Electrochemical Energy Storage
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Module - 10
Li - Sulfur batteries
Lecture - 50
State of the art Li-S Batteries: Case Study - II

Welcome to my course Electrochemical Energy Storage. And we are in module number 10, where we are talking about lithium-sulfur batteries. So, this is the last lecture of this module lecture number-50 State of the art Lithium-Sulfur battery, and Case Study number II we will be talking about.

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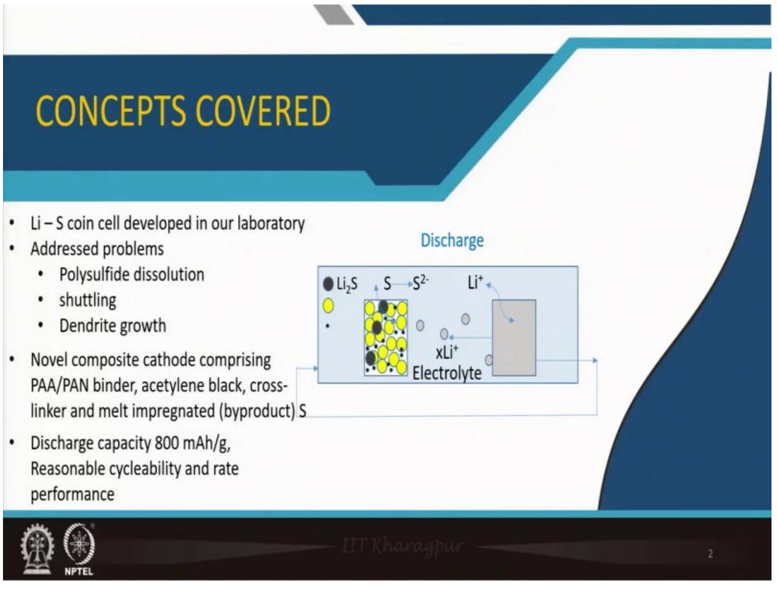

Now, as you can see that in the last lecture we talked about lithium-sulfur coin cell which was developed in our laboratory, and we addressed the problem of polysulfide dissolution problem, shuttling of this long chain polysulfides, then the growth of the dendritic growth on the metal electrode surface.

Then we talked about a novel composite cathode, but it was quite complicated. So, next we tried to use a proper binder which are polar binder we use polyacrylic acid and PAN binder with acetylene black, and a special cross linker that was developed by an industry which is some polymer based cross linker that was also used along with the sulfur which was melt impregnated. And this kind of structure was far simpler as compared to the structure already we talked about. And this simple structure also started to give us acceptable electrochemical performance. So, this is my case study number 2 for lithium-sulfur batteries.

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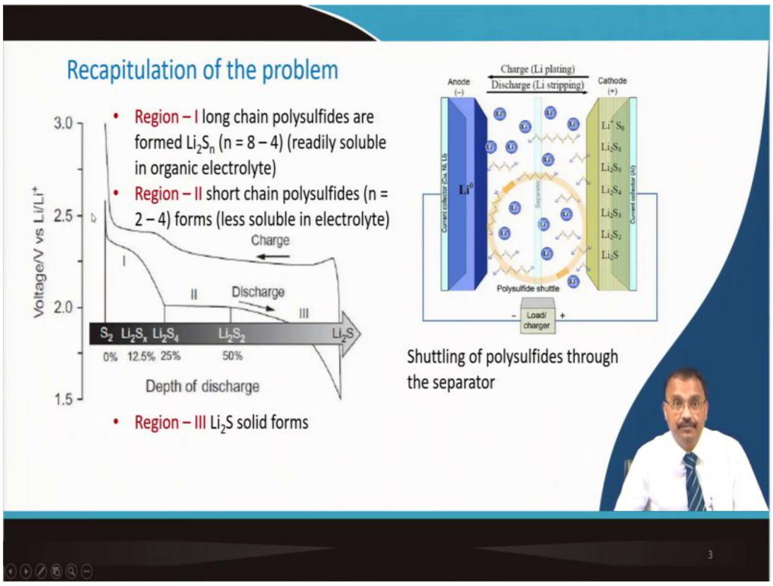

If you recapitulate this is the typical discharge and charge profile of any standard lithium-sulfur battery. You can identify region number I, here actually long chain polysulfides they are formed by long chain I means the general formula is Li 2 Sn. So, this value of n is in between 4 to 8. And these are actually readily soluble in the organic electrolyte, and that creates problem.

