Electrochemical Energy Storage
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Module - 10
Li - Sulfur batteries
Lecture - 49
State of the Art Li - S Batteries: Case Study - I

Welcome to my course Electrochemical Energy Storage and this is module number 10 where we are talking about Lithium Sulfur batteries and this is lecture number 49. In earlier lectures, we talked about lithium sulfur batteries, its principle operation principle of operation and then what are the advantages and disadvantages. And then separately we talked about the positive electrode material, the negative electrode materials and the electrolyte.

And you have seen that lot of experimental studies that have been done. So, in the laboratory from the knowledge whatever we have gained out of this literature work we have decided to start working on lithium sulfur battery. So, as a case study we will describe our effort and what we have gotten is part of one of my M Tech students experimental results and that I am going to describe.

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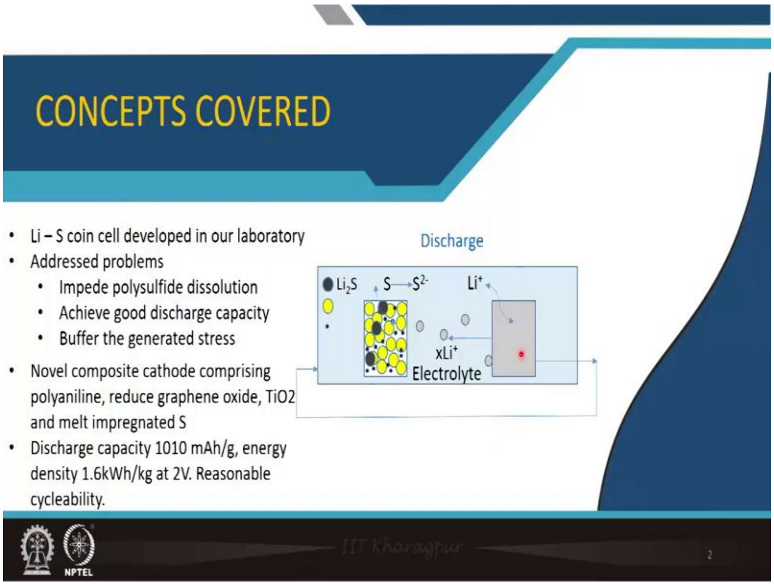

CONCEPTS COVERED

- Li – S coin cell developed in our laboratory
- Addressed problems
  - Impede polysulfide dissolution
  - Achieve good discharge capacity
  - Buffer the generated stress
- Novel composite cathode comprising polyaniline, reduce graphene oxide, TiO2 and melt impregnated S
- Discharge capacity 1010 mAh/g, energy density 1.6kWh/g at 2V. Reasonable cycleability.

So, lithium sulfur cell this is in a coin cell configuration that was developed in our laboratory. And we have addressed this problem that polysulfide dissolution whether we can and whether we can control it to get a good discharge capacity and what are the other effect that one can have. And what is the exact novelty of our work based on the based on the knowledge that we have gained out of different types of literature report that we have reviewed.

And based on that we have used a composite cathode which is having a polymer. Then a conducting carbonaceous material then a oxide additives and sulfur we have used as a melt impregnated way just to control the particle size effect and we have gotten a descent discharge capacity and energy density and reasonable cycleability also we have gotten. So, we were very excited about this piece of work this has also been published and in fact, the published paper that is your study material along with all the cited literatures.

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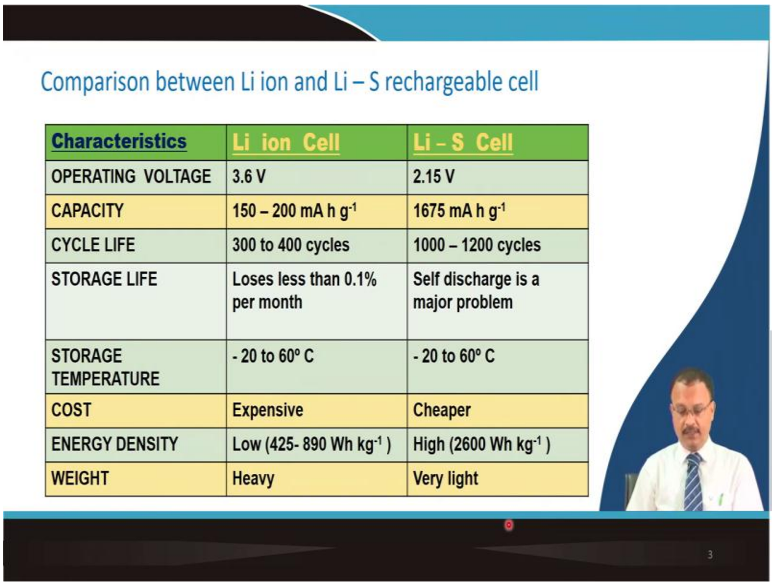

Comparison between Li ion and Li – S rechargeable cell

Characteristics	Li ion Cell	Li – S Cell
OPERATING VOLTAGE	3.6 V	2.15 V
CAPACITY	150 – 200 mA h g^{-1}	1675 mA h g^{-1}
CYCLE LIFE	300 to 400 cycles	1000 – 1200 cycles
STORAGE LIFE	Loses less than 0.1% per month	Self discharge is a major problem
STORAGE TEMPERATURE	- 20 to 60° C	- 20 to 60° C
COST	Expensive	Cheaper
ENERGY DENSITY	Low (425- 890 Wh kg^{-1})	High (2600 Wh kg^{-1})
WEIGHT	Heavy	Very light

So, if you compare this lithium ion cell and lithium sulfur cell you know the operating voltage lithium ion cell, the nominal voltage is 3.6 volt and here it is quite low about 2.15 volt in case of lithium sulfur. Capacity is pretty large the theoretical capacity I am talking about 1675 milli ampere hour per gram. So, it is of no comparison lithium the good quality or best quality lithium ion cell does not have this kind of capacity.

Cycle life it is possible to get 1000 to 1200 cycles. In fact, we have we also reached about 300 400 cycles using our lithium sulfur which I will be describing as a part of the case study. Storage life here is an age about 0.1 percent per month and here self discharge is a major problem. And why the self discharge takes place? You know that because in my last three lectures I talked about it.

Storage temperature is almost same minus 20 to 60 degree Celsius it can be operative it is cheaper than the lithium ion cell because no expensive cobalt or nickel that you are using sulfur is cheap and lithium is only the expensive material. Energy density also is of no match here 2600 watt hour per kg as compared to this one and it is very lightweight. So, you have all the reasons to start working on lithium sulfur batteries.

