Electrochemical Energy Storage
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Module - 10
Li - Sulfur batteries
Lecture - 48
Electrolyte and Negative Electrodes for Li - S Battery

Welcome to my course Electrochemical Energy Storage and this is module number 10 where I am describing Lithium Sulfur batteries. This is lecture number 48 where I will be talking about Electrolyte and Negative Electrodes for Lithium Sulfur Batteries in the last lecture, lecture number 47 we talked about the positive electrode.

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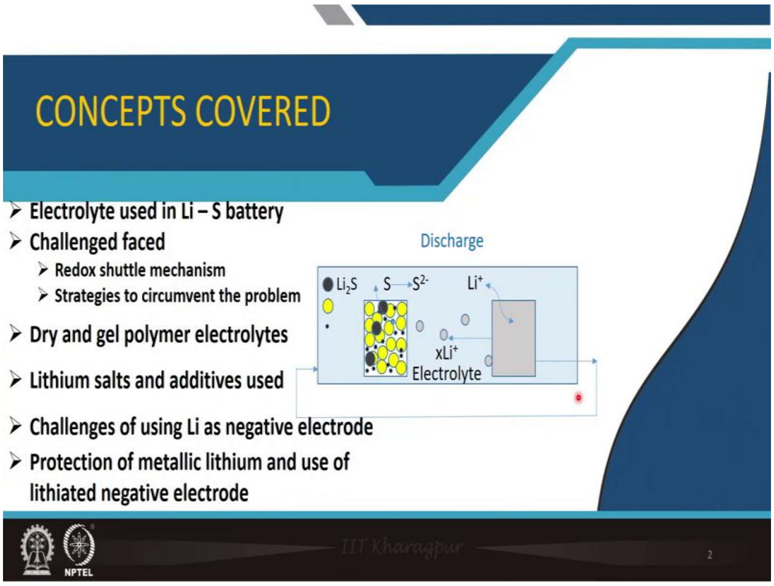

CONCEPTS COVERED

- Electrolyte used in Li – S battery
- Challenged faced
  - Redox shuttle mechanism
  - Strategies to circumvent the problem
- Dry and gel polymer electrolytes
- Lithium salts and additives used
- Challenges of using Li as negative electrode
- Protection of metallic lithium and use of lithiated negative electrode

And this lecture we will talk about the electrolyte used in lithium sulfur batteries. Again we will talk about the challenge faced introducing a concept of redox shuttle mechanism which is operative related to the electrolyte that is used and the strategies that is adopted to circumvent this problem. Apart from this liquid state electrolyte dry or gel polymer electrolyte is also used for lithium sulfur batteries.

So, we will shed light on that the lithium salts that are used and also certain additives that is used in the electrolyte what are their functions we will be talking about it. And what are the challenges of lithium metal as negative electrode and what kind of protection that is given for this negative electrode which is lithium and lithiated negative electrode is also used under certain by certain groups, so we will talk about it.

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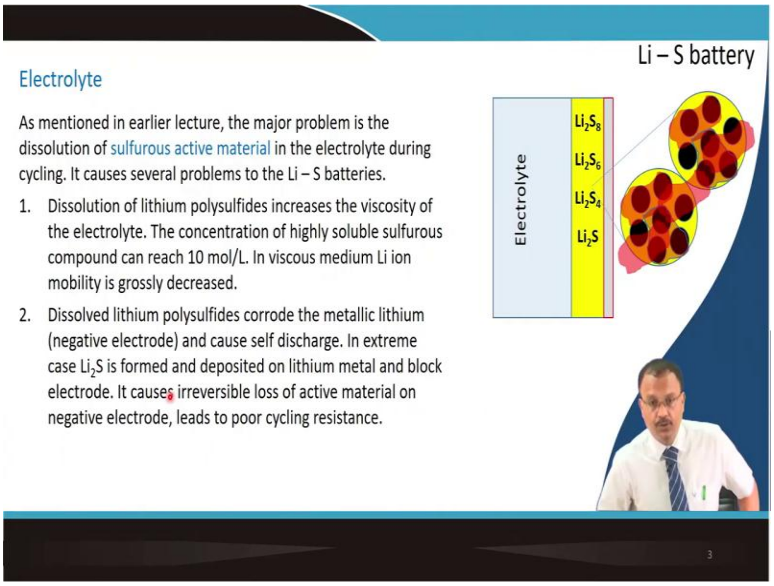

Li – S battery

Electrolyte

As mentioned in earlier lecture, the major problem is the dissolution of sulfurous active material in the electrolyte during cycling. It causes several problems to the Li – S batteries.

1. Dissolution of lithium polysulfides increases the viscosity of the electrolyte. The concentration of highly soluble sulfurous compound can reach 10 mol/L. In viscous medium Li ion mobility is grossly decreased.
2. Dissolved lithium polysulfides corrode the metallic lithium (negative electrode) and cause self discharge. In extreme case Li_2S is formed and deposited on lithium metal and block electrode. It causes irreversible loss of active material on negative electrode, leads to poor cycling resistance.

So, the problem of electrolyte that is already mentioned in my last lecture and the major problem is the dissolution of this sulfurous active material which forms during discharge. So, during cycling more and more active material goes into the cathode lyte catholyte and this creates problem of lithium sulfur battery. So, if you enlarge the part of this positive electrode you can see that the yellow part is your sulfur and then that is coated with the carbon black which is conducting agent.

Because sulfur itself its having very poor electronic conductivity then you have binder PVDF or something like that which can hold not only this sulfur and carbon particles, but also it is it helps the whole composite mass to get adhered on the current collector which is aluminum.

So, what will happen that if this lithium polysulfides they are progressively dissolve into the electrolyte then the first thing that happens that will increase the viscosity of this electrolyte.