And region II they are usually short chain polysulfides they form, where the value of n is in between 2 to 4, and relatively they are less soluble. So, once this kind of polysulfides forms, they start to shuttle between these two electrode, so that already we described this shuttling effect. And in region number III, basically Li 2 S form and this is in its solid state form. So, our idea is to bind this polysulfides in its soluble state, so that it does not get out of the electrode into the electrolyte.

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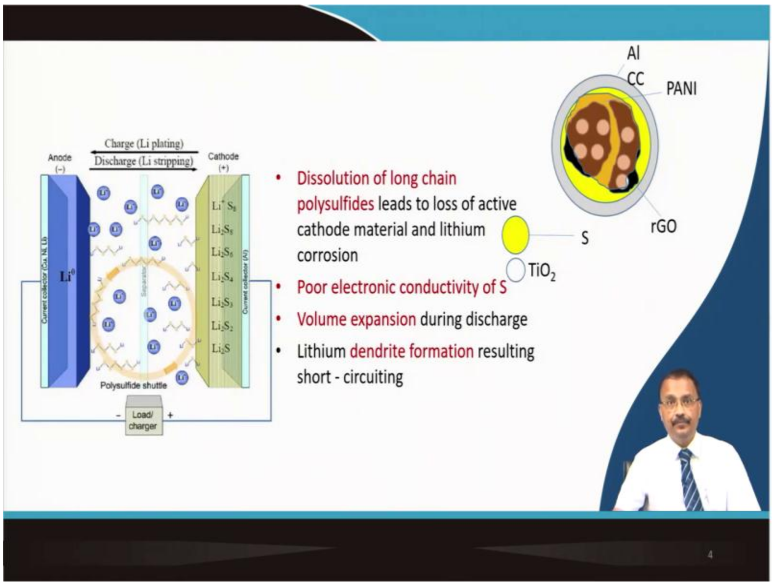

So, dissolution of long chain polysulfides that basically leads to the active cathode material, and also it leads to the corrosion of lithium. This already we have talked about. And electronic conductivity of sulfur that is also poor, so that is another problem. And the during discharge in particular you know that this polysulfides form, so there is a chance of volume expansion.

And finally, since you are using lithium metal, then always there is a chance of lithium dendrite formation. So, we will have to address this problem, so that the electrochemical performance is actually effectively you can control the electrochemical performance. So, if you see this schematic, so here the structure that we are proposing now is quite straight forward.

You see the current collector is aluminum because in this voltage range aluminum will not get corroded. Then you have melt impregnated sulfur this yellow portion. Then you have this oxide you know what is the role of the oxide it helps in binding this polysulfides, and that is embedded in a reduced graphene sheet. So, that kind of structure we thought that it might be helpful the combination of Ti O 2 and the PANI binder. So, this might help the performance.

Now, this kind of structure is quite complicated for industrial application. Already we talked about it. This structure works reasonably well, but so many things are involved melt impregnation of sulfur, then use of graphene or reduced graphene oxide, then titanium oxide, then a conducting polymer in terms of PANI, the binder is used PVDF, and this is a relatively complicated structure.