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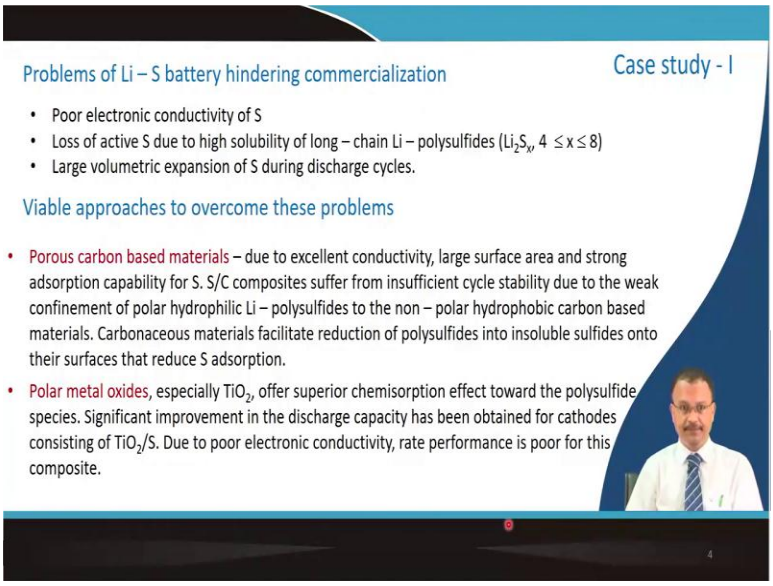

Problems of Li – S battery hindering commercialization

Case study - I

- Poor electronic conductivity of S
- Loss of active S due to high solubility of long – chain Li – polysulfides (Li_2S_x, $4 \leq x \leq 8$)
- Large volumetric expansion of S during discharge cycles.

Viable approaches to overcome these problems

- Porous carbon based materials – due to excellent conductivity, large surface area and strong adsorption capability for S. S/C composites suffer from insufficient cycle stability due to the weak confinement of polar hydrophilic Li – polysulfides to the non – polar hydrophobic carbon based materials. Carbonaceous materials facilitate reduction of polysulfides into insoluble sulfides onto their surfaces that reduce S adsorption.
- Polar metal oxides, especially TiO_2, offer superior chemisorption effect toward the polysulfide species. Significant improvement in the discharge capacity has been obtained for cathodes consisting of TiO_2/S. Due to poor electronic conductivity, rate performance is poor for this composite.

The problem is the poor conductivity of the sulfur. So, you need to add a conducting agent and loss of sulfur because of this lithium polysulfides usually this x anywhere in between 4 to 8. So, it is the starting point and then it goes to 6, it goes to 4, sometimes 5 and 3 is also reported and Li 2 S 2 and Li 2 S they are in solid state.

And third one is the volumetric expansion when sulfur incorporates lithium. So, there is a change in the volume. So, these three are the major problems and also the redox shuttle mechanism once this soluble product goes into the electrolyte. So, we will have to work on that.

So, there are viable approaches to overcome these problems and part of this approaches I have already described porous carbon based material that one can use because of their excellent conductivity, surface area is large because the particle size is pretty small and they have strong adsorption capability of sulfur to make the sulfur carbon composite.

And which actually form some kind of insufficient cycle stability and that is basically the weak confinement of the polar hydrophilic polysulfides that time and again I have talked about to the non polar hydrophobic material. So, it comes out it does not have proper adhesion particularly long chain polysulfides and comes back to the electrolyte.

So, this carbonaceous material to some extent they facilitate the reduction of the polysulfides into soluble sulfides onto their surface and that reduce this sulfur adsorption. So, you remember that we talked about carbon nanotube and porous carbon structure. So, they have this kind of tendency to adsorb the long chain polysulfides.

So, we also talked about this polar metal oxide and in this case we have used titanium oxide. So, they also offer a chemisorption towards the polysulfides to bind it. So, we took advantage of that.

So, we made this titanium oxide sulfur composite, but one problem that we have to solve is to make it conducting titanium oxide is not electronically conducting. So, if you just barely use sulfur TiO 2 you can bind polysulfides, but the rate performance will not be that good.

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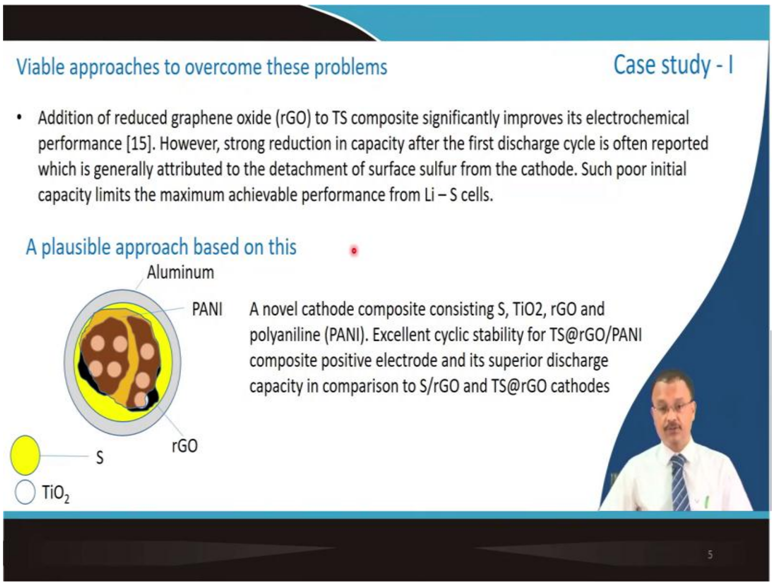

Viable approaches to overcome these problems

Case study - I

- Addition of reduced graphene oxide (rGO) to TS composite significantly improves its electrochemical performance [15]. However, strong reduction in capacity after the first discharge cycle is often reported which is generally attributed to the detachment of surface sulfur from the cathode. Such poor initial capacity limits the maximum achievable performance from Li – S cells.

A plausible approach based on this

A novel cathode composite consisting S, TiO2, rGO and polyaniline (PANI). Excellent cyclic stability for TS@rGO/PANI composite positive electrode and its superior discharge capacity in comparison to S/rGO and TS@rGO cathodes

So, reduced graphene oxide rGO to this composite titanium oxide sulfur this TS composite that actually improves the electro chemical performance because this acts as a conducting path. So, this reference we have cited in the our original paper that how exactly it works.

And the reduction capacity in the first discharge cycle that is important. And that basically tells you the detachment of the sulfur from the cathode. So, poor initial capacity if you get if it is 400, 500, 300 milli ampere hour per gram. So, you know that the performance of your lithium sulfur cell is not that good going to be because it will not increase the capacity anyway after beyond first discharge. So, that is one indicator that something is wrong.

So, the plausible approach that we found after a lot of iteration we started with titanium oxide type of oxide material incorporation into the sulfur and whether the sulfur will be as received sulfur or it will be reduced particle size or we will go for a molten sulfur that was another issue and different types of composite we made.

So, finally, this structure that was attractive aluminum current collector, then you have this sulfur and then you have this rGO binding the titanium oxide sulfur composite. And then finally, a conducting polymer. So, it is a quite complicated structure it has the sulfur which is also melt impregnated inside the as prepared titanium oxide which is in it is anatase phase.

And then we introduced rGO it is a conducting layer not only conducting layer, but it acts as a buffer to take some of the stress generated due to Li 2 S formation and then additionally we have a PANI layer polymeric layer that also we have introduced. So, this is a complicated structure that finally, we could end up with in our work as a part of the case study.

So, what we got excellent cycling stability for this titanium oxide sulfur coated with rGO and making it a composite with PANI and discharge capacity was quite good as compared to sulfur composite made with rGO or titanium oxide sulfur coated with rGO without the PANI layer. So, it worked, how it worked that we tried to understand it, but we do not have the whole story yet unfolded for this particular kind of configuration.