So, concentration of this polysulfides that will increase cycle by cycle and it can be as high as 10 moles per liter this kind of viscous medium if it is there at all then the lithium conduction will get hampered will get impeded. So, that is the major problem for using such electrolyte. Also this polysulfides they will also travel to the other part where lithium metal is there it is not shown in this schematic.

So, it will cause the so called self discharge at open circuit voltage that also I have mentioned in my earlier lectures. In the extreme case what will happen this lithium Li 2 S that will start to form on the lithium metal and that is electronically insulating material that will block the electrode.

So, eventually it will cause irreversible type of capacity loss coulombic efficiency will be poor and cycleability will get hampered. So, that is going to happen if proper precaution is not taken in designing this electrolyte material.

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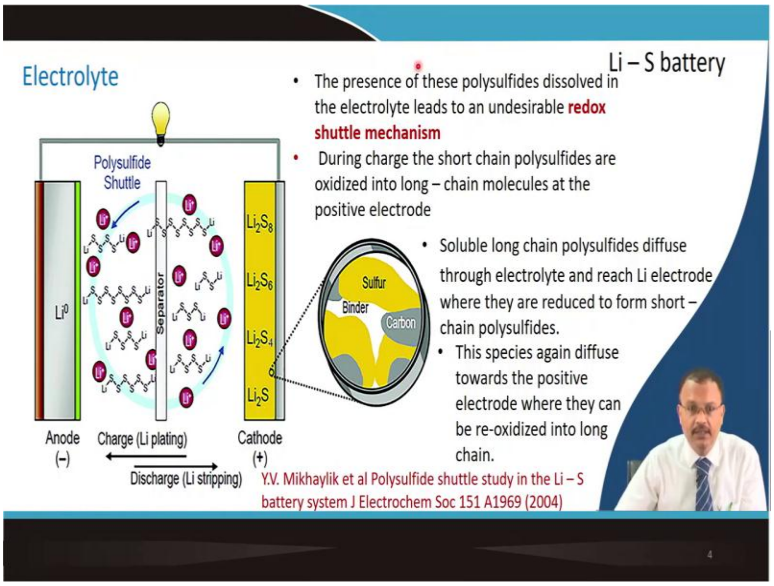

Electrolyte

Li – S battery

- The presence of these polysulfides dissolved in the electrolyte leads to an undesirable **redox shuttle mechanism**
- During charge the short chain polysulfides are oxidized into long – chain molecules at the positive electrode
- Soluble long chain polysulfides diffuse through electrolyte and reach Li electrode where they are reduced to form short – chain polysulfides.
  - This species again diffuse towards the positive electrode where they can be re-oxidized into long chain.

Y.V. Mikhaylik et al Polysulfide shuttle study in the Li – S battery system J Electrochem Soc 151 A1969 (2004)

So, the polysulfide material they undergoes an interesting phenomena which is called this redox shuttle mechanism. So, this is the schematic of the lithium sulfur battery you know that the composite cathode is here and it is deposited on aluminum as current collector.

So, if you take a look at this composite cathode it constitutes a binder then sulfur particle and carbon black or other carbon conducting carbon to impart sufficient electronic conductivity for the sulfur because it is getting reduced anyway during discharge.

Then you have a separator here which is same like Celgard 24 is used, then lithium metallic lithium is there the formation of an S e i during the forming cycle it is unavoidable. And you may or may not have this copper, but lithium also you can take the electron out of it, so that is the common schematic. So, what happens that the polysulfides which goes to the electrolyte as a dissolved mass that actually there that is responsible for this so, called redox shuttle mechanism.

So, during charge the short chain polysulfides. So, short chain polysulfides are somewhere here they are oxidized into the long chain molecules at the positive electrode. So, the positive electrode the short chain gets converted to the long chain polysulfides and the soluble long chain polysulfides they start to diffuse through the electrolyte through the separator and eventually reach to the lithium electrode.

So, where they are reduced? So, reduced to form a short chain polysulfides. So, again during charge the species again diffuses back towards positive electrode where they can again re oxidize into long chain. So, this phenomena occurs. So, this is a separate redox that is taking place during this process. So, this whole phenomena is called the redox shuttle mechanism and it is almost inevitable for lithium sulfur batteries.

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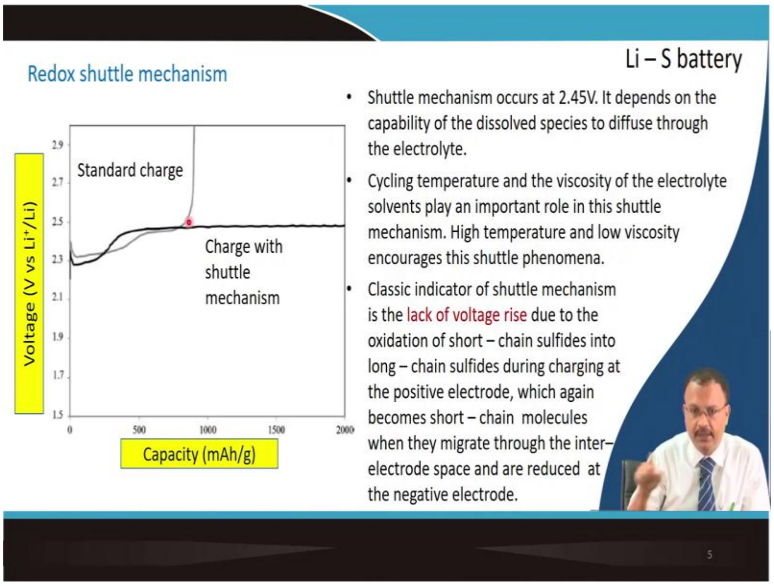

Li – S battery

Redox shuttle mechanism

- Shuttle mechanism occurs at 2.45V. It depends on the capability of the dissolved species to diffuse through the electrolyte.
- Cycling temperature and the viscosity of the electrolyte solvents play an important role in this shuttle mechanism. High temperature and low viscosity encourages this shuttle phenomena.
- Classic indicator of shuttle mechanism is the lack of voltage rise due to the oxidation of short – chain sulfides into long – chain sulfides during charging at the positive electrode, which again becomes short – chain molecules when they migrate through the inter–electrode space and are reduced at the negative electrode.

