

**Electrochemical Energy Storage**  
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**Module - 10**  
**Li - Sulfur batteries**  
**Lecture - 47**

**Advantages and Disadvantages of Li - S Batteries, Positive Electrodes**

Welcome to my course Electrochemical Energy Storage, we are in module number 10 discussing Lithium Sulfur Batteries. This is lecture number 47, where I will be talking about the Advantages and Disadvantages of Lithium sulfur Batteries and then we will introduce the Positive Electrodes in a detailed way.

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**CONCEPTS COVERED**

- A promising technology
- Limitation of Li - S battery
- Positive electrode
  - Conducting additives
  - Additives to adsorb lithium polysulfides
  - Method for preparation of carbon /sulfur composite
  - Li<sub>2</sub>S based composite electrodes

Discharge

Li<sub>2</sub>S   S → S<sup>2-</sup>   Li<sup>+</sup>

Electrolyte

xLi<sup>+</sup>

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So, as I have mentioned that this is a promising technology, but we should understand well what are the limitations of lithium sulfur batteries. And we will start with the positive electrode as a part of this lecture, where we will be talking about the nature of the conducting additives, certain additives which are used to adsorb the lithium polysulfides. So, they can retain into the electrode material.

Then how to prepare this composite cathode materials for the lithium ion lithium sulfur cells and certain other lithiated sulfide based composite electrode will be introduced.

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**Advantages to Li-S batteries**

- As estimated in last lecture, Li-S technology is capable to yield 3517 Wh/kg of sulfur.
- As indicated in the accompanied diagram, in practice, given the mass of the whole battery and the intrinsic electrochemical limitations – it is only capable of delivering 700 Wh/kg – 1000 Wh/kg.
- The value is still much higher than that for other technologies.
- Sulfur is abundant, cost effective and non-toxic – These criteria are very important for PHEV and EV.

Cost of the positive electrode is one third of the total price of the conventional lithium-ion battery, we understand the need to develop alternative storage technologies such as Li-S

The Ragone plot shows Gravimetric Power (W/kg) on the y-axis (log scale from 10<sup>0</sup> to 10<sup>4</sup>) and Gravimetric Energy (Wh/kg) on the x-axis (log scale from 10<sup>-1</sup> to 10<sup>3</sup>). Ultracapacitors (Supercapacitors) are located in the top-left region (high power, low energy). Li-ion capacitors and Li-ion Batteries are in the middle. Li-S Batteries are in the top-right region (high power, high energy). Goals for LSCs, PHEV, EV, HEV, and EV are also marked.

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So, advantage of this advantages of this lithium sulfur batteries already I have talked about mostly in the last lecture, the theoretical energy density is pretty high about 3517-watt hour per kg and if you take only the weight of sulfur.

So, here we have drawn the Ragone plot the interrelation between the power and the gravimetric energy. So, you can see that ultracapacitor they have large power density, but the energy density is low. Lithium ion batteries come in this way and lithium ion capacitor also I have introduced a part of my earlier code earlier lectures. So, it lies here still the energy density is a bit poor lithium sulfur battery comes here.

So, it is a wide range, but you can see it can deliver both power and good energy density and it is very close to the electric vehicles goal. So, we are targeting something around 700-watt hour per kg to 1000-watt hour per kg. So, theoretically is far far above, but as I said that we will have to take into consideration of the weight of other electro electrical electrochemically inactive materials into consideration.

So, considering this; this technology is far superior than all this ultracapacitors or lithium ion capacitors or lithium ion batteries. So, one should pursue it with an increased activity and sulfur as I said it is abundant, it is cost effective and I will describe later that this lithium if you use in a metallic form recycling is also a bit easier. So, if you consider the electric vehicles application, this technology is very very efficient it is going to be very efficient.

Now, if you consider the cost of the positive electrode that is one third roughly one third of the total price of the lithium ion battery. So, we should use alternate technology because to reach the goal of this plug in hybrid electric vehicles or electric vehicles as such. So, lithium sulfur is a very very promising technology that is well established.

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**Limitations and disadvantages of Li-S batteries**

Limitations of Li-S battery are needed to be addressed. These limitations are related to the electrode, electrolyte and separator.

**Positive electrode**

- Sulfur is electronically insulating ( $\sigma = 5 \times 10^{-30} \text{ S/cm}$  at  $25^\circ\text{C}$ ). Conducting carbon black additives are needed to increase the electronic conductivity of the composite cathode. It also facilitates the redox reaction. Carbon black contents need to be optimized. The discharge reaction of Li-S is a slow reaction.
- $\text{S}_8$  is partially soluble in organic solvents. Dissolved sulfur diffuses through the liquid electrolyte to reach metallic lithium anode. It corrodes metallic lithium. Self discharge of Li-S cell is significant (both open circuit and during operation).
- $\text{Li}_2\text{S}$  is insoluble in organic solvents. It precipitates at the end of discharge onto positive electrode. This is electronic insulator, therefore, passivate the positive electrode (create inactive area on its surface).