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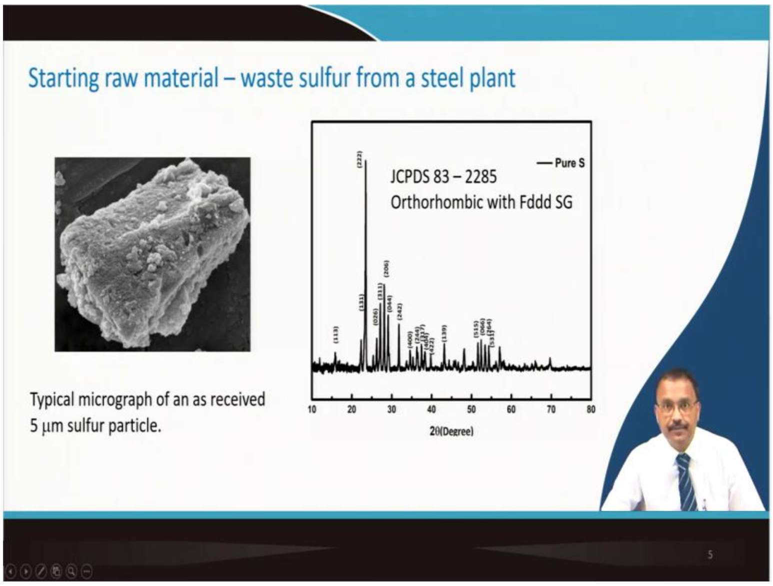

Now, the second part of the study is to use the sulfur which is a waste product of an industry. So, the sulfur is costless I mean we get it free, but it is having a chunk like this. So, typical size is about 5 micron. So, we tested that sulfur, and we found that this is orthorhombic nature with the space group Fddd, and pure sulfur we felt that this is good for making lithium-sulfur battery.

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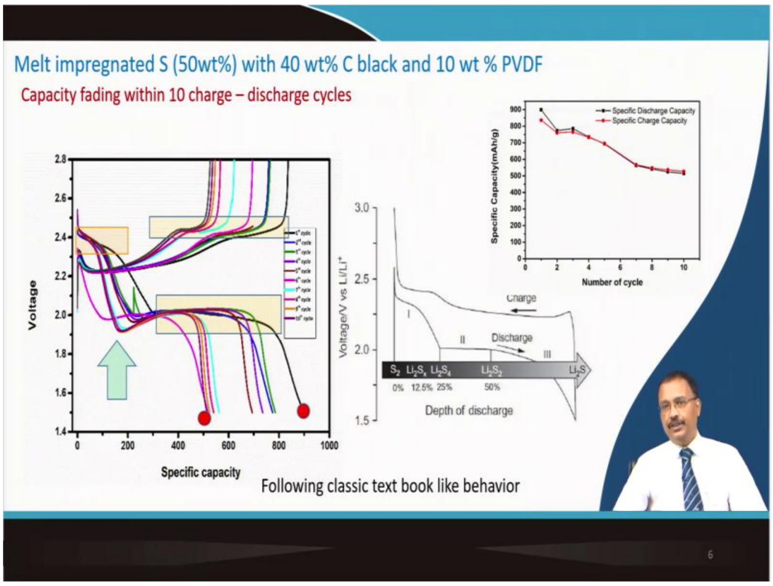

Now, a simple initially the structure that I showed you which worked it was quite complicated that PANI was used, titanium oxide was used, RGO was used commercial sulfur as well as sulfur we prepared also in the laboratory, so that was tried. So, it was a quite complicated structure. So, we directly use this sulfur which is about 50 weight percent and 40 weight percent carbon black, and PVDF 10 weight percent was used.

So, you will be able to explain this discharge and charge curve. So, initially you know that this is a small slope and this was reasonably flat here. And finally, it was down. So, where the long chain polysulfide forms, where the short chain forms will both are soluble, and where Li 2 S forms that you will be able to correlate with the standard textbook graph which is given here also.

And it follows exactly the similar kind of charge discharge profile, so that told us that this industrial waste we did not do any kind of modification, and we used that sulfur as it is. So, it gaves us the performance the electrochemical performance which is we were happy that this can be used.

But if you see that here also you can see after progressive cycle, first to 10 cycles, the capacity drops from about 900 milli ampere hour per gram to about 500. So, there is a huge capacity drop. And although the coulombic efficiency is not that bad, but this as it is you cannot use it. So, there is dissolution will be there and the problem which is quite common for lithium-sulfur battery, it is cannot be avoided.