So, this shuttle mechanism if it is operated, it can be easily identifiable from the charge profile as you can see that if this is operative the long chain to short chain and back to long chain and this redox with cycling takes place then it gives you a plateau around specific 2.45 volt. So, of course, it depends on the capability of the dissolved species to diffuse through the electrolyte. So, that actually controls this, but you can readily identify it, so this is one of the indications.

Now, other two factors which are important for this, one is temperature and the viscosity of the electrolyte. So, these two factors they play an important role for this redox shuttle mechanism usually temperature if it is high and viscosity is low. So, this is a bit contradicting, but rise in temperature or if the viscosity is low due to the dissolution of this kind of polysulfides dissolvable polysulfides from the positive electrode back into the electrolyte takes place then the shuttle phenomena you cannot avoid.

So, the classic example as I said that you will get a plateau around two point four five volt. So, normal sulfur battery there is a rise in voltage sudden rise in voltage, but that will not occur if this is operative. So, this is due to the fact of oxidation of short chain sulfides into the long chain sulfides during charging at the positive electrode and again they are going back through the separator and became become short chain molecules um and reduce at the negative electrode.

So, it is an indicative of this redox shuttle mechanism which is occur concurrently with the actual charge and discharge electrochemically active reaction for lithium sulfur batteries.

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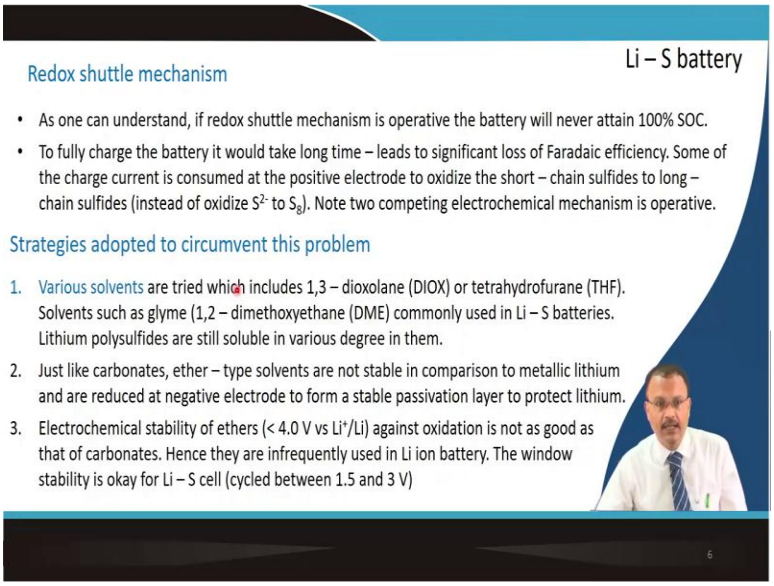

Li – S battery

Redox shuttle mechanism

- As one can understand, if redox shuttle mechanism is operative the battery will never attain 100% SOC.
- To fully charge the battery it would take long time – leads to significant loss of Faradaic efficiency. Some of the charge current is consumed at the positive electrode to oxidize the short – chain sulfides to long – chain sulfides (instead of oxidize S^{2-} to S_8). Note two competing electrochemical mechanism is operative.

Strategies adopted to circumvent this problem

1. Various solvents are tried which includes 1,3 – dioxolane (DIOX) or tetrahydrofurane (THF). Solvents such as glyme (1,2 – dimethoxyethane (DME) commonly used in Li – S batteries. Lithium polysulfides are still soluble in various degree in them.
2. Just like carbonates, ether – type solvents are not stable in comparison to metallic lithium and are reduced at negative electrode to form a stable passivation layer to protect lithium.
3. Electrochemical stability of ethers (< 4.0 V vs Li^+/Li) against oxidation is not as good as that of carbonates. Hence they are infrequently used in Li ion battery. The window stability is okay for Li – S cell (cycled between 1.5 and 3 V)

So, this is operative when the battery will never be 100 percent of SOC, so that is the problem, so redox circle mechanism is not actually desirable. And you can actually allow long time, so to get the full SOC, but Faradaic efficiency that you will have to compromise with.

So, because some of the charge current that is consumed the positive electrode to oxidize the short chain sulfide to long chain sulfide. So, this in opposed to the actual mechanism from S 2 minus to back to sulfur during charging. So, concurrently it is occurring the short chain is transferred into long chain.

So, addition current you will have to put. So, this two competitive electrochemical mechanism is operative because of this redox shuttle. So, that is one of the problems one of the major problems where this electrolyte is involved.

So, what are the solution to circumvent this problem because we do not want that separate mechanism redox mechanism is operative during the charge discharge of the lithium sulfur battery. So, one way to tackle is that to use various solvent. So, for example, DIOX this 1, 3 dioxolane or the so called THF which is tetrahydrofurane this kind of solvent or the glyme that is 1, 2 dimethoxyethane they are commonly used for lithium sulfur battery.

But unfortunately lithium in if you use this kind of solvent this polysulfides they are still soluble only thing the degree of the solubility in various types of solvent they are a bit different. So, that is one way to tackle it to reduce the solubility of the long chain polysulfides carbonate solvents they are not used for lithium sulfur battery. Ether type of solvents they are also not stable in comparison to metallic lithium and they are reduced at the metallic lithium and it forms a stable layer to protect the lithium.