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Now, there are several limitations of lithium sulfur battery and as I have already explained this limitations are related to the positive electrode, electrolyte is also certain things we will have to address I will take it in the next class, separator that is also should be taken into account and also negative sorry the negative electrode material that is lithium certain issues are also attached to the use of lithium metal.

So, in this particular lecture we will be talking about the positive electrodes and as you understand sulfur electronic conductivity is too poor about  $10^{-30}$  Siemens per centimeter at ambient temperature. So, we need to use carbon black additives to increase the electronic conductivity of the composite cathode.

And this redox reaction whatever I have explained earlier this carbon some way this carbonaceous material I should say you know some way it also expedite that redox reaction, but carbon content needs to be optimized you know the last lecture I was talking about that there is in fact, no limit to use this sulfur content. So, there should be some kind of limit that you will have to use sulfur beyond a certain weight fraction.

So, at present it is about 60 to 70 weight percent sulfur you will have to use you cannot use indefinitely indefinite amount of exceeding amount of this carbon black. So, this carbon black content that needs to be optimized to impart sufficient electronic conductivity of this otherwise non conducting sulfur. And the discharge reaction as a whole whatever I have shown in the earlier lecture, this is a basically slow reaction it takes time to have this reaction in operation.

So, the pure sulfur that the organic solvent that usually we use for lithium sulfur battery even in that solvent, this cyclic sulfur is partially soluble. So, if you just take sulfur electrode and dip it into the organic electrolyte, you will find that the sulfur is coming out from the electrode and it is going into the electrolyte itself.

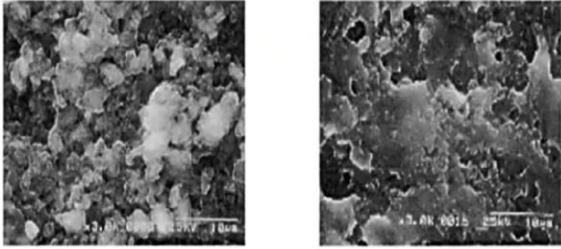
So, this sulfur what is coming out from the positive electrode that diffuses through the liquid electrolyte and eventually it reacts with lithium anode that which is metallic lithium.

So, once this is done it happens like this then we can term it as self-discharge because the discharge reaction will take place as soon as you put the positive electrode, electrolyte and lithium metal into place. So, during the open circuit condition as well as when you are really discharging it by applying a load, you will find that the self discharge is one of the major problems of the lithium sulfur battery. Fortunately, the end product  $\text{Li}_2\text{S}$  that is insoluble in organic solvent.

But, what happens, it precipitates at the end of the discharge on to the positive electrode and this  $\text{Li}_2\text{S}$  that is also electronic insulator. So, once an electronic insulator that actually precipitate on the positive electrode, it passivates the positive electrode and those passivated area they are electronically I mean electrochemically they are inactive area on the surface. So, that also you will have to take care of.


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Limitations and disadvantages of Li-S batteries



Left SEM micrograph shows the SEM image of Sulfur composite electrode before discharge. The right micrograph shows after discharge at 1.5V with a current density of 3 mA/cm<sup>2</sup>. Significant deposit of Li<sub>2</sub>S are apparent in the discharged electrode.

Micrographs taken from : S.E. Cheon et al " Rechargeable lithium – sulfur battery – I. structural change of sulfur cathode during discharge and charge" J. Electrochem. Soc., 149, A1437 – 1441 (2002)