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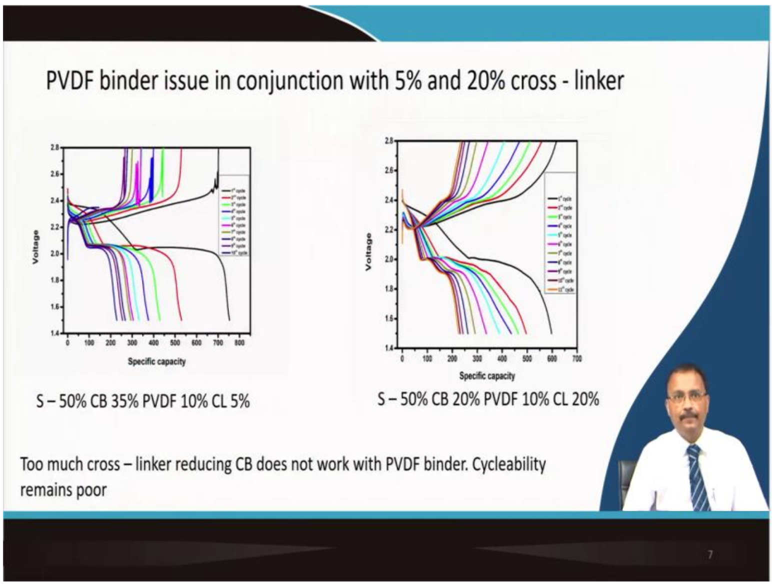

So, then we try to use this cross linker the so called cross linker which we thought that this can bind the polysulfide in the composite electrode efficiently. The nature of this cross linker this is not even known to me because that is their patented process for their for that industry I am working with.

But with PVDF kind of binder as you can see that if you increase the binder content from 5 to 10 percent, the profile which is characteristics to the lithium-sulfur battery that is changed something is happening here, we did not try to understand that what exactly is happening.

Because of the fact that this capacity is dropping down, certainly it will drop down because you are using a material which is not electrochemically active. So, the capacity is progressively dropping down with the increase of this cross linker. And with PVDF binder, it is not working the cross linker was not functioning, and we thought that this is not a good idea to pursue that.

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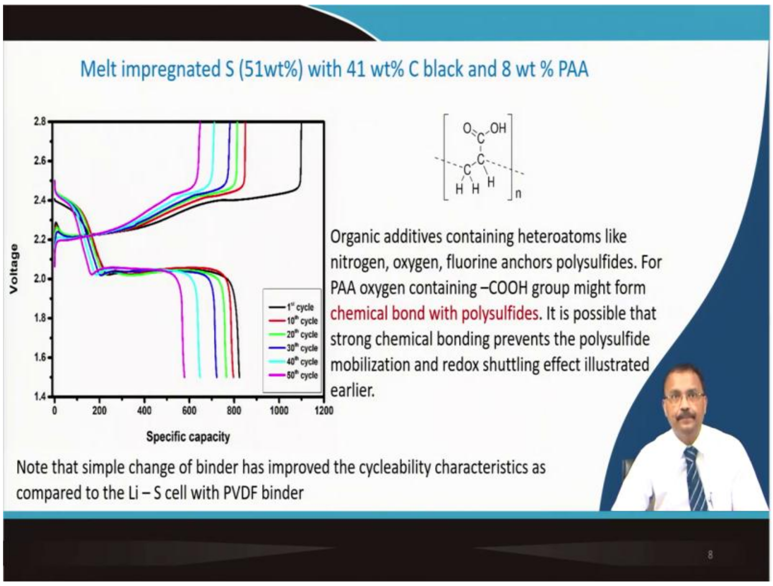

Now, we change the binder. So, we change the binder from PVDF to polyacrylic acid. So, this is an binder which is an organic additive that contains lot of heteroatoms. So, nitrogen you can see, oxygen, fluorine.