So, that is one part that is good, but ether one can use carbonate material they have the stability window is not that good as the carbonate the ether one can use, but it should be less than 4 volt. So, in lithium ion battery you know that it operates at 4 volts.

So, they are the carbonate the mixture of the carbonate solvent cyclic and linear type of carbonate ECDNC that we have used. But here in lithium sulfur battery stability is ok because your voltage window is lowered 1.5 to 3 volt. So, ether can be used for this. In fact, infrequently this ether is used for your lithium sulfur battery.

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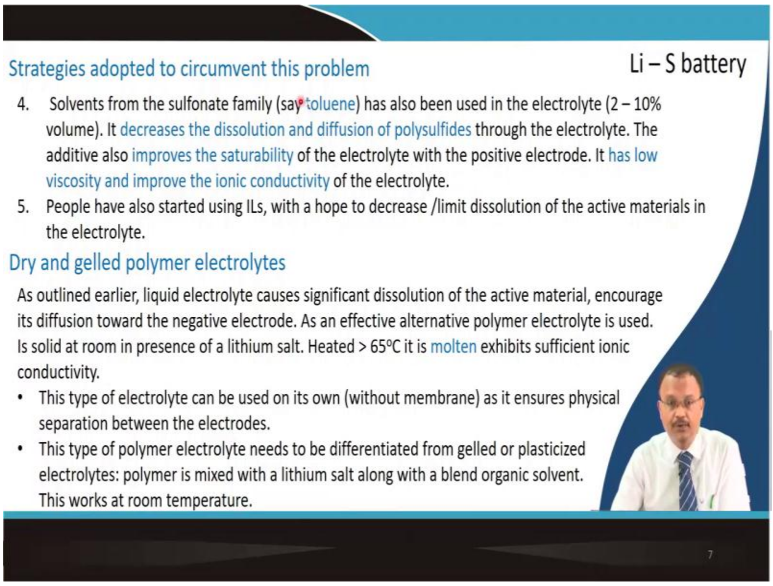

Strategies adopted to circumvent this problem

Li – S battery

4. Solvents from the sulfonate family (say toluene) has also been used in the electrolyte (2 – 10% volume). It decreases the dissolution and diffusion of polysulfides through the electrolyte. The additive also improves the saturability of the electrolyte with the positive electrode. It has low viscosity and improve the ionic conductivity of the electrolyte.
5. People have also started using ILs, with a hope to decrease /limit dissolution of the active materials in the electrolyte.

Dry and gelled polymer electrolytes

As outlined earlier, liquid electrolyte causes significant dissolution of the active material, encourage its diffusion toward the negative electrode. As an effective alternative polymer electrolyte is used. Is solid at room in presence of a lithium salt. Heated > 65°C it is molten exhibits sufficient ionic conductivity.

- This type of electrolyte can be used on its own (without membrane) as it ensures physical separation between the electrodes.
- This type of polymer electrolyte needs to be differentiated from gelled or plasticized electrolytes: polymer is mixed with a lithium salt along with a blend organic solvent. This works at room temperature.

Sulfonate base solvent example is toluene that is also used typically 2 to 10 percent by volume that is used in the electrolyte. So, it is reported that this toluene based solvent the sulfonate family, they decrease the dissolution of the polysulfides not only that the diffusion of this polysulfides that is also embedded and actually this solvent they also improve the saturatability of the electrolyte with the positive electrode.

So, they are going into the positive electrode the saturation level is quite good, but viscosity is a problem and also ionic conductivity for this type of solvent is not that good. So, ionic liquid is another thing although very limited reports one can find and the use of ionic liquid which already I have described part of my earlier lectures. So, it is reported the certain ionic liquid they decrease or at least limit the dissolution of the active material in the form of this long chain polysulfides into the electrolyte.

So, electrolyte is still a problem and you do not have a perfect solution except for the patented technology for the two companies I will be talking about they are they have commercialized lithium sulfur batteries.

So, that is there, but apart from that this the use of this solvent is not that much optimized. So, gel polymer electrolyte or dry electrolyte that is also used, but liquid electrolyte the dissolution of the active material is too much and diffusion of this polysulfides from one electrode to another electrode providing this shuttle mechanism that also should be retarded.

So, polymer electrolyte is one solution with of course, a lithium based salt it should be heated at high temperature more than 65 degree Celsius to make it molten. So, that it exhibits enough ionic conductivity. So, that is one strategy this type of electrode this is self supporting it can be used on its own and actually the idea is to have a positive electrodes separated from the negative electrode.

And this type of molten electrolyte that basically should be differentiated from the gelled electrolyte as I already described that one can use plasticizer in the polymer mix polymer based electrolyte where lithium salt and a binder organic solvent is used to form a gel type of electrolyte.

So, the advantage of this gel type of electrolyte is that it can work at room temperature for this polymer based electrolyte you need to use it in the molten state. So, temperature should be high in order to operate it efficiently.