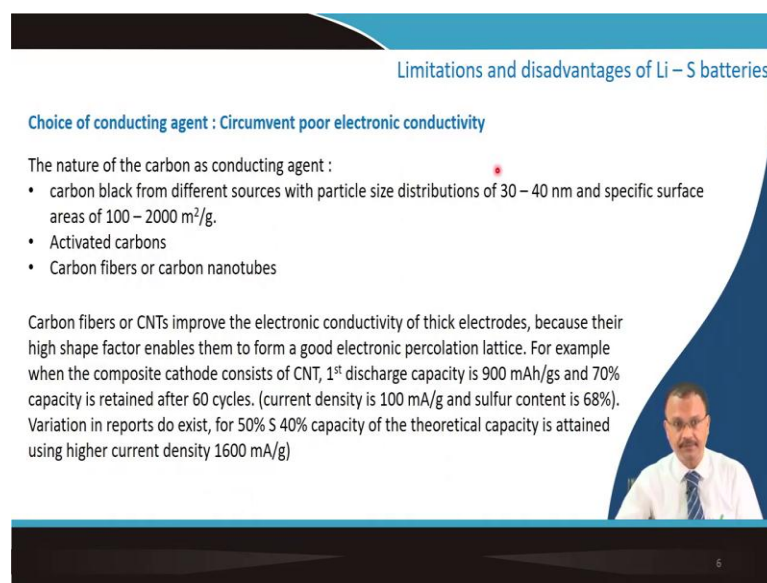


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So, the left micrograph that use that is shown and it is taken from this literature and I would like you to read this particular paper. So, this micrograph shows that it is basically a sulfur composite. So, it is having sulfur, then it is having conducting carbon, binder. So, this is during discharge and after discharge it forms something like this. So, usually the potential window is 3 to 1.5 volt or little bit lower.

So, a typical current density that was used for this kind of discharge is 3 milliamperere per centimeter square. So,  $\text{Li}_2\text{S}$  is deposited on the positive electrode and as I said that since they are electronically insulating. So, this kind of deposition a bulk deposition of lithium  $\text{Li}_2\text{S}$  that particularly in the discharge electrode will make the electrode surface which is not electrochemically active for the subsequent charge operation.

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Limitations and disadvantages of Li-S batteries

Choice of conducting agent : Circumvent poor electronic conductivity

The nature of the carbon as conducting agent :

- carbon black from different sources with particle size distributions of 30 – 40 nm and specific surface areas of 100 – 2000 m<sup>2</sup>/g.
- Activated carbons
- Carbon fibers or carbon nanotubes

Carbon fibers or CNTs improve the electronic conductivity of thick electrodes, because their high shape factor enables them to form a good electronic percolation lattice. For example when the composite cathode consists of CNT, 1<sup>st</sup> discharge capacity is 900 mAh/gs and 70% capacity is retained after 60 cycles. (current density is 100 mA/g and sulfur content is 68%). Variation in reports do exist, for 50% S 40% capacity of the theoretical capacity is attained using higher current density 1600 mA/g)

So, there are various choice of the conducting agent and you will have to use conducting agent to circumvent the poor electronic conductivity of the cyclic sulfur that you are using. And usually carbon black that is a common conducting agent which is also used for lithium ion battery that is used and here the important part is its particle size distribution, final particle will give you larger specific surface area.

So, typically if you have a 30 to 40 nanometer of particle size of the conducting carbon black, then specific surface area b t surface area comes around 100 to 2000 meter square per gram so, that can be used. Activated carbon which usually we talked about in one of our lecture model where I was talking about super capacitor you understand the role of activated carbon.

And also carbon nanotube and carbon fibers they have also been used, but as you understand this carbon fiber and carbon nanotube you will have to make it you will have to synthesize it and that basically improves the electronic conductivity particularly for the thicker electrode because you need to increase the mass loading to have more capacity.

So, for thicker electrode this carbon nanotube they have the large length as compared to the diameter. So, the shape factor is important and they actually percolate in a thicker electrode from one end to another end from current collector to the surface of the electrode. So, they act as a conducting path.

So, some examples I have cited that composite electrode if you use carbon nanotube, then typically 1st discharge capacity of the lithium sulfur you are getting say for example, 900 milliampere hour per gram of sulfur and typically 70 percent of the capacity is retained at 60 cycles..

And you know that the capacity depends on the discharge current. So, here typically 100 milliampere per gram this kind of discharge current was used and as I said that the sulfur content is important and indefinitely you cannot increase the content of the conducting carbon.

So, here in this case 68 percent of sulfur was used. So, typically you get this kind of discharge capacity and decent cycleability I should say. So, after 60 cycles 70 percent retention not very great, but it is acceptable. So, if you review several reports variation do exist. So, for example, 50 percent sulfur, 40 percent capacity of the theoretical capacity is attained theoretical capacity is in the order of 1600 milliampere hour per gram.

So, reduce the sulfur content increase the carbon. So, it is more conducting in the composite electrode. So, this you can achieve a good capacity discharge capacity even if the discharge current is pretty large 1600 milliampere per gram.

It is almost 1 C rate you are discharging still you get a reasonable good capacity that is due to the high content of the conducting carbon, that is why I told there should be a limit of the use of sulfur. So, you cannot reduce the sulfur content beyond certain limit to exaggerate your data.

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Limitations and disadvantages of Li-S batteries

Additive to adsorb lithium polysulfides

CNT or certain carbon blacks with large surface area exhibit absorbing effect to limit the dissolution of the active material. These active materials are adsorbed on the surface of the carbonaceous materials. As mentioned earlier, one could get initial discharge capacity of 1200 mAh/gs (at 100 mA/g with less than 60% S in the composite electrode) and reasonably good cycleability.