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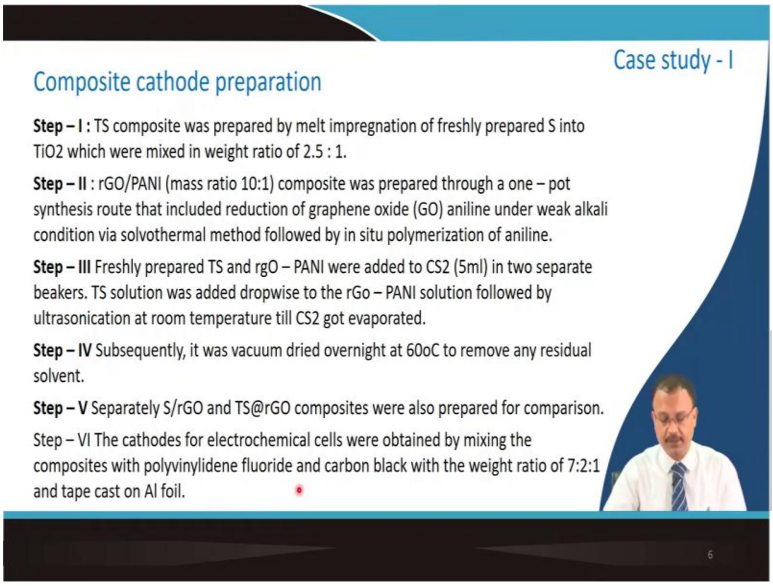

Case study - I

Composite cathode preparation

Step – I : TS composite was prepared by melt impregnation of freshly prepared S into TiO2 which were mixed in weight ratio of 2.5 : 1.

Step – II : rGO/PANI (mass ratio 10:1) composite was prepared through a one – pot synthesis route that included reduction of graphene oxide (GO) aniline under weak alkali condition via solvothermal method followed by in situ polymerization of aniline.

Step – III Freshly prepared TS and rgO – PANI were added to CS2 (5ml) in two separate beakers. TS solution was added dropwise to the rGo – PANI solution followed by ultrasonication at room temperature till CS2 got evaporated.

Step – IV Subsequently, it was vacuum dried overnight at 60oC to remove any residual solvent.

Step – V Separately S/rGO and TS@rGO composites were also prepared for comparison.

Step – VI The cathodes for electrochemical cells were obtained by mixing the composites with polyvinylidene fluoride and carbon black with the weight ratio of 7:2:1 and tape cast on Al foil.

So, if you want to make it there are several steps involved the first step is titanium oxide and sulfur composite that was prepared by melt impregnation of freshly prepared sulfur; that means, the sulfur has received we melt it and then titanium oxide also we prepared by a sol gel technique and then we mixed it initially in the ratio of 2.5 is to 1; where 2.5 is your titanium oxide sorry sulfur and 1 part is a your titanium oxide.

So, this was melt impregnated sulfur dissolve melt at a relatively lower temperature. So, that was the advantage. Then rGO PANI that mass ratio 10 is to 1 this composite was prepared through a one pot synthesis that includes what reduction of graphene oxide which we prepared by a hummers method and then aniline under weak alkali condition via a solvothermal method and then in situ polymerization from aniline to polyaniline. So, that was second step to make this rGO PANI composite.

Then freshly prepared this TS and rGO PANI that was added with carbon disulfide which is a solvent in two separate beakers, now, this composite this TS that was added to this composite rGO PANI and we ultrasonicated it at room temperature and to that extent where all the solvents gets evaporated for us to get the powder.

This powder that was vacuum dried as a part of step four in a vacuum overnight at 60 degree Celsius. So, all the residual solvent they got evaporated. So, following this we also prepared sulfur and rGO composite and this titanium sulfur coated rGO composite that was made this was made to compare with our final composite the schematic already I showed.

So, then finally, the cathodes for electrochemical cells this that was prepared by mixing the composite with the binder polyvinylidene fluoride and carbon black was the conducting agent and the weight ratio was 7 is to 2 is to 1. So, we have used sufficient amount of sulfur not confined to 20 percent or 30 percent sulfur and mostly conducting carbon, but this is the concentration and then finally, we tape cast on aluminum foil.

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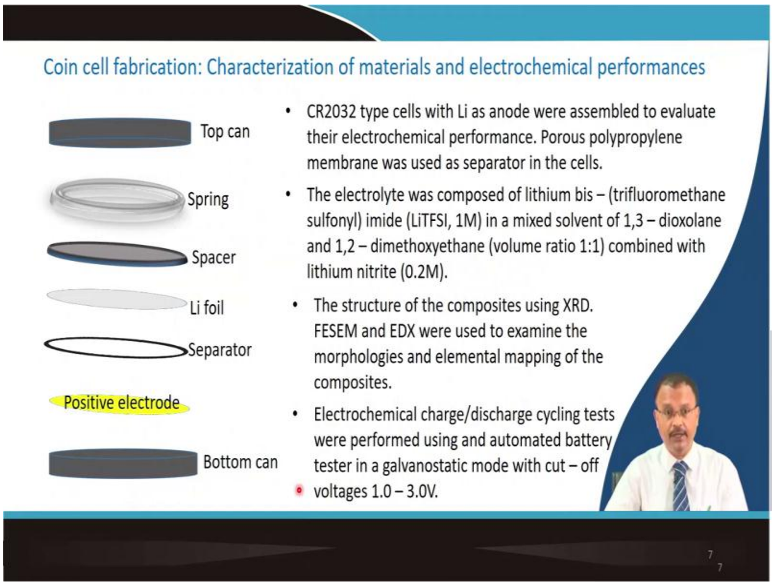

Coin cell fabrication: Characterization of materials and electrochemical performances

- CR2032 type cells with Li as anode were assembled to evaluate their electrochemical performance. Porous polypropylene membrane was used as separator in the cells.
- The electrolyte was composed of lithium bis – (trifluoromethane sulfonyl) imide (LiTFSI, 1M) in a mixed solvent of 1,3 – dioxolane and 1,2 – dimethoxyethane (volume ratio 1:1) combined with lithium nitrite (0.2M).
- The structure of the composites using XRD. FESEM and EDX were used to examine the morphologies and elemental mapping of the composites.
- Electrochemical charge/discharge cycling tests were performed using and automated battery tester in a galvanostatic mode with cut – off voltages 1.0 – 3.0V.

So, constructed a CR2032 type of coin cell this by this time you know. So, it has a spring, a spacer, then lithium foil, then separator which is soaked with electrolyte, then the positive composite electrode and then everything is crimped inside a globe box in organ ambient to form a coin cell.

So, anode was pure lithium and separators separator was porous polypropylene membrane normal cell guard membrane. Electrolyte we use LiTFSI this lithium bis trifluoromethane sulfonyl imide. So, this salt 1 molar and the mixed solvent was we have used dioxolane and 1, 2 dimethoxyethane volume is 1 is to 1 and this additive you know that to protect the lithium metal we already explained it in the last lecture that 0.2 M we added into it.

So, the structure of the as prepared composite electrode that was examined by X ray diffraction for its phase purity and FESEM also we did the composite electrode to know the particle size and if we can identify separately where is titanium oxide or where is silica as where is sulfur etcetera.