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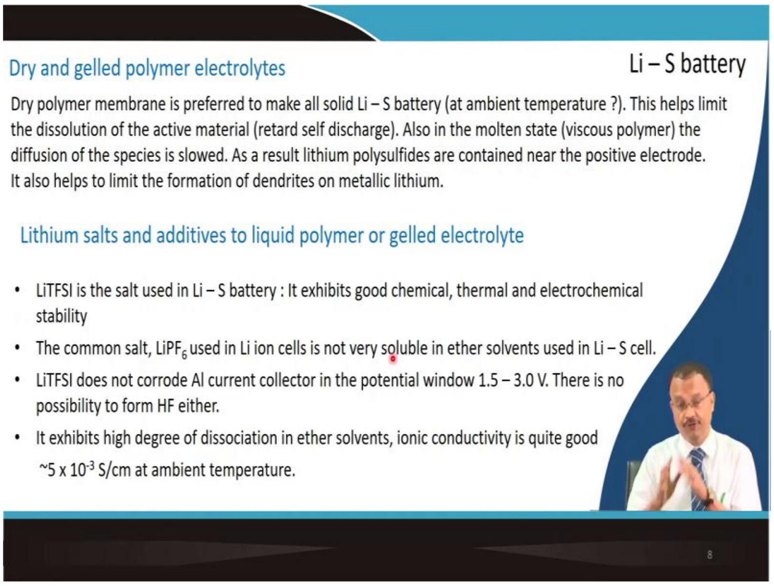

Dry and gelled polymer electrolytes

Li – S battery

Dry polymer membrane is preferred to make all solid Li – S battery (at ambient temperature ?). This helps limit the dissolution of the active material (retard self discharge). Also in the molten state (viscous polymer) the diffusion of the species is slowed. As a result lithium polysulfides are contained near the positive electrode. It also helps to limit the formation of dendrites on metallic lithium.

Lithium salts and additives to liquid polymer or gelled electrolyte

- LiTFSI is the salt used in Li – S battery : It exhibits good chemical, thermal and electrochemical stability
- The common salt, $LiPF_6$ used in Li ion cells is not very soluble in ether solvents used in Li – S cell.
- LiTFSI does not corrode Al current collector in the potential window 1.5 – 3.0 V. There is no possibility to form HF either.
- It exhibits high degree of dissociation in ether solvents, ionic conductivity is quite good $\sim 5 \times 10^{-3}$ S/cm at ambient temperature.

So, if one can make dry polymer based membrane one can make all solid lithium sulfur battery whether it will be at ambient temperature it is questionable because polymer electrolyte you cannot use you will not get sufficient lithium ion conductivity in it.

So, that is a question mark and in solid state of course, the dissolution of this active material including the self discharge that can be grossly limited molten state we call it is a viscous polymer the diffusion of the species is a bit slowed, so that this redox shuttle mechanism will also be impeded.

So, basically this lithium polysulfides they will be confined in the positive electrode and also the dendrite formation in the lithium metal that will also be grossly limited. So, people are started working on this also listed then sulfur battery, but I do not believe that the exact solution for what kind of solid state polymer they will use that has not yet been finalized.

Now, you need not only the solvent right, you need lithium salts and certain additives also into this liquid polymer or gelled electrolyte you need to use it. So, LiP LiPF 6 which is so common for lithium ion batteries they are not stable in ether based solvent which is actually used for lithium sulfur battery.

So, this salt usually it is not used, but LiTFSI this kind of salt that is used for lithium sulfur battery. And the reason for use for this is a good chemical thermal as well as electrochemical stability it has sufficient large window certainly from 1.5 to 3 volt you can safely use this kind of salt.

Also, unlike this LiPF 6 this particular salt they do not corrode the aluminum current collector which usually you use for the composite lithium sulfur composite battery particularly in this voltage range 1.5 to 3 volt it does not corrode the current collector. And in other words you remember we talked about one mechanism where this LiPF 6 salt they produce hydrofluoric acid and that actually causes the corrosion.

So, this part is also not very prominent for if you use Li LiTFSI this kind of salt. So, it also exhibits a good dissociation in almost various types of solvents are used in the electrolyte. So, it dissociates well ionic conductivity is in the order of 10 raised to minus 3 siemens per centimeter at ambient temperature which is considered to be quite good for their use.

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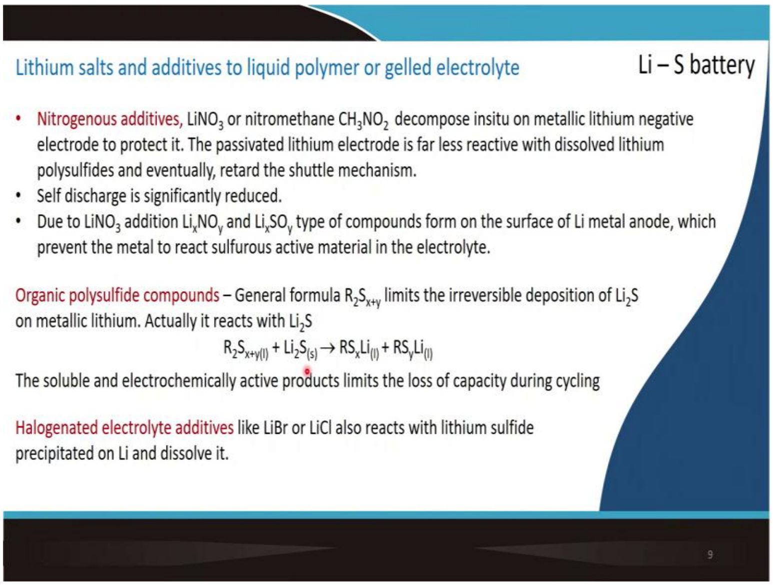

Lithium salts and additives to liquid polymer or gelled electrolyte

Li – S battery

- Nitrogenous additives, $LiNO_3$ or nitromethane CH_3NO_2 decompose insitu on metallic lithium negative electrode to protect it. The passivated lithium electrode is far less reactive with dissolved lithium polysulfides and eventually, retard the shuttle mechanism.
- Self discharge is significantly reduced.
- Due to $LiNO_3$ addition Li_xNO_y and Li_xSO_y type of compounds form on the surface of Li metal anode, which prevent the metal to react sulfurous active material in the electrolyte.