Adsorbing effect is also exhibited by oxides of aluminum, vanadium etc. Also  $Mg_{0.6}Ni_{0.4}O$  is used to yield stable discharge capacity 1000 mAh/gs for more than 50 cycles (C/10 rate). One should carefully interpret these data as in such case sulfur content is too low (20% only)

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So, carbon nanotube and also certain carbon blacks which are having very large surface area, they actually exhibit some kind of absorbing effect. Absorbing to what? Absorbing to the discharge product so, that they do not dissolve into the active material. So, in that they will be binding this longer chain polysulfides into the positive electrode.

So, in the surface of this carbonaceous material, this active materials are absorbed. So, we will consider that is active material because eventually again they will be dissociated to lithium ion sulfur. So, initial discharge capacity in certain report it is 1200 milliamper hour per gram of sulfur and typically at 100 milliamper per gram with the current and again it is less than 60 percent.

So, you will have to use sufficient amount of the carbon black in the composite electrode. So, this kind of composite electrode also exhibited reasonable good cycleability. So, apart from this carbonaceous material if you use certain oxides and one typical example is this magnesium nickel oxide, this is basically nickel doped magnesium oxide. So, vanadium oxide also people have used and in our work also we have used certain oxide I will show it in as a part of the case study.

So, this oxide material they also yield very stable discharge capacity and anything around in and around 1000 milliamper hour per gram is good and 50 cycles although the rate as you can see is little bit low C by 10 rate, but still one could achieve with this oxide additives about 1000 milliamper hour per gram of sulfur. So, as I said one should



interpret this data with a caution that sulfur content particularly for this example it was only 20 percent.

So, 20 percent is not acceptable. So, in a composite material your active electrochemically active phase fraction; phase weight fraction should not be 20 percent, but as you understand that several reports they have reported like this. So, one should be little bit cautious to compare the electrochemical activity of different types of composite electrode which has been reported in recent literature.

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**Preparation of carbon/sulfur composite**

Different modes of preparation

- Mixing of conducting carbon and polymer binder by vacuum mixing into a stable suspension before tape casting the slurry. Carbon needs to be evenly distributed around sulfur particle to create a carbon percolating composite positive electrode.
- Sometimes an additional milling is introduced to homogenize the particle size of the constituents. Usually the milling is done in dry environment to surface coat sulfur with carbon. Carbon coating can also be done in vapor phase.
- Coating of carbon black with a layer of sulfur is also done. Core is carbon with an active skin of sulfur.
- Precipitation of sulfur from  $\text{SO}_2$  onto carbon nanoparticle in accordance to the following (in liquid medium : water or ethanol)

$$\text{SO}_2 + 2\text{S}^{2-} + 4\text{H}^+ \rightarrow 2\text{S} \downarrow + 2\text{H}_2\text{O}$$

The slide includes a small inset image of a man in a white shirt and tie, and two diagrams: one showing a yellow circle with a black outline and another showing a black circle with a yellow outline.

So, preparation of this carbon and sulfur composite that is important. So, first important thing is that you will have to mix this conducting carbon with a polymer binder and usually vacuum mixing is used, it forms a stable suspension and it is a deflocculated suspension.

So, it is stable the things should not get precipitate out because you are using particles of different size they have different density. So, it should not be phase separated. So, the slurry, the ink for the tape casting it should be stable enough and it is very important that carbon is very evenly distributed in the inside the slurry, it should not form agglomeration. And if it forms agglomerate then certainly the electronic path will not be that great.

So, it should be evenly distributed around the carbon I mean sorry sulfur particle. So, if it is something like this it is good. So, some kind of porosity is also there. So, this carbon if you consider another sulfur.

So, this carbon actually form a percolative path from current collector to the surface to the electrolyte of the battery. So, that is one way to get good performance. Sometimes you do need additional milling if the particle size of the sulfur is large as well as carbon black usually they are finer.

So, sometimes the milling is also introduced to homogenize the particle size not always spherical the way it is shown, but the distribution should be narrow you should have a narrow size distribution towards the final limit of the active sulfur site. So, this carbon coating also has been tried. So, the carbon coating you can do in the vapor phase which is expensive of course. So, that also can impart a uniform carbon coating across the sulfur material.

Another way is that you take the sulfur as a coating. So, sulfur is a coating material where core is carbon and active skin is sulfur. So, this kind of configuration is also possible. Third one is the chemicals precipitation of sulfur and usually it is done from sulfur dioxide onto this carbon nanoparticle.

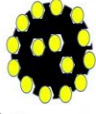

And this is the reaction which is involved the medium is taken either water or ethanol and sulfur is precipitated on to the carbon nanoparticle. So, something of this kind you can get that is used as the active material for lithium sulfur batteries.

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**Preparation of carbon/sulfur composite**

**Different modes of preparation**


Sulfur could also be deposited (by physical vapor deposition) into the pores of the carbon. It might cause polarization during discharge as one need to spend additional energy to break C-S bonds formed by close contact between carbon and sulfur.