So, that was there and along with that we did energy dispersive photometry to know the elemental mapping throughout the electrode material. Then we did electrochemical charge discharge cycling test in a automated battery tester in our laboratory, cut off voltage is 1 to 3 volt because that is the range that is required for lithium sulfur battery.

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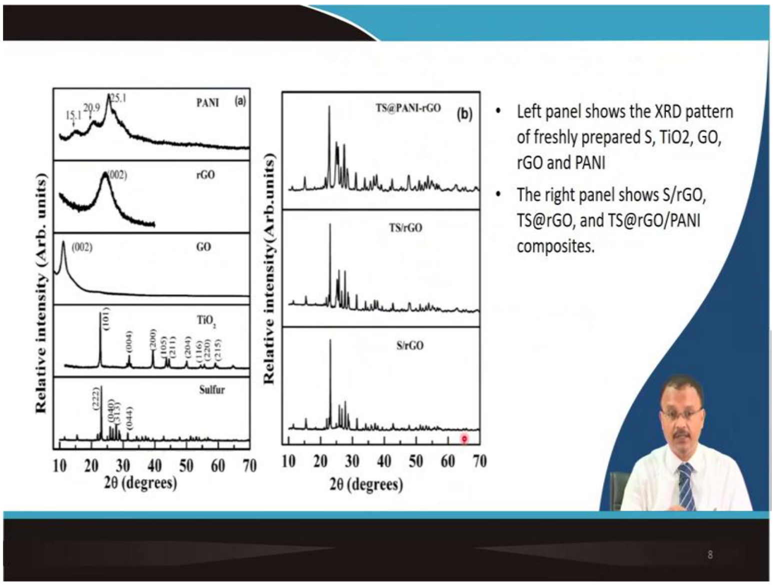

- Left panel shows the XRD pattern of freshly prepared S, TiO2, GO, rGO and PANI
- The right panel shows S/rGO, TS@rGO, and TS@rGO/PANI composites.

So, here you can see that sulfur after melt impregnation no impurity is there. Titanium oxide prepared by a normal sol gel root so, that is anatase type titanium oxide and the GO is characteristic X ray diffraction peak and then reduced GO to form rGO and finally, the semi crystalline polymer PANI.

So, they are all phase pure and then the separate composite which we have used one is sulfur with rGo, another one is titanium oxide sulfur composite coated with rGO and finally, titanium oxide sulfur composite coated with PANI and rGO. So, X ray diffraction tells us that these are phase pure material and we went ahead with the cell preparation with this.

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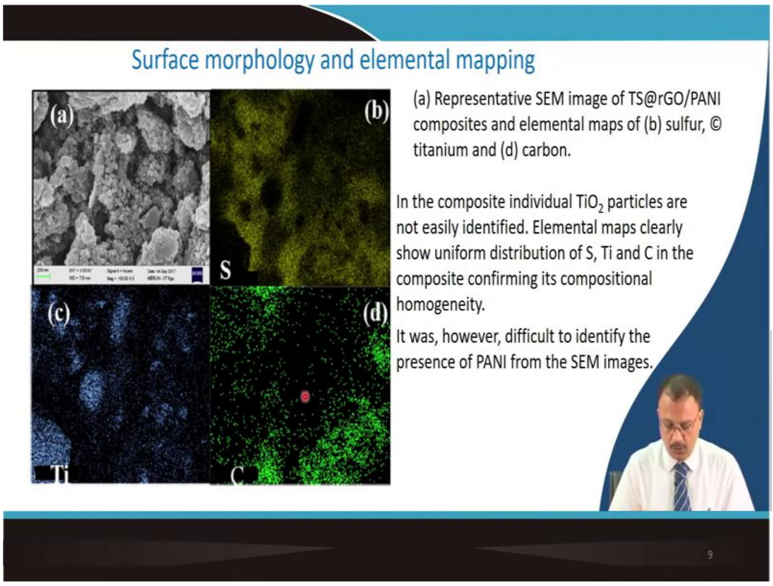

Surface morphology and elemental mapping

(a) Representative SEM image of TS@rGO/PANI composites and elemental maps of (b) sulfur, © titanium and (d) carbon.

In the composite individual TiO_2 particles are not easily identified. Elemental maps clearly show uniform distribution of S, Ti and C in the composite confirming its compositional homogeneity.

It was, however, difficult to identify the presence of PANI from the SEM images.

If you see the surface morphology there it is difficult to identify where is sulfur, but if you do the composition mapping I mean elemental mapping then the b this one is for sulfur. So, sulfur is present almost everywhere and the c one c is for titania. So, titania is also titanium is also there and carbon is everywhere.

So, actually the individual titanium oxide particle they are not easily identifiable in the normal FESEM Field Emission Scanning Electron Micrograph, but the distribution of sulfur, titanium, carbon that tells us that they are homogeneously dispersed. So, there are compositional uniformity of the composite sulfur electrode that we have used.

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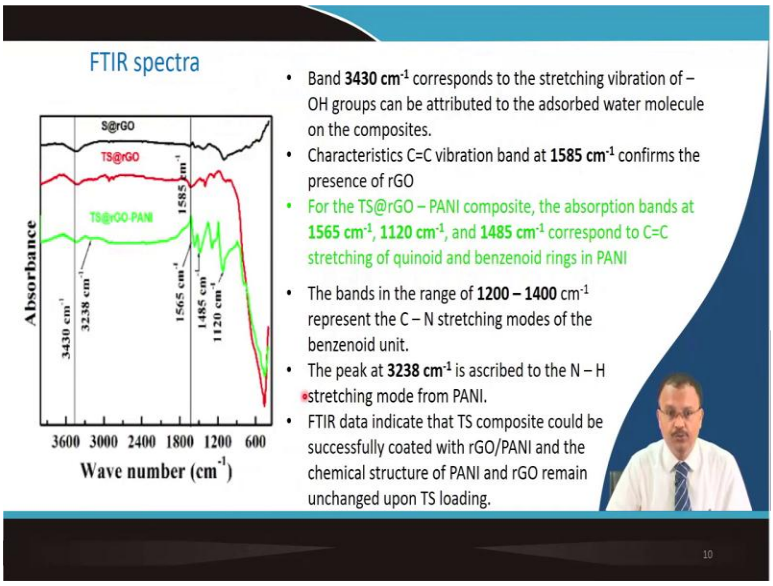

FTIR spectra

- Band **3430 cm^{-1}** corresponds to the stretching vibration of –OH groups can be attributed to the adsorbed water molecule on the composites.
- Characteristics C=C vibration band at **1585 cm^{-1}** confirms the presence of rGO
- For the TS@rGO – PANI composite, the absorption bands at **1565 cm^{-1}**, **1120 cm^{-1}**, and **1485 cm^{-1}** correspond to C=C stretching of quinoid and benzenoid rings in PANI
- The bands in the range of **1200 – 1400** cm^{-1} represent the C – N stretching modes of the benzenoid unit.
- The peak at **3238 cm^{-1}** is ascribed to the N – H stretching mode from PANI.
- FTIR data indicate that TS composite could be successfully coated with rGO/PANI and the chemical structure of PANI and rGO remain unchanged upon TS loading.

