to pass through the electrolyte from the negative to positive electrode and there are several problems that is associated.

Now, a straightforward way to use the Faraday law to know the theoretical capacity, you know this reaction equation that already I had mentioned. And you apply the Faraday law. I think by this time, you are quite familiar how to calculate the theoretical capacity. The total number of electron that you need to know and molecular mass of sulfur which

is 32 grams per mol that you need to know and put that in the equation, so you get enormous specific capacity.

You remember the specific capacity of lithium cobalt oxide or NCA or NMC, kind of cathode material, they are all under around 200 to 300. So, 200 is the limit I should say, not even 300; but as compared to that, if the voltage is 0.1 and if the capacity is this much, then you will get huge energy density and specific energy density is also quite high. For example, lithium cobalt oxide, you can take only 0.5 moles of lithium and it will give you about 137 milliampere hour per gram.

So, this gravimetric energy, they are expressed usually in milliampere hour per gram and this is based on the sulfur that is contained in the positive electrode. So, here is the trick, you know that the sulfur content, sometimes you know people make a trick out of it. So, sulfur content is say 20 percent. So, still they will report the theoretical energy density or theoretical capacity only by taking the weight of sulfur. That is why this gram, I put a sulfur. So, it is based on the sulfur weight.

So, I am not considering the weight of carbon in some case because it is electronically non-conducting. So, you will have to put lot of carbon in it and sometime the carbon usually one should use about 10 weight percent to 20 weight percent, you will find in the literatures which I have cited that they have put 40 weight percent, 50 weight percent and thereby, reducing the active material content. So, that is not a good way, but still people report like that.

So, it contains the inactive material. I am not considering the cell material, cell fabrication material that I am not including into it. I am not considering the electrolyte whatever being used, but still you will find that the capacity is quite high. Even if you consider only sulfur and the material which are not electro active in nature like carbon black or PVDF, still you will get a reasonable good capacity at least 3 to 4 times than normal cathode whatever we are using.

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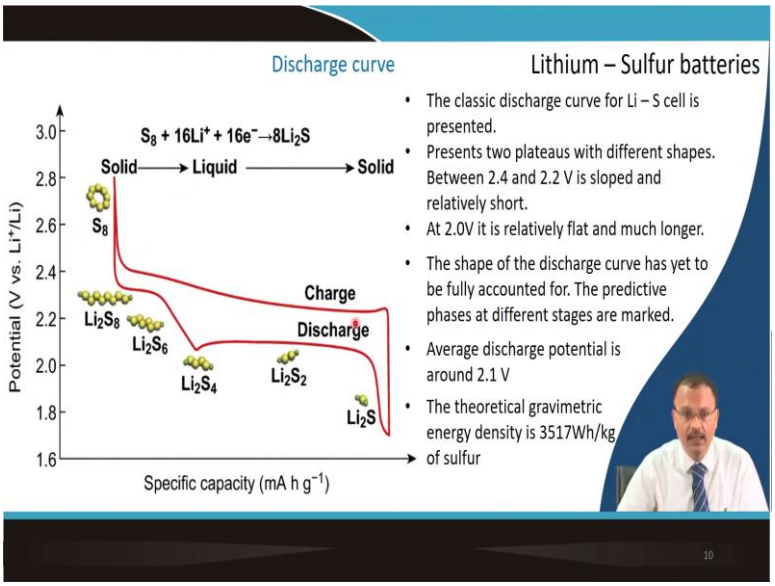

So, if you see the discharge and charge profile, so first it will get discharged. You can see that this cyclic kind of sulfur, they form this kind of intermediate products; several intermediate products it can form.

And in fact, if you go deep into this problem by knowing this kind of capacity whatever you are getting and truly analyzing this discharge profile in terms of differential capacity plot, you can exactly identify that what kind of linear chain, linear long chain or linear short chain kind of materials, they are being produced during discharge.