Mesoporous carbon structure formed between aligned carbon tubes. High volume of pores, good electronic conductivity and possibility of confining **active materials** in channels left between the tubes

Mesopores 2 – 50 nm, micropores < 2nm, macropores > 50 nm

X. Li et al "A highly ordered nanostructured carbon – sulfur cathode for lithium – sulfur batteries" *Nature Materials*, 8, 500 – 506, 2009



So, sulfur can be deposited by physical vapor deposition into the pores of carbon. So, it actually forms a percolative layer and you know that the polarization during discharge that is important. So, one need to spend additional energy to break this kind of carbon sulfur bond, once this sulfur is deposited into the pores between this carbon.

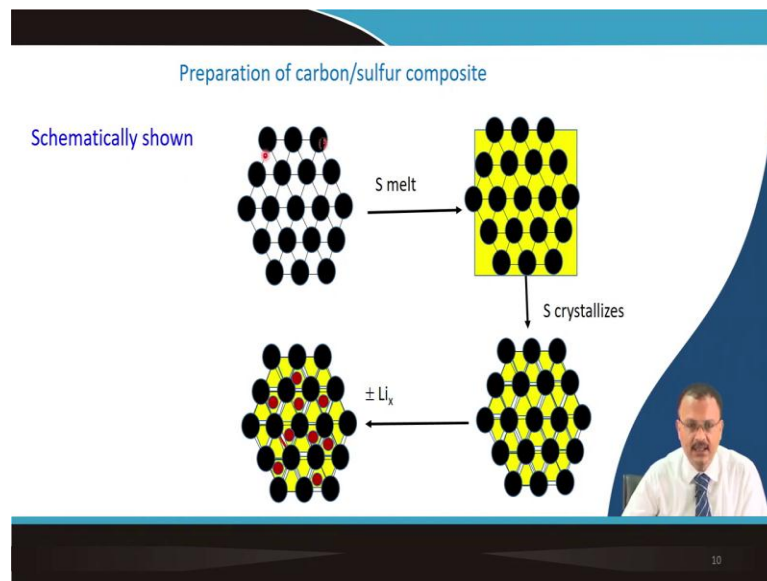
So, here one example is there. So, it is a mesoporous carbon structure and you know the dimension of mesopores are usually 2 to 50 nanometer and we term this is micro pores when the size is less than 2 nanometer and macro pores when the size is more than 50 nanometer.

So, if I consider this mesoporous carbon and then sulfur is deposited particularly by physical vapor deposition, then there is a bond possibility of bond formation between carbon and sulfur and you need to spend energy to break this bond to make it free so, that it can react with lithium.

So, that polarization that will lead to the polarization. So, one should be cautious about this so, but it is always effective you if you have high volumes of pores. So, good conductivity and there is also a possibility to confine the active materials that is the long chain polysulfides into this channel into this channel. So, this is one kind of configuration that is described in this nature papers.

And you can see that the diameter of this carbon nanotube is about 6.5 nanometer and the pore here is 3 nanometer. So, sulfur is deposited inside the pore and this kind of material except the problem of this breakage of this carbon sulfur bond because it forms a bond. Otherwise, this is a good strategy because when lithium will react with this sulfur and form the polysulfides then inside this channels between these tubes, it can be partially adhered. So, you can hold this so, that it does not go back to the catholytes to the electrolyte.

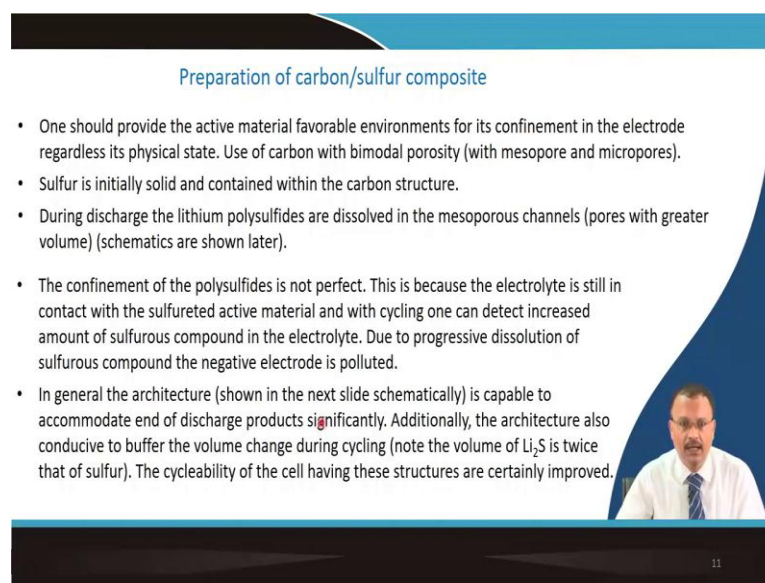
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So, the strategy is that this carbon is form of a porous structure and then instead of mixing it with the sulfur, you can melting point of sulfur is pretty low. So, you can melt the sulfur. So, once you melt it, it will go into this porous structure to form a liquid melt like this and then you can recrystallize this sulfur.