So, if you do the FTIR of the composite electrode, then you get the indication of the formation of a good composite. For example, this range 3430 this is due to the stretching vibration of OH group. So, this is the adsorbed water molecule in the composite. So, that is during the measurement you cannot avoid the water absorption, but before putting the electrode for coin cell fabrication we did the vacuum drying. So, that water tress water even is not there.

Then you can see this characteristics C C double bond 1585 the small one that confirms the presence of rGO, rGO in the composite. And this is our interesting composite titanium oxide sulfur coated with rGO PANI. So, this bands at 1565, then 1120, then 1485 they actually correspond to carbon carbon double bond stretching of this so, called quinoid and benzenoid rings of the PANI.

So, the composite is formed in the actual material which I have used for lithium sulfur battery. And the band that is in the range of 1200 to 1400 wave number that basically represent the carbon nitrogen this is stretching mode and that is basically due to this benzenoid rings.

And the peak that you can see at 3238; 3238 wave number this is ascribed to the nitrogen hydrogen stretching mode of PANI. So, this is just to identify that our material is homogeneous and phase pure and successfully the titanium oxide sulfur composite coated with rGO and PANI and actually the structure of the PANI and this rGO that there is no major change upon the loading of this titanium oxide and sulfur. So, that the FTIR analysis tells us.

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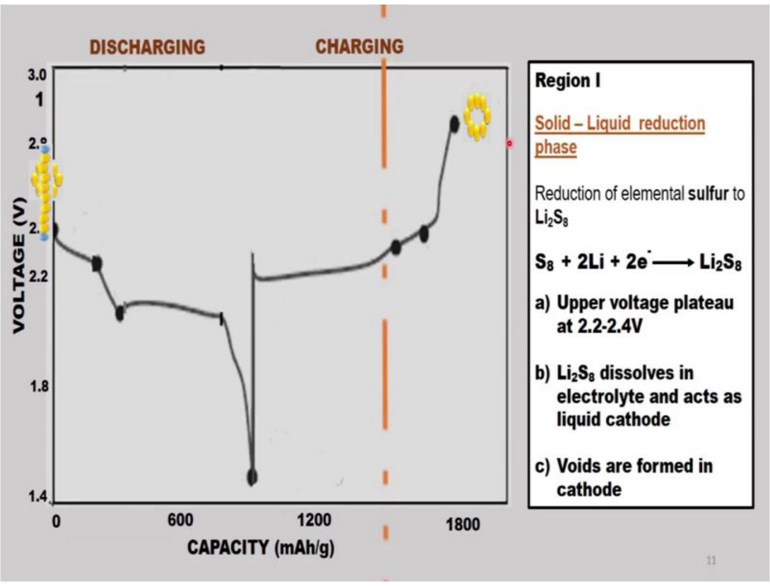

Region I

Solid – Liquid reduction phase

Reduction of elemental sulfur to Li_2S_8

$S_8 + 2Li + 2e^- \longrightarrow Li_2S_8$

a) Upper voltage plateau at 2.2-2.4V

b) Li_2S_8 dissolves in electrolyte and acts as liquid cathode

c) Voids are formed in cathode

Now, this thing is important this already I have described. This is the discharge profile we start with the ring sulfur and then finally, you get the solid phase here around 1.5 volt around and then during charging it again goes back to the ring sulfur. So, this step already we talked about. So, we are talking about region number 1.

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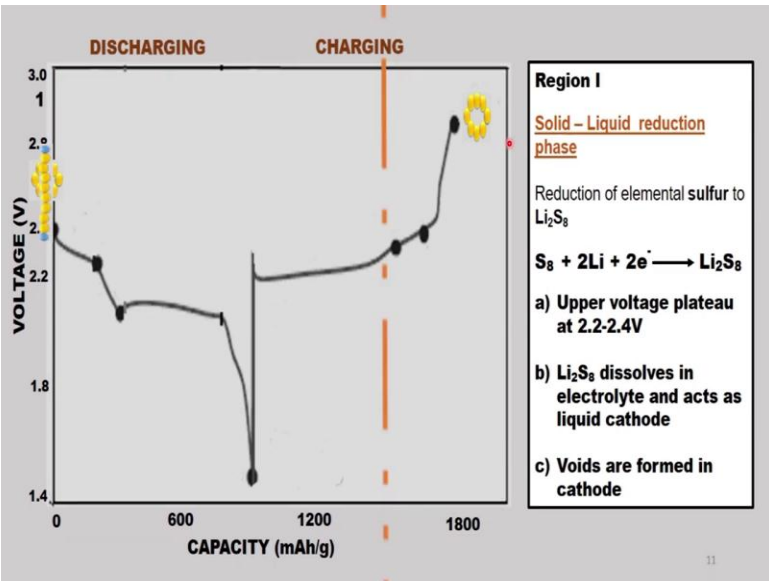

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c) Voids are formed in cathode

Where S 8 is basically reacting with lithium. So, we start from here. So, discharge we are starting from here. So, it forms Li 2 S 8 kind of structure.

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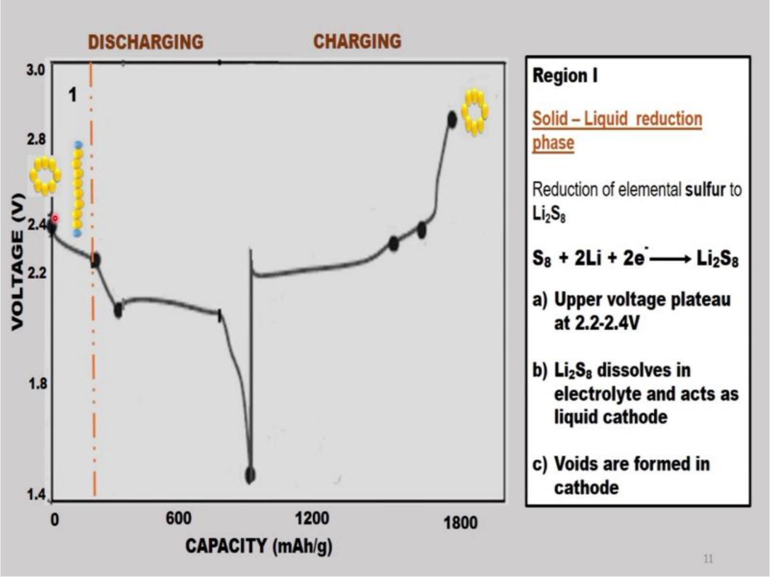

Region I

Solid – Liquid reduction phase

Reduction of elemental **sulfur** to Li_2S_8

$S_8 + 2Li + 2e^- \longrightarrow Li_2S_8$

- a) **Upper voltage plateau at 2.2-2.4V**
- b) **Li_2S_8 dissolves in electrolyte and acts as liquid cathode**
- c) **Voids are formed in cathode**

And then progressively it goes. So, this is basically region 1.