And the charge is exactly opposite where the formed Li 2 S, they will get dissociated to lithium and sulfur go back to its original position. So, this is a classic textbook discharge curve for lithium sulfur cell.

So, broadly, you can see here is one plateau; this is in between 2.2 to 2.4 volt and if you consider the slope, the slope is little bit slope is there. But if you consider this slope, this plateau, it is relatively flat and you have a large capacity in this region as compared to this region.So, as I said, this kind of discharge curve that is not yet fully understood.

So, that is why we will review the case study, where I will show for our kind of material composite material; what kind of discharge profile we are getting. But one thing is clear that average discharge potential, you can see about 2.1 volt and if you consider the capacity here, you can multiply the capacity with the voltage and you get a huge energy

density about 351 c 17 watt hour per kg. And this is considering only sulfur. So, it is a very very promising technology for EV also. So, we all are very excited about lithium sulfur battery.

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So, one company, I could find it is oxy Oxisenergy and they are developing innovative lithium sulfur battery chemistry. So, it is innovative because nothing much is given in their website. So, they consider that it will revolutionize the storage industry. You can see the small cars, cars are there and then, scooty type of vehicles are also there and for the storage also, it is important. Although it is quite light weight, but renewable energy storage, this batteries are very safer.

So, they have made two things; one god knows what kind of positive electrode they have made. So, they are they have come up with the battery module and they are working on it. There is another industry, I will explain it later on. They are also in the business and they claim that this lithium sulfur technology is lighter, safer and maintenance free and theoretical energy density, they are five times higher than lithium ion. So, this is a good technology for the EV as well, so that is their views.

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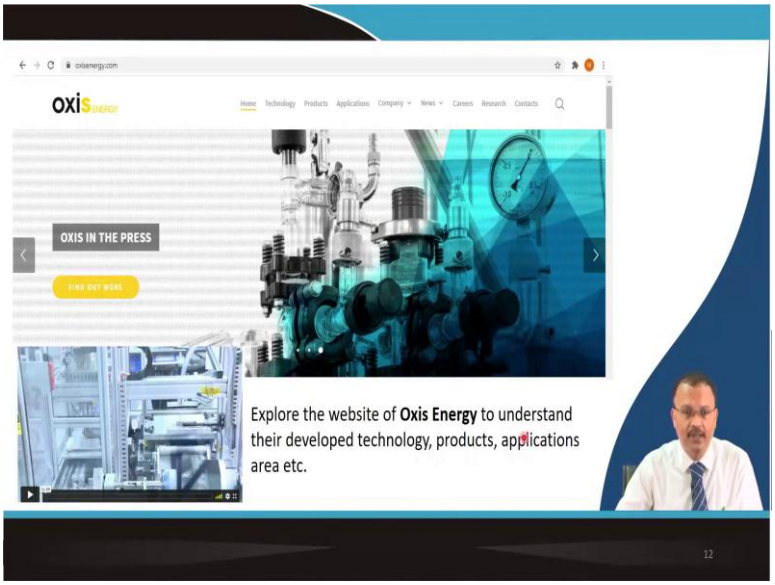

So, I would like you to go through their website and explore their website, what are the products they are having and understand the development, they have made. They have a reasonably good battery making facilities and provided a small video. Because you know that unlike the other battery forming technology, we described; a part of my earlier lectures it is a bit different because here you are using lithium metal plate. So, mostly, pouch kind of cells they have made.

So, I would like you to go through the technology, you will not find much that how they can arrest this long chain polysulfide dissolution into the electrolyte or how exactly they protect the negative lithium metal.

So, that they have not disclosed. But a general idea about how they are making the cell, what are their products and what are the future markets, what are the news, latest news in terms of the technology; I would like you to go through the site of Oxisenergy and explore their website to have a better understanding.