So, we have thought that this can anchor the polysulfides. And additionally this PAA is a oxygen containing C double O O H bond, this we thought that it might form a chemical bond with the polysulfide. Later we actually propose a tentative model that how exactly it is done.

So, this strong chemical bonding if you can provide, then this polysulfide mobilization will be retarded, and the redox shuttling when it comes to the electrolyte it tries to shuttle between the positive and negative electrolyte that will also get retarded. So, that was the idea of using just changing this binder instead of this PVDF, we just change this binder. And it helped.

It helped because you see that it can withstand earlier within 10 cycles the battery was losing most of its capacity, but now the battery is not losing its capacity, initial capacity is also not that bad also it is not in the range of 1000 using our complicated structure of Ti O 2 PANI reduced graphene oxide melt impregnated sulfur which I presented in my last lecture, but as compared to that this is showing some kind of positive signature.

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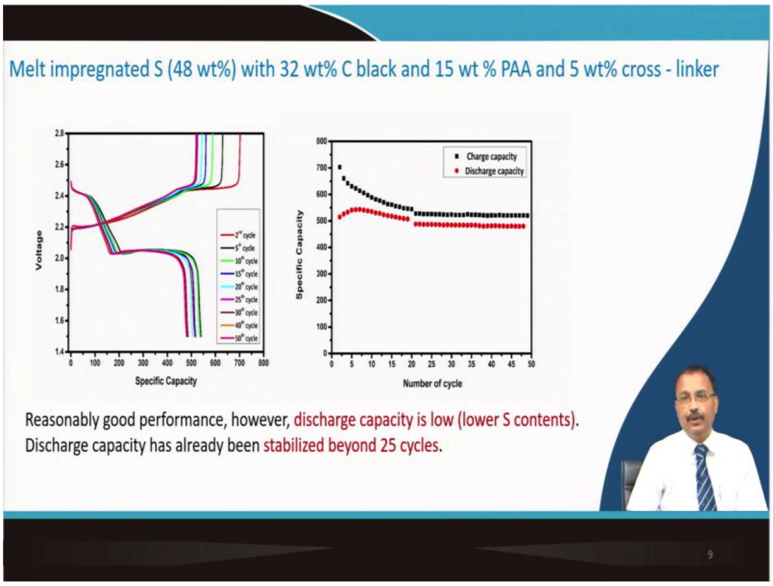

Then we try to play about this binder and the cross linker whatever was developed in that industry we also started using it. So, always we were trying to do something, so that this anchoring effect is in force, so that the we do not lose this polysulfide when it forms.

So, you can see that this is a melt impregnated sulfur, I must say there sulfur content is 48 percent because thirty two percent carbon black is there. And 15 weight percent binder we had to use, and 5 percent of cross linker.

So, as you can see that initial capacity will certainly be less because we are not calculating the capacity based on only the active sulfur, but we took the weight of this materials as well. So, the initial capacity was about 550, 500 around. And then basically it was stabilized after 50 cycles, so it is almost constant. So, after 25 cycles in fact it got stabilized.

So, lower sulfur content that actually yield lower capacity, but the concept works the binder, the polar binder, and the cross linker, the combined effect this is giving a reasonably good result.

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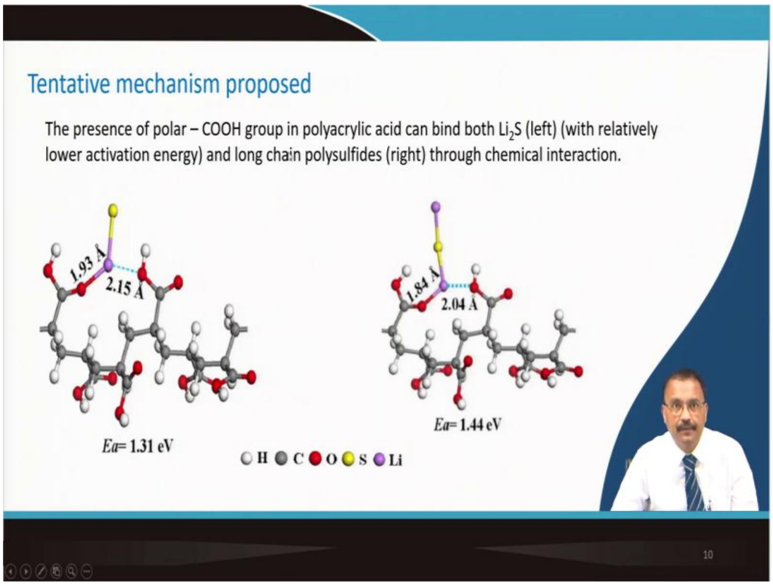