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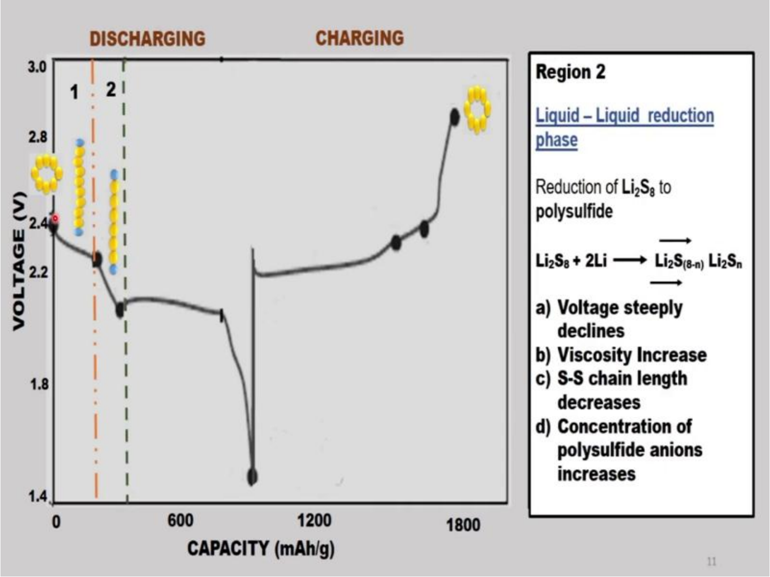

Region 2

Liquid – Liquid reduction phase

Reduction of Li_2S_8 to polysulfide

$Li_2S_8 + 2Li \longrightarrow \overset{\longrightarrow}{\underset{\longrightarrow}{Li_2S_{(8-n)}}}\ Li_2S_n$

- a) **Voltage steeply declines**
- b) **Viscosity Increase**
- c) **S-S chain length decreases**
- d) **Concentration of polysulfide anions increases**

Then you have region 2 where it forms Li 2 S and something 8 minus n Li 2 S n. So, that forms so, again it is a long chain molecule.

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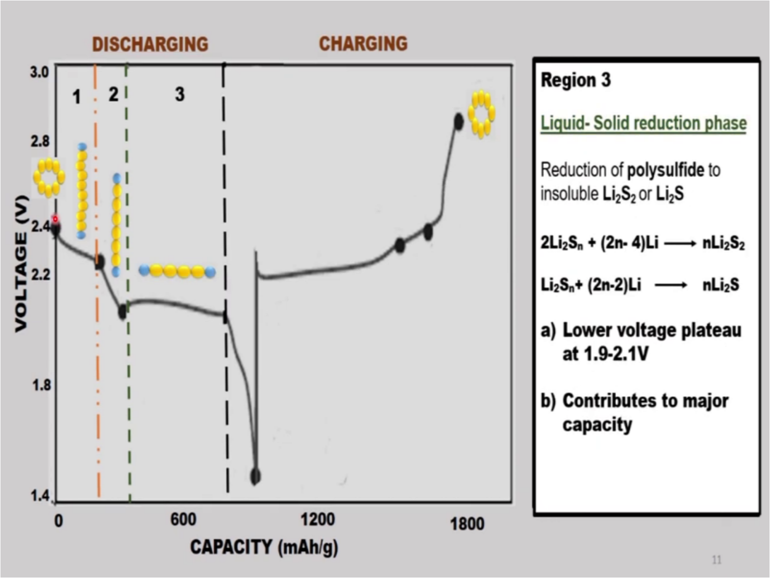

Region 3

Liquid- Solid reduction phase

Reduction of **polysulfide** to insoluble **Li_2S_2** or **Li_2S**

$2Li_2S_n + (2n- 4)Li \longrightarrow nLi_2S_2$

$Li_2S_n + (2n-2)Li \longrightarrow nLi_2S$

a) **Lower voltage plateau at 1.9-2.1V**

b) **Contributes to major capacity**

Then it forms relatively short chain.

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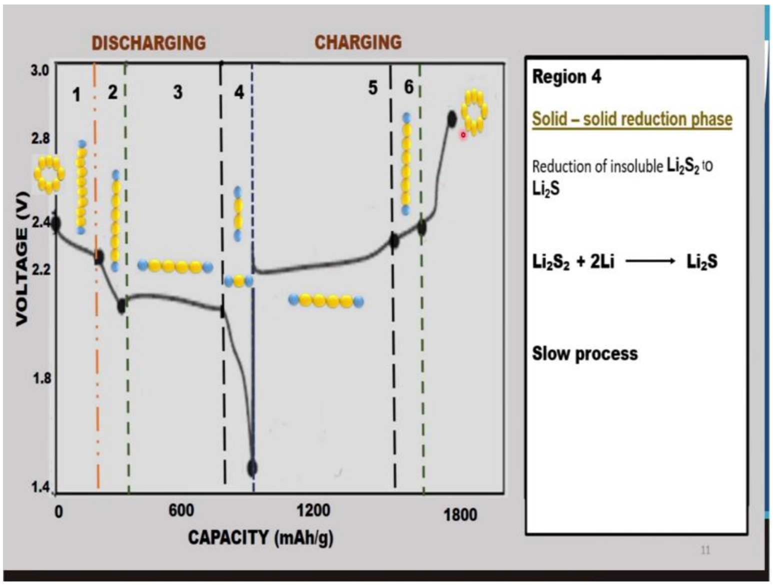

Region 4

Solid – solid reduction phase

Reduction of insoluble **Li_2S_2** to **Li_2S**

$Li_2S_2 + 2Li \longrightarrow Li_2S$

Slow process

And then finally, in this region; region 4 it is solid. So, this 1, 2, 3 they all dissolve into the electrolyte and this 4 is the solid state that is there. And then 5 again this is solid solid reaction phase it goes back finally, to the ring structure at the end.

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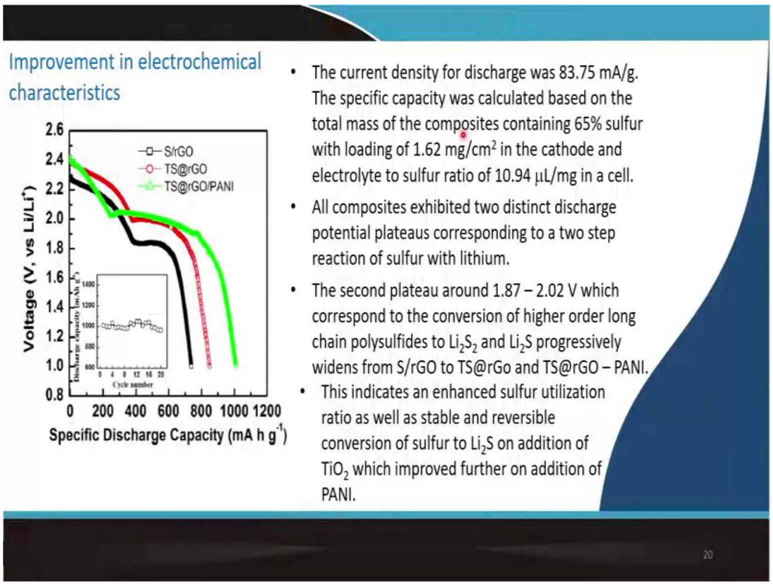

Improvement in electrochemical characteristics

- The current density for discharge was 83.75 mA/g. The specific capacity was calculated based on the total mass of the composites containing 65% sulfur with loading of 1.62 mg/cm² in the cathode and electrolyte to sulfur ratio of 10.94 µL/mg in a cell.
- All composites exhibited two distinct discharge potential plateaus corresponding to a two step reaction of sulfur with lithium.
- The second plateau around 1.87 – 2.02 V which correspond to the conversion of higher order long chain polysulfides to Li_2S_2 and Li_2S progressively widens from S/rGO to TS@rGo and TS@rGO – PANI.
- This indicates an enhanced sulfur utilization ratio as well as stable and reversible conversion of sulfur to Li_2S on addition of TiO_2 which improved further on addition of PANI.