Organic polysulfide compounds – General formula R_2S_{x+y} limits the irreversible deposition of Li_2S on metallic lithium. Actually it reacts with Li_2S

$$R_2S_{x+y(l)} + Li_2S_{(s)} \rightarrow RS_xLi_{(l)} + RS_yLi_{(l)}$$

The soluble and electrochemically active products limits the loss of capacity during cycling

Halogenated electrolyte additives like LiBr or LiCl also reacts with lithium sulfide precipitated on Li and dissolve it.

Now, you need certain additives inside the electrolyte and this additives are usually nitrogenous additives like lithium nitrate LiNO 3 or nitromethane that is used and this basically decomposed into the lithium metal electrode to passivate it. And this is less reactive with the dissolved lithium polysulfides and that eventually retard the so called shuttle mechanism.

How exactly it works this is not very clear, but the it is related to the decomposition of this particular materials which are nitrogenous additive and it works. Because several literature report including we have also found that it is quite effective to protect the lithium metal and also to impede the this redox cycle this mechanism shuttle mechanism it retard eventually.

So, if the lithium Li 2S does not get precipitated onto the lithium metal then of course, the self discharge will get reduced. And in certain literature it says that this LiNO 3 when it added then the layer which it forms on the surface of the metal the nature of this layer is some kind of lithium nitrogen base or lithium sulfur based compounds which basically prevents the metallic lithium to react with the sulfurous active material in the electrolyte.

So, you remember that we discussed that in the positive electrode the long chain that get reduced to the negative electrode in lithium and then vice versa it goes back to the positive electrode and this cycles are grossly impeded. Apart from this nitrogenous additives organic polysulfide compounds which is having a general formula this is some kind of alkyl group that is and also with sulfur that is also added. So, this is also reported to limit the position of Li 2 S on metallic lithium.

So, a possible mechanism is that this kind of polysulfide compound they basically react with this Li 2 S make it soluble. So, it is in solid state this is added in the liquid electrolyte. So, these two reacts and it forms liquid component. So, this does not get precipitate on the lithium sulfide Li 2 S is electronically non conducting. So, you never want that your metallic lithium surface is actually blocked by this non conduct non conducting precipitate.

So, it brings it back to the solution. So, that soluble and electrochemically active products they basically limit the loss of capacity during cycling. So, this organic polysulfides they have a good influence to improve the cycleability. Halogenated electrolyte additives that is lithium bromide, lithium chloride that also reacts with the lithium sulfide that is precipitated on lithium and dissolved.

So, in that way this and this function is quite identical. In fact, many of this additives people have added and actually the recipe which basically works for a good lithium sulfur battery you need high capacity, you need to have the coulombic efficiency quite good. Then the dissolution problem you will have to tackle the cycleability should be improved. So, redox shuttle mechanism will have to be impeded and finally, it should have good rate performance.

So, lot of things people kept trying based on their understanding to get this kind of optimized electrochemical performance, but still the actual thing a optimized system is yet to be developed.

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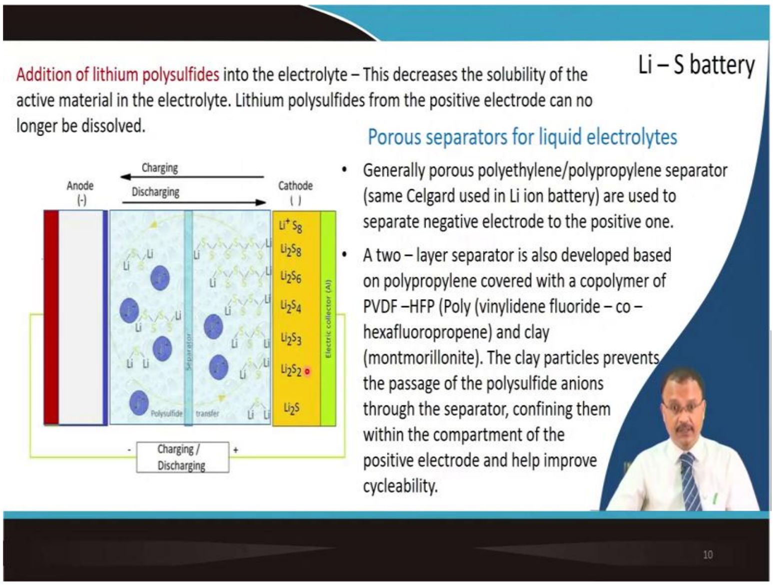

Li – S battery

Addition of lithium polysulfides into the electrolyte – This decreases the solubility of the active material in the electrolyte. Lithium polysulfides from the positive electrode can no longer be dissolved.

Porous separators for liquid electrolytes

- Generally porous polyethylene/polypropylene separator (same Celgard used in Li ion battery) are used to separate negative electrode to the positive one.
- A two – layer separator is also developed based on polypropylene covered with a copolymer of PVDF –HFP (Poly (vinylidene fluoride – co – hexafluoropropene) and clay (montmorillonite). The clay particles prevents the passage of the polysulfide anions through the separator, confining them within the compartment of the positive electrode and help improve cycleability.

Now, addition of lithium polysulfides into the electrolyte that is another way. So, if the long chain or short chain lithium polysulfide dissolution into the electrolyte is a problem then additionally you add it.

So, any material if you add then basically it has a solubility limit right. So, if you add additional lithium polysulfides into the electrolyte. So, that will basically decrease the solubility of the active material during the operation of this lithium sulfur battery and they will no longer get dissolved. So, that strategy also quite good and one should try it.

So, these are the way where you can manipulate the electrolyte composition now this is the situation which I was talking about the same thing already I have described it. Now I have included all types of polysulfides.

So, these two are solid this Li 2 S and Li 2 S these are all liquid and this is partially this is also go to the solution and as you can see this is a long chain polysulfide they get dissolved they pass through this separator goes here get reduced and then again during the subsequent cycling it comes back here.