Now, if you see the presence of the polar group COOH group as I was talking about in poly acrylic acid, it can bind both Li 2 S, so this is the structure of Li 2 S. So, it can form a bond it can bind both Li 2 S and also the long chain polysulfides.

Although the activation energy will be little bit lower in case of Li 2 S, but as you can see that this is a possibility, it has not been experimentally verified yet but we have enough signature that this kind of binder that basically forms with the cross linker of course.

The nature of cross linker is not identifiable not, I cannot disclose it, but they can bind this polysulfides and that actually improves the electrochemical performance.

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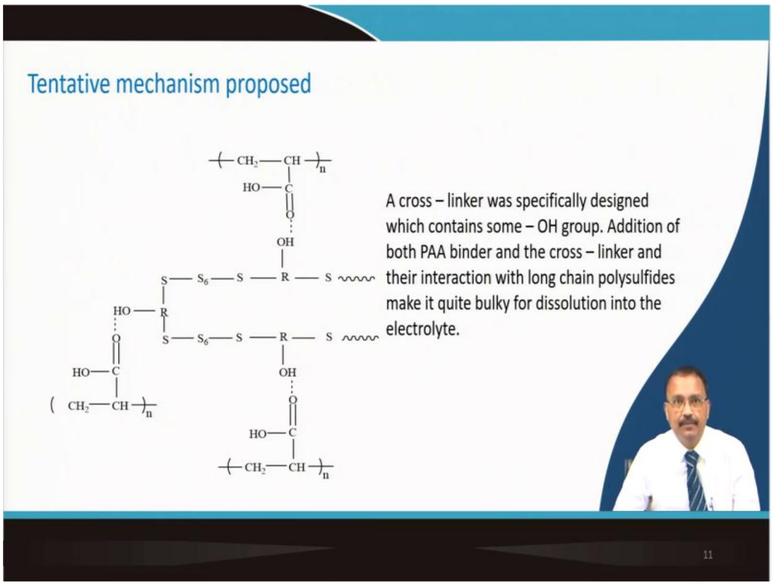

And some tentative kind of way it does it. So, as I said the cross linker was specifically designed for with something, so that it has some OH group. And once you add PAA binder and the cross linker, they interact with the long chain poly sulfides. And basically make it quite bulky group, so that it cannot dissolute inside the electrolyte material.

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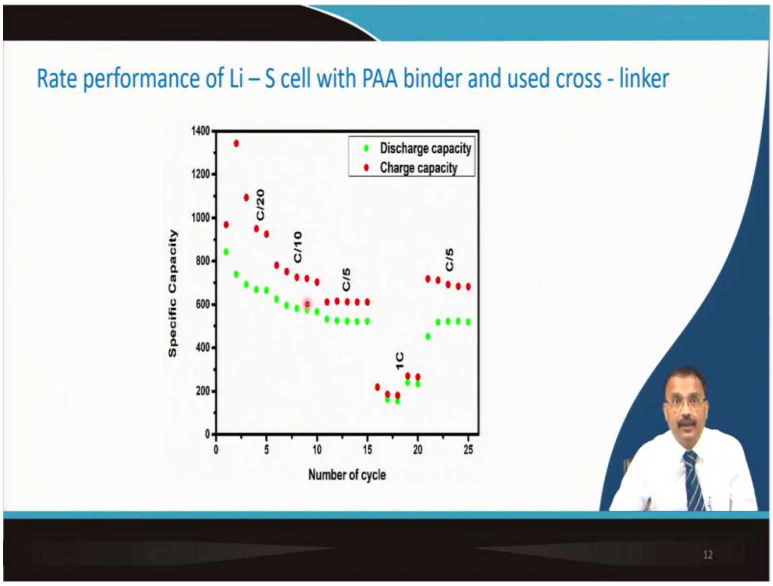