So, I am sorry for the animation part. I mean basically what I try to convey I am pretty sure that you could understand it, but sudden problem I faced due to this animation, but the idea I think this is conveyed and finally, I would like to say that this is a very slow process. So, this where the solid state it forms Li 2 S 2 and Li 2 S both these two this is a quite slow process and relatively faster process when it get into the cathode light.

So, now you look at the electrochemical performance. Now, this kind of three types of composite we have talked about. So, typically the current density was some value 83.75 milli ampere per gram. So, considering this is 1000 milli ampere hour per gram this kind of capacity you are getting.

So, this is not a very high rate discharge. So, that specific capacity we calculated based on the total mass of the composite. So, about 65 percent of sulfur was there loading was 1.62 milligram per centimeter square in the cathode and electrolyte to sulfur ratio was 10.95 micro liter per milligram in a cell because you will have to put sufficient amount of electrolyte also for the diffusion to take place.

So, that was the experimental condition. So, you can see there are two distinct discharge potential plateau. So, one is somewhere here and another one is here that is for the final composite and this sloping profile is a bit more as compared to your rGO or TS rGO kind of composite.

So, it is a typical two step process and the second step that is important that actually gives the solid one that that formation. So, this which is around 1.87 to 2 volt this is the conversion of higher order long chain polysulfides to Li 2 S 2 and Li 2 S progressively. So, that is widen because you see that here it is quite short it is slightly larger here and it is more here.

So; that means, suddenly it is working and progressively you see that this capacity increases from about 800 to 900 to more than 1000. So, we could get good capacity and the voltage is around 2 volt. So, that is not a bad performance of our lithium sulfur cell of course, I will I would like to say that this is a bit complicated structure.

So, this actually indicates the sulfur utilization more and it is a reversible conversion. So, reversible conversion is good that is given by this cycleability. So, here I have shown up to 20 cycles, but actually the cell data ran for 400 cycles with very marginal about 10 percent of capacity loss from the initial stage. So, 1000 it started and it dropped down around that level.

So, cycleability is also quite good only thing that we are yet to do is the rate performance because the rate is still quite low, but faster rate we will have to see that how it performs. But, as a initial demonstration that based on the our developed concept on the long chain polysulfide formation its dissolution and its confinement into the positive electrode.

And stabilization of the lithium anode by putting this lithium nitrate base additives this thing works. So, that is I considered a good I mean once you know about what to do and then design your material and if it performs well then you feel good that your achievable knowledge is working.

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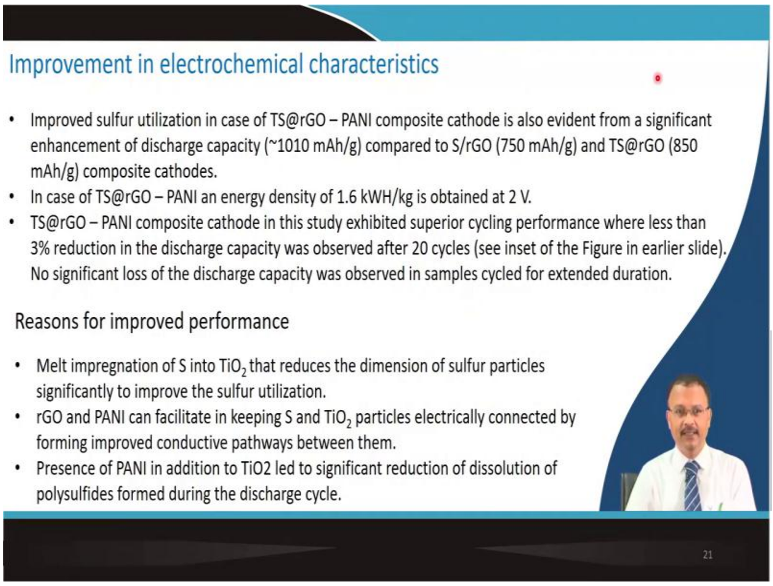

Improvement in electrochemical characteristics

- Improved sulfur utilization in case of TS@rGO – PANI composite cathode is also evident from a significant enhancement of discharge capacity (~1010 mAh/g) compared to S/rGO (750 mAh/g) and TS@rGO (850 mAh/g) composite cathodes.
- In case of TS@rGO – PANI an energy density of 1.6 kWH/kg is obtained at 2 V.
- TS@rGO – PANI composite cathode in this study exhibited superior cycling performance where less than 3% reduction in the discharge capacity was observed after 20 cycles (see inset of the Figure in earlier slide). No significant loss of the discharge capacity was observed in samples cycled for extended duration.

Reasons for improved performance

- Melt impregnation of S into TiO_2 that reduces the dimension of sulfur particles significantly to improve the sulfur utilization.
- rGO and PANI can facilitate in keeping S and TiO_2 particles electrically connected by forming improved conductive pathways between them.
- Presence of PANI in addition to TiO2 led to significant reduction of dissolution of polysulfides formed during the discharge cycle.

So, that is the case study want and in fact, people got interested some industry approached us that they have lot of sulfur in the next lecture we will talk about it. So, whether you can just make the process less complicated and use our waste product sulfur to make lithium sulfur battery. This is TATA Steel they approached us and my another M. Tech student I just engaged him to work on it. So, next lecture we talk about it.

But, this part we could show that improved sulfur utilization to make this kind of structure and significant enhancement of the discharge capacity 1000 up we have gotten and in case of the composite for sulfur rGO and this titanium oxide sulfur rGO without PANI this was slightly lower.

And the energy density if you calculate it is quite good 1.6 kilowatt hour per kg of sulfur not of sulfur, but we considered the other additives as well at 2 volt range. And superior cycling performance that I showed 20 cycles data, but we extended it to 300 to 400 cycles no major change in the cycleability is obtained.

Now, based on the knowledge that we have gained the reason for the improvement is you see the melt impregnation of sulfur into the titanium oxide that basically reduces the sulfur dimension and you know that recrystallization that reduces the particle size. So, though your sulfur is having lot of different particle size just melt it and recrystallize it. So, particle size will be uniform. So, that was the strategy and it worked.

Then rGO and PANI they facilitated sulfur and titanium particle electrically connected because PANI is also conducting and your rGO is also conducting. So, it formed improved conductive pathway between them although we have not yet studied the rate performance, but it is a good way to use both of them.

And this PANI and titanium oxide significant reduction of this polysulfides takes place. You know that had it been a actually a redox shuttle mechanism which is operative then 2.4 volt charging is a constant plateau is observed although I have not shown it here, but we could not observe that one. So; that means, somehow the dissolution is also arrested.

Although it is a very preliminary state it is working based on the concept we have developed we have designed this kind of composite electrode material, but it needs to be further investigated that how exactly what is happening so, that the dissolution during the discharge cycle the polysulfide whatever is forming that is getting arrested. Because progressively you can see that the plateau at that lower voltage this is enhancing and as it enhances then the electrochemical performance also is better.