So, this redox cycle operates you need to put more current into it and that creates the polarization effect, so this problem remains. So, the porous separator is important generally. So, far this Celgard whatever we use for lithium ion battery the same Celgard that is used. In some of the cases a two layer separator and I also talked about it when in general I was discussing different types of separator used for lithium ion batteries. So, this separator is also found to be effective which is polypropylene the same material for Celgard with a copolymer of PVDF and this hexafluoropropene.

So, that is used the, so this copolymer and some kind of clay which is montmorillonite. So, it forms a bilayer structure a two layer structure. So, it is told that it is understood. In fact, the clay particle they prevent the passage of this polysulfide anions through the separator and they confine them within this channel I mean, within this compartment of the positive electrode. So, that basically improves the cycleability of the lithium sulfur cell.

So, some of the research groups they have also used instead of a single separator a two layer separator to improve the cycliability of the lithium sulfur cell.

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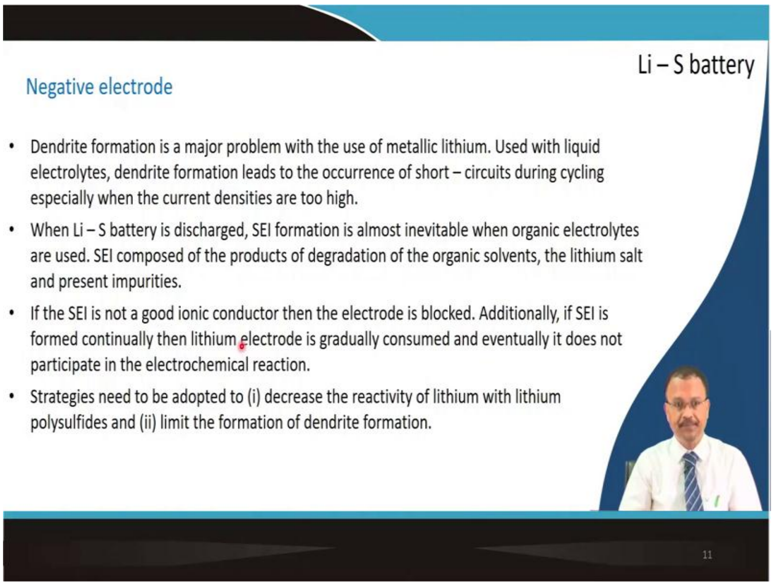

Li – S battery

Negative electrode

- Dendrite formation is a major problem with the use of metallic lithium. Used with liquid electrolytes, dendrite formation leads to the occurrence of short – circuits during cycling especially when the current densities are too high.
- When Li – S battery is discharged, SEI formation is almost inevitable when organic electrolytes are used. SEI composed of the products of degradation of the organic solvents, the lithium salt and present impurities.
- If the SEI is not a good ionic conductor then the electrode is blocked. Additionally, if SEI is formed continually then lithium electrode is gradually consumed and eventually it does not participate in the electrochemical reaction.
- Strategies need to be adopted to (i) decrease the reactivity of lithium with lithium polysulfides and (ii) limit the formation of dendrite formation.

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Now, we will talk about the negative electrode and in negative electrode as you can understand dendrite formation is a major problem. So, lithium get precipitated during the charging operation and then dendrites form and it leads to the short circuiting because it forms a dendrite kind of structure. So, when this battery is discharged SEI formation is almost inevitable that you know by this time particularly when organic electrolytes are used.

So, this SEI whatever is formed that is basically comes from the degradation of the organic solvent and the lithium salt which is present some kind of impurity also is there in the electrolyte solution. So, they form this SEI layer, SEI layer if they are ionically non conductor then it is a problem because this SEI continuously will start to form and then eventually your material will not be electrochemically active.

So, SEI layer formation is good because it gives some kind of protection to the metallic lithium, but it should not grow and you can easily identify it by EIS spectroscopy of the lithium sulfur battery which I talked about. So, the strategies that one should adopt is to decrease the reactivity of lithium with lithium polysulfides which is dissolved in electrolyte and also the formation of the lithium dendrite.

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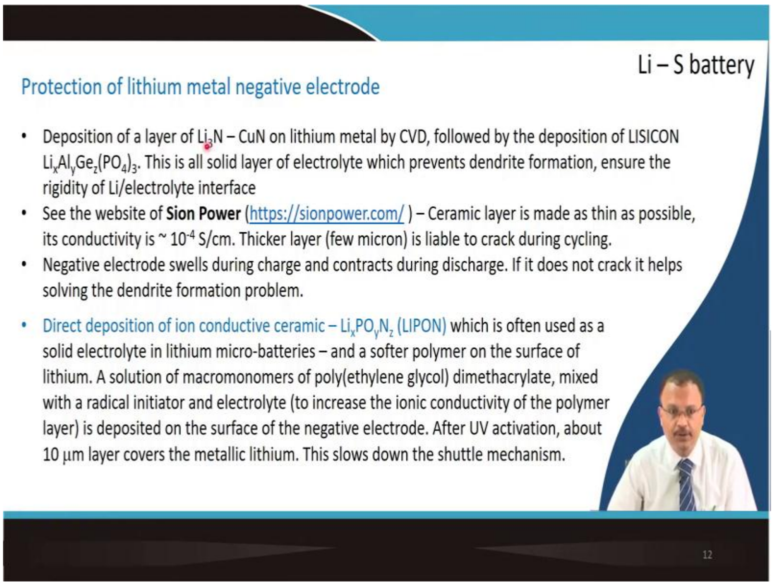