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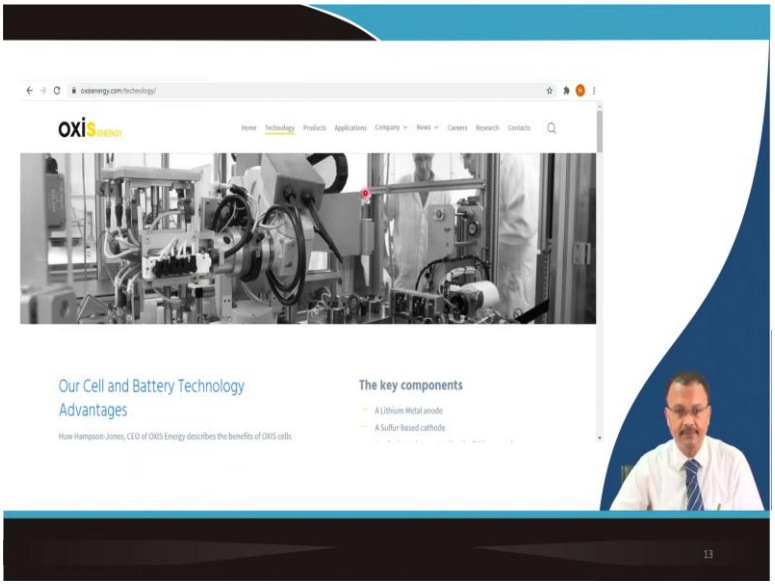

So, the advantage of their technology, they have given some kind of brochure also. I could not find much knowledge what exactly they are doing. But finally, they have done something to arrest this polysulfide dissolution and protective protect the lithium anode. So, in that way, they are successful to run this company.

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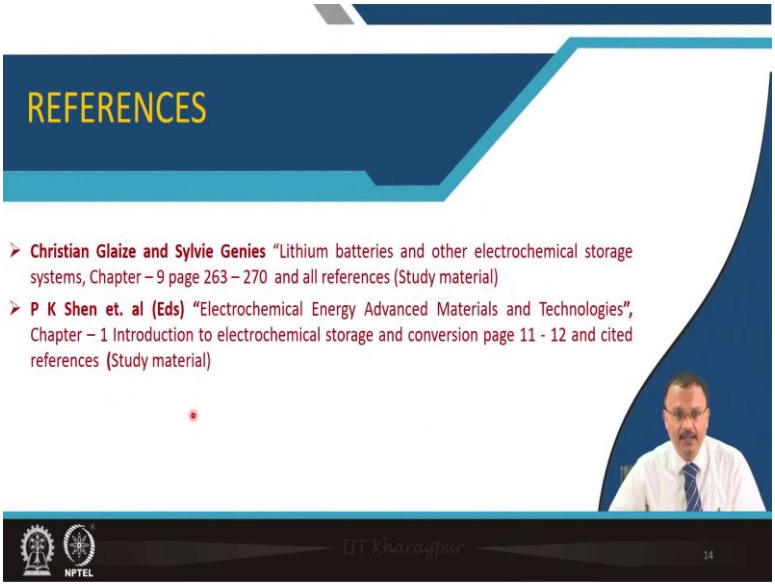

So, the study material is again the book by Christian Glaize, chapter number 9 and all the references, they are important. Because they are a bit earlier references so that will give you some kind of insight and I would like you to study the published papers. And the book by this Shen, edited volume, only the first chapter that is important because they have not talked much on this advanced technology lithium sulfur.

So, as a textbook, you will not find much source; only you will have to rely on suitable review articles and the references those have been cited in my lecture as well as in the study material.

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So, we have introduced a promising technology, which is very different from lithium ion or sodium ion rechargeable batteries. Lithium air is also another exploratory technology, people are working on it. Principle of operation, it is very straight forward; what are the reactions and discharge charge schematics, the formation of long chain molecules from the cyclic sulfur and getting back Li 2 S which is solid in nature. Mechanism of its operation how to calculate the theoretical capacity and the insight on the discharge profile, we have talked about.

Thank you for your attention