So, this type of positive electrode helped us to carry out the rate performance. In the last lecture, the last case study whatever I presented the performance at higher current was not that good, but here you can see it actually performs not that good, but performance is there even at 1 C. And it performs reasonably good at lower current rate, this PAA binder.

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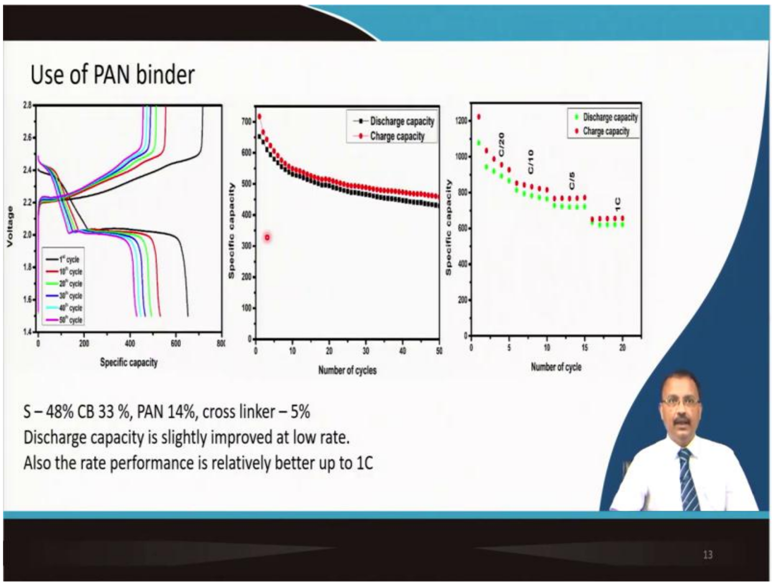

Then we change the binder to PANED. So, PAN binder we changed and the composition was 48 percent sulfur melt impregnated, then conducting black was 33 percent, PAN 14 and cross linker 5. The discharge capacity was a bit low 700, a bit high I should say earlier it was 500. So, discharge capacity is slightly improved at low rate. And it performs 50 cycles and you can see the cycleability plot.

So, it is getting faded for sure, but it is performing. Some manipulation is still required to change the cross linker concentration, or increase the sulfur, or reduce the PAN or use of other anchoring agent like graphene one can use. So, whatever possible things that you that you fill that will anchor the polysulfides that one should try to make it a better battery, but for this type of binder you can see that even if it at high current rate also it works.

It works reasonably good because it gives more than 600 milliampere hour per gram capacity. So, we try to make a simplified structure, so that to make a battery which works well.

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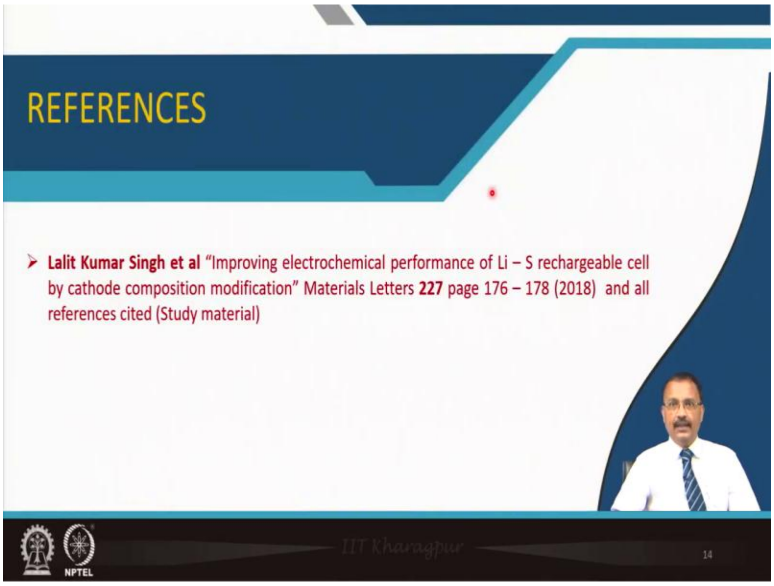