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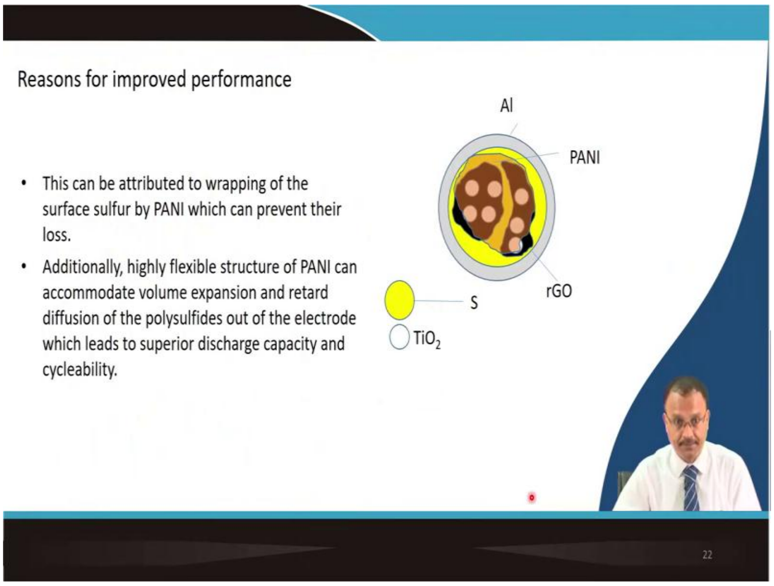

Reasons for improved performance

- This can be attributed to wrapping of the surface sulfur by PANI which can prevent their loss.
- Additionally, highly flexible structure of PANI can accommodate volume expansion and retard diffusion of the polysulfides out of the electrode which leads to superior discharge capacity and cycleability.

So, one possible way could be the wrapping of the surface of sulfur by PANI although this is just a speculation we do not have a quality transmission electron microscope data where exactly you can show that whatever we are predicting yes that is happening is still a prediction that it is happening like that.

And another way is this flexible structure of the PANI. So, this polymer is having a flexible structure and this volume expansion which I am talking about when sulfur reacts with lithium to form Li 2 S the volume expansion takes place. So, this volume expansion and retard the diffusion of polysulfides out of the electrode which leads to the superior discharge capacity as well as cycleability. So, that is the model that we have in mind that it is happening like that.

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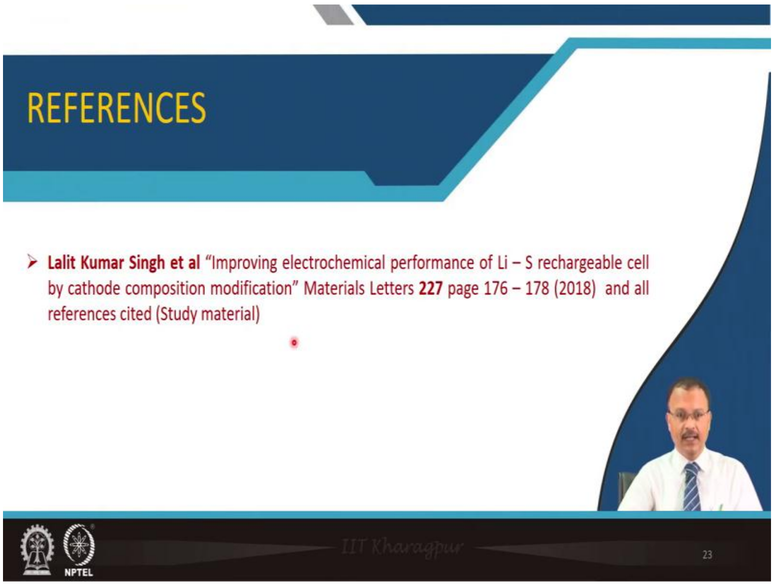

REFERENCES

- **Lalit Kumar Singh et al** "Improving electrochemical performance of Li – S rechargeable cell by cathode composition modification" Materials Letters **227** page 176 – 178 (2018) and all references cited (Study material)

So, this paper was published by an M. Tech student of myself and one of my colleagues they were involved. And lot of good literature you will find because we studied the literature, well understood the problem then designed our material and it worked. It is not a full fledged study lot of things we will have to do, but it got enough attention, industries involved I mean industry got excited about this. And then in the next lecture we will have a simplified version of this work and see that how it performs. So, that will be my final lecture in this module.

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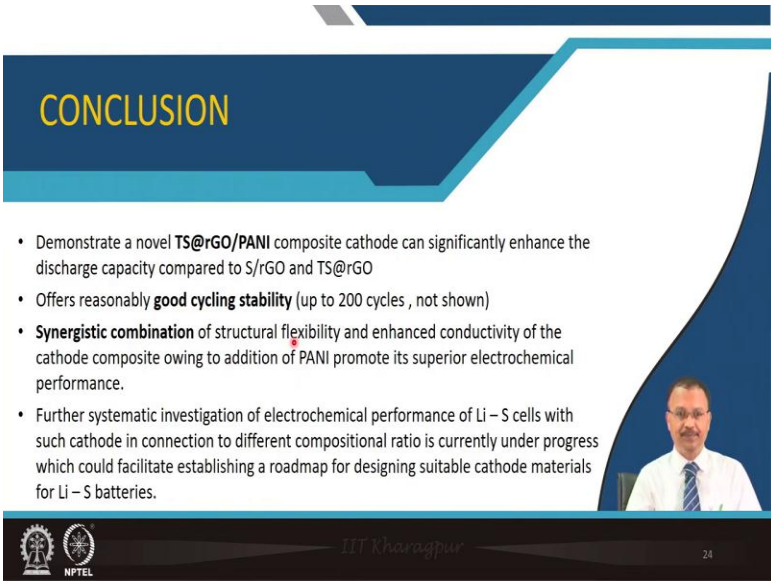

CONCLUSION

- Demonstrate a novel **TS@rGO/PANI** composite cathode can significantly enhance the discharge capacity compared to S/rGO and TS@rGO
- Offers reasonably **good cycling stability** (up to 200 cycles , not shown)
- **Synergistic combination** of structural flexibility and enhanced conductivity of the cathode composite owing to addition of PANI promote its superior electrochemical performance.
- Further systematic investigation of electrochemical performance of Li – S cells with such cathode in connection to different compositional ratio is currently under progress which could facilitate establishing a roadmap for designing suitable cathode materials for Li – S batteries.

So, in this particular lecture we demonstrate that a novel composite one can make that significantly enhance the discharge capacity as compared to the simple sulfur rGO or titanium sulfur coated rGO it is quite good. Reasonably good cycling stability that we have achieved. It is due to a synergistic combination of the structural flexibility that enhance the conductivity of the cathode into the addition of the PANI that promotes its superior electrochemical performance this is our speculation and probably it is true.

And further investigation with such cathode in connection to different compositional ratio that we will keep doing. Instead of PANI some other polymer is also being tried, instead of titanium oxide we will use other oxide as well to make it a success because in my opinion this technology needs to be taken seriously.

Thank you for your attention.