So, it is in a recrystallized form and then you get it reacted with lithium to form the polysulfides and depending on the size of the channel there is a possibility to hold this long chain polysulfide into this pore. So, that it does not go into the electrolyte solution. So, this strategy is also quite effective which just now I described.

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Preparation of carbon/sulfur composite

- One should provide the active material favorable environments for its confinement in the electrode regardless its physical state. Use of carbon with bimodal porosity (with mesopore and micropores).
- Sulfur is initially solid and contained within the carbon structure.
- During discharge the lithium polysulfides are dissolved in the mesoporous channels (pores with greater volume) (schematics are shown later).
- The confinement of the polysulfides is not perfect. This is because the electrolyte is still in contact with the sulfureted active material and with cycling one can detect increased amount of sulfurous compound in the electrolyte. Due to progressive dissolution of sulfurous compound the negative electrode is polluted.
- In general the architecture (shown in the next slide schematically) is capable to accommodate end of discharge products significantly. Additionally, the architecture also conducive to buffer the volume change during cycling (note the volume of  $\text{Li}_2\text{S}$  is twice that of sulfur). The cycleability of the cell having these structures are certainly improved.

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So, the active material one should provide the favorable environment for its confinement to the electrode and regardless its physical state, whether it is in the sulfur powder form or it is having the molten form.

So, it has been demonstrated that the carbon which is having a bimodal porosity two different size of the porosity, particularly in the mesopore which is 2 to 50 nanometer and micro pore which is less than 2 nanometer. This kind of situation if you can generate it is advantageous. So, sulfur usually is initially solid and that is contained into the carbonaceous structure.

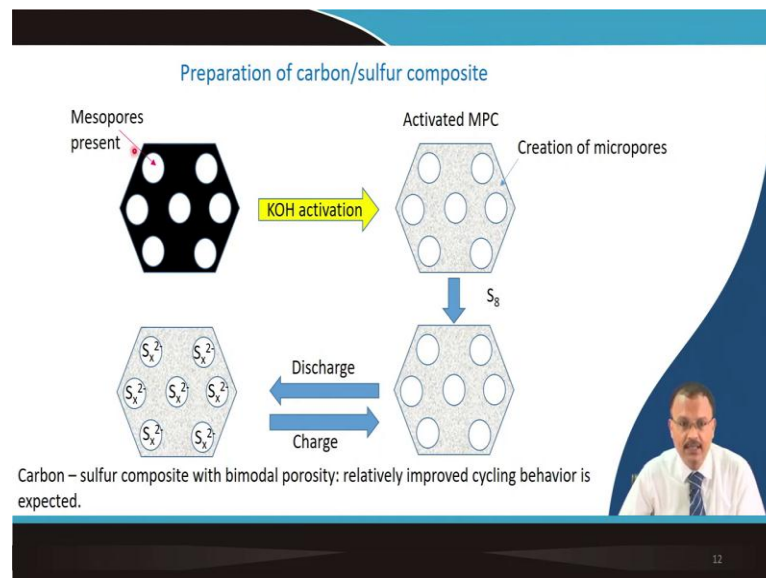
So, as I have explained that during discharge this lithium polysulfides they form and they dissolve into the mesoporous channels. So, mesoporous channels are having larger volume, I will show the schematic later on how exactly it is done. So, sometimes this confinement of this polysulfides they are not very perfect because you know the electrolyte they are not sitting separate from the positive electrode.

So, if it is a porous structure electrolyte also they can diffuse inside the positive electrode and they are in contact with this polysulfides. So, during cycling there is a possibility to leach out of this long chain polysulfides and one can actually detect this sulfurous compound into the electrolyte. So, progressive dissolution of the sulfurous compound actually goes to the negative electrode that is lithium and this is also detrimental for the battery.

So, the architecture whatever I have described that is actually possible possibly they are capable to accommodate the end of discharge product which is  $Li_2S$  significantly they can hold this inside the positive electrode material. Another advantage is that you know that when sulfur that is reduced with lithium during discharge and forms this polysulfide there is a volumetric expansion.

So, this kind of structure they can buffer this volumetric expansion. In fact, in one of my lectures we talked about the role of carbonaceous material when I was talking about the alloy based anode material. So, it buffers the stress generated due to this expansion. So, something similar here also it is possible since the volumetric expansion takes place particularly this expansion is buffered by this kind of structure.