Li – S battery

Protection of lithium metal negative electrode

- Deposition of a layer of Li_3N – CuN on lithium metal by CVD, followed by the deposition of LISICON $Li_xAl_yGe_z(PO_4)_3$. This is all solid layer of electrolyte which prevents dendrite formation, ensure the rigidity of Li/electrolyte interface
- See the website of **Sion Power** (https://sionpower.com/) – Ceramic layer is made as thin as possible, its conductivity is ~ 10^{-4} S/cm. Thicker layer (few micron) is liable to crack during cycling.
- Negative electrode swells during charge and contracts during discharge. If it does not crack it helps solving the dendrite formation problem.
- Direct deposition of ion conductive ceramic – $Li_xPO_yN_z$ (LIPON) which is often used as a solid electrolyte in lithium micro-batteries – and a softer polymer on the surface of lithium. A solution of macromonomers of poly(ethylene glycol) dimethacrylate, mixed with a radical initiator and electrolyte (to increase the ionic conductivity of the polymer layer) is deposited on the surface of the negative electrode. After UV activation, about 10 μm layer covers the metallic lithium. This slows down the shuttle mechanism.

So, people have tried to deposit a layer of this material lithium nitride and copper nitride and this is a complicated process by CVD they grew a thin layer. And then a lithium iron conducting super conducting material lithium aluminum germanium phosphate just like nasicon we have lithium super ionic conductor lisicon material.

So, these are all solid electrolyte and that basically prevents the dendrite formation. And only problem is that that these are ceramic material it is fragile in nature and it adds to the cost of making the battery for large scale production it is not a good idea.

So, this is another company Sion Power you can have a look at their website they are working with this kind of ceramic layer I could not get with what is the composition of this kind of ceramic layer. And conductivity also reported is not that great it is 10 raised to minus 4 siemens per centimeter at least we need a order of magnitude lower any conductivity. Thicker layer will not work because it cracks and also the conductivity is not that great. So, very thin layer is required on lithium.

So, dendrite formation is inhibited and probably something some patented technology they have devised. So, I would like you to see, so I mean check you the recent progress in this area that how to protect this lithium metal during the operation of lithium sulfur batteries. Another way you directly deposit this lipon which is a known solid electrolyte for lithium ion battery along with a softer polymer on the surface of the lithium. So, it is a polymer and this lithium ion conducting electrolyte.

So, the polymer is in many case PEG and dimethacrylate mixed with a radical which is acts as a initiator and an electrolyte that is to increase the ionic conductivity of the polymer layer. So, you can deposit it on the lithium metal surface and usually the polymerization is better in a we activated way about 10 micron layer on metal lithium that has been proved that its lower this so called shuttle mechanism.

But it is extremely anything to do with the lithium metal it is a complicated process and it is not I am not very sure that in terms of its commercial adaptability how effective will they be.

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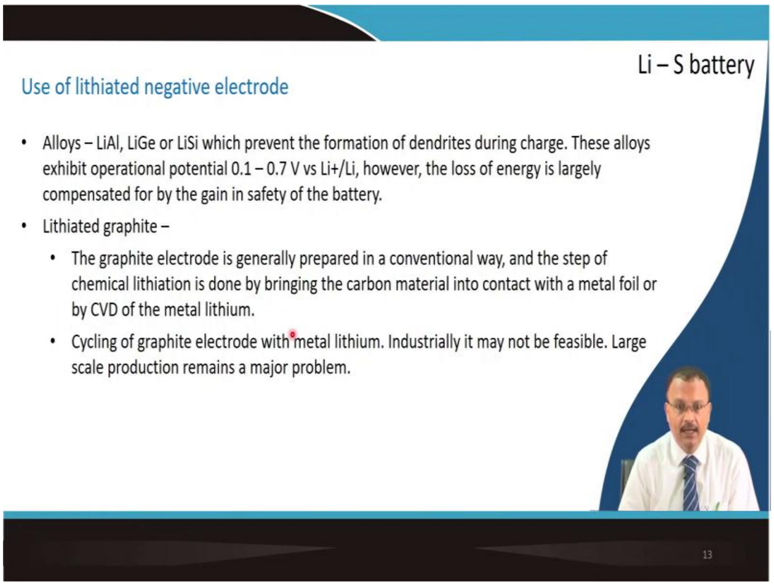

Li – S battery

Use of lithiated negative electrode

- Alloys – LiAl, LiGe or LiSi which prevent the formation of dendrites during charge. These alloys exhibit operational potential 0.1 – 0.7 V vs Li+/Li, however, the loss of energy is largely compensated for by the gain in safety of the battery.
- Lithiated graphite –
  - The graphite electrode is generally prepared in a conventional way, and the step of chemical lithiation is done by bringing the carbon material into contact with a metal foil or by CVD of the metal lithium.
  - Cycling of graphite electrode with metal lithium. Industrially it may not be feasible. Large scale production remains a major problem.

Another very good way is to use lithiated negative electrode. So, you know lithium aluminium, lithium germanium, lithium silicon this kind of negative electrode you can use instead of pure lithium.

So, dendrite formation that will not be there and you will have slightly larger operation potential it is not against metallic lithium which is considered 0. So, slightly more, but not much 0.1 to 0.7 lithium versus lithium this kind of voltage basically will lose because sulfur you know that you are getting 2.1 volt and 0.7 is gone from there.

So, eventually you are reducing the voltage and eventually you are compromising your energy density. So, but the loss of energy is largely compensated by the gain of safety of the battery.

So, you do not have the formation of the dendrite and short circuit problem that is grossly removed. Another way to use instead of this is lithiated graphite. So, the preparation could be a conventional way and chemical lithiation usually is done by bringing this carbonaceous material in contact with the lithium metal foil.

Or you can deposit lithium by CVD another way you can prepare it is just like a half cell of graphite you have lithium and you have carbon and then you make lithiated carbon, but as you understand the large scale production of this kind of lithiated graphite is problematic. So, I do not know that whether this will be a good solution to address the problem of lithium.

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