Now, you will find numerous report on lithium-sulfur battery because lithium-sulfur battery, lithium-air batteries, sodium-ion batteries, lithium-ion batteries, hybrid batteries, super capacitor whatever I have covered in the course so far I try to give you the basic idea about the understanding the fundamentals or understanding the presented papers, but this is not a textbook kind of material. So, the performance yet we do not understand well, the mechanism yet we do not understand well.

So, always you will have to go through the recent literature. And this course will give you just the foundation to understand those literature things. So, you will have to see when you see a lithium-sulfur battery, we will have to see let us see what kind of binder they have used, whether it is really getting this polysulfide formation anchored inside the electrode and improving the cycleability, or improving the discharge capacity, or improving the rate performance.

And if they have improved the rate performance what are the science behind it that has been explained in this paper, and whether it fits well to the understanding that I have gotten through my course, so that should be the approach to understand the things well it is a dynamic process.

And many of you will start working on the lithium-ion type of battery or rechargeable batteries. I am pretty sure that this kind of knowledge gained through this course will help you to do better research in this area. So, I am not giving any specific literature because both this study was based on two M. Tech., works that was carried out in our laboratory.

And you are free to study the literature report and we can discuss it that if you can find some better result that sir this fellow have done this kind of work, and which is giving you a better values whatever you showed us during the case study. I appreciate that if you can do it.

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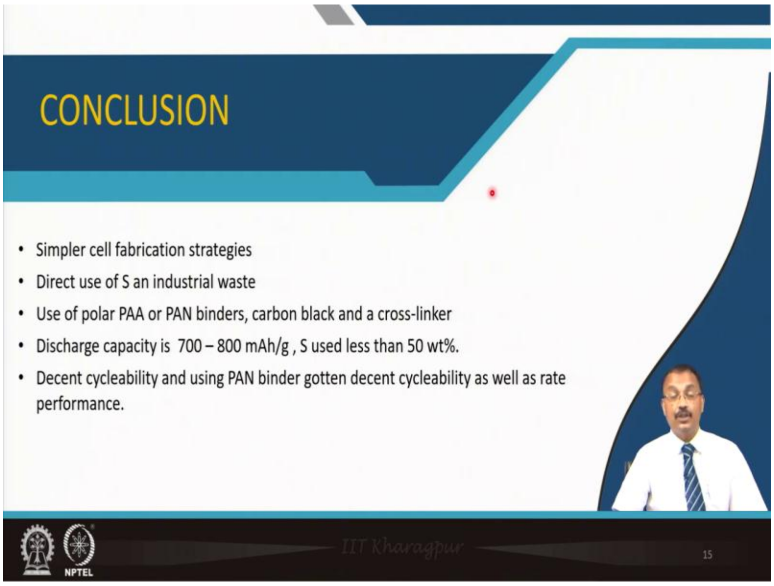

So, the idea was to use a simpler cell fabrication strategies. And direct use of sulfur from an industrial waste without any kind of modification, take it the waste material, melt it and use it. And use of polar binder like PAA we have studied, and PANI binders with carbon black and the cross linker, and it showed us some positive result in as far as the simplicity of the battery is concerned.

Usually we report or we got the discharge capacity about 700 to 800 milli ampere per per gram, but sulfur is used in this case less than 50 percent. We will have to increase sulfur to get good capacity. Cycleability was decent. And using the pan binder, we got decent cycleability as well as rate performance.

Thank you for your attention.