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So, here you can see the typical example of mesopores and micro pores. So, mostly mesopores here. So, with potassium hydroxide you can basically this carbon material you can introduce more micro pores in it to have a bimodal kind of distribution. So, earlier it was mesoporous region and this region you introduced more micro pores this finer size pores which is much finer as compared to your mesoporous size.

And then you use your cyclic sulfur and then during discharge this sulfur is confined into the mesoporous region and it reacts with lithium. So, this long chain kind of polysulfides they are actually bonded into this mesoporous region.

So, for this kind of structure, it also helps to buffer the resultant expansion which is taking place because lithium is going into the structure the volume expansion takes place as compared to pure active sulfur. So, that stress is also buffered and for this kind of structure with bimodal porosity which is artificially generated cycling behavior is a bit improved.

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**Preparation of carbon/sulfur composite**

**Pretreatment of the active material**

Two popular methods are widely reported:

1. Sulfur is milled to reduce the particle size to increase the surface area. Particle size distribution of the active material influence the nature of percolation. Finer is the particle size greater is the surface area of contact between sulfur and carbon. For example reduction of the particle size from 20 to 5  $\mu$  increase the percent usages of the active material from 35 to 50%. Usually larger active particles are sieved out before making the composite electrode.
2. Elementary sulfur is couple with a conductive polymer (polythiophene or polypyrrole) to improve the electronic conductivity. The electrode could bind the polysulfides as well. Presence of conducting polymer also prevents the accumulation of active material during cycling.

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Another popular way to improve the positive electrode material there are in fact, two prominent methods that has been used the first one is straight forward to reduce the particle size and to increase the surface area.

So, particle size distribution of the active material they influence the percolation and finer particle size they have greater surface area. So, carbon and sulfur they are in good contact and carbon can percolate this electronic conducting path. So, as an example the reduction of particle size if you do from 20 micron to 5 micron that increase the percent uses of the active material from 35 to 50 percent.

So, larger active particle basically you can sieve it out so, that you have some kind of uniform finer particle size distribution. So, this is commonly usually it is done and as an effective alternative you can recrystallize the molten sulfur, sulfur is in the molten form and then it is recrystallized. So, finer particles you will get with more surface area. So, that is also another way to use sulfur effectively.

The second one is the sulfur you can couple with a conducting polymer and conducting polymer could be polythiophene or polypyrrole and this basically increases the electronic conductivity and usually this kind of electrode incorporate oxide material as well.

So, it is a pretty complicated structure, you have sulfur which is fine structure then you embed it into a polymer wrapper and then this polymer is more electronically conducting if you have oxide particle embedded in it and usually it is found that this kind of electrode they could bind the polysulfides.

So, the whole aim is to bind the polysulfide so, that it does not go back to the electrolyte solution increase its viscosity. And also once you have this conducting polymer with your active sulfur the chances of the agglomeration of this active material because as you know the sulfur if you reduce the particle size its surface area increases.

So, the energy is more surface free energy is more. So, they have a tendency to form the soft agglomerate. So, this formation of the soft agglomerate that is also grossly reduced. So, due to the use of this kind of polymer.

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The slide is titled "Preparation of carbon/sulfur composite" and discusses the formulation of  $\text{Li}_2\text{S}$  based composite electrodes. It lists the positive electrode as  $\text{Li}_2\text{S}$  (with a theoretical capacity of approximately 1170 mAh/g) and the negative electrode as Graphite, Si, or Sn. It notes that this is Li ion battery technology and lists three key points: it eliminates the problem of Li dendrite formation, the charge-discharge mechanism ( $\text{S}_8/\text{S}^{2-}$ ) remains unchanged (avoiding dissolution and poor conductivity), and  $\text{Li}_2\text{S}$  like elementary sulfur is an electronic insulator that must be coated with carbon. A small video inset shows a man in a white shirt and tie. The slide footer includes a citation: "J. Hassoun et al Rechargeable lithium sulfide electrode for a polymer tin/sulfur lithium ion battery J. Power Sources, 196, 343 -348 2011" and the number 14.

Preparation of carbon/sulfur composite

Formulation of  $\text{Li}_2\text{S}$  based composite electrodes

Positive electrode –  $\text{Li}_2\text{S}$  (estimate its theoretical capacity ~ 1170 mAh/g)  
Negative electrode – Graphite, Si, Sn

This is Li ion battery technology.

- Eliminates the problem of Li dendrite formation
- Charge – discharge mechanism  $\text{S}_8/\text{S}^{2-}$  remains unchanged : dissolution, poor electronic conductivity, passivation at the end of cycle
- $\text{Li}_2\text{S}$  like elementary sulfur is an electronic insulator. It has to be coated with carbon.

J. Hassoun et al Rechargeable lithium sulfide electrode for a polymer tin/sulfur lithium ion battery  
J. Power Sources, 196, 343 -348 2011

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Another straight forward use is the formulation of  $\text{Li}_2\text{S}$  based composite electrode. So, if I want  $\text{Li}_2\text{S}$ , I know it is solid it does not get dissolved into the electrolyte then why not to use positive electrode itself which is lithiated sulfide. So, you can estimate the



theoretical capacity, I leave it on you to estimate the theoretical capacity to show that it is 1170 milliampere hour per gram.

Compare it with the theoretical capacity of sulfur it is slightly lower and in this case since lithium is already there in your sulfur the negative electrode you can use graphite you can use silicon you can use tin.

This is a good technology, but certain report we have in recent time as well, but this is one of the literature which explains its well. So, it eliminates the problem of lithium dendrite formation because you are not using metallic lithium and charge discharge mechanism this  $S_8$  to  $S_2$  that part remains unchanged because initially starting point is  $S_2$  minus and you can bypass the all long chain polysulfide formation in this way dissolution, poor electronic conductivity, passivation at the end of the cycle.

So, that is partially resolved, but I am not pretty sure that whether it will be direct  $L_2S$  to sulfur or in this case also the intermediate long chain formation is also there. I need to check that, but certainly as compared to pure sulfur this is certainly reduced. This paper says that it is grossly reduced, but the problem like  $Li_2S$  is still an electrical insulator. So, you need to use considerable amount of conducting agent to make it operative. So, that part you cannot avoid.

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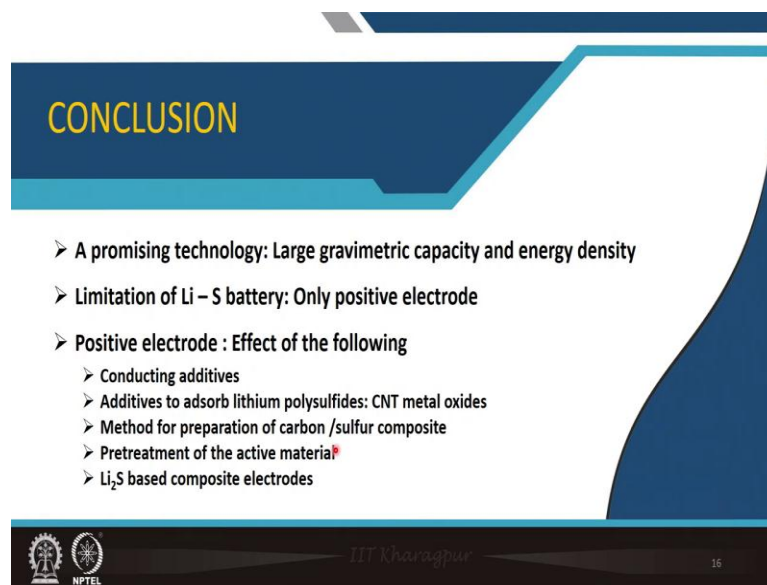
**REFERENCES**

- **Christian Glaze and Sylvie Genies** "Lithium batteries and other electrochemical storage systems, Chapter – 9 Lithium – Sulfur Batteries page 271 – 277 and all references cited (Study material)

The slide features a dark blue header with the word "REFERENCES" in yellow. Below the header, a red arrow points to a citation. In the bottom right corner, there is a small video inset showing a man in a white shirt and tie. The footer contains the NPTEL logo, the text "IIT Kharagpur", and the number "15".

So, this part of the lecture is the study material is this book chapter 9 and all the references they are good references innovative and informative references you can find. I would like you to read those literature for a better understanding.

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**CONCLUSION**

- A promising technology: Large gravimetric capacity and energy density
- Limitation of Li – S battery: Only positive electrode
- Positive electrode : Effect of the following
  - Conducting additives
  - Additives to adsorb lithium polysulfides: CNT metal oxides
  - Method for preparation of carbon /sulfur composite
  - Pretreatment of the active material
  - Li<sub>2</sub>S based composite electrodes

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So, it is still a promising technology, large gravimetric capacity and energy density. Limitations by this time you are well aware of it, but only positive electrode I have described. In the next lecture we will talk about the electrolyte and we will also talk about the lithium metal, the negative electrode material.

And in case of positive electrode conducting additives they play a major role, then additives to adsorb carbon polysulfides, we have talked about CNT, we have talked about metal oxides. Then the method of preparation of a quality carbon sulfur composite the bimodal distribution then the use of carbon nanotube with mesoporous structure to confine the polysulfides that was introduced..

Pretreatment of the active material by reducing the particle size that was also talked about and finally, Li<sub>2</sub>S based composite electrode and their functionality we have touched upon.

Thank you for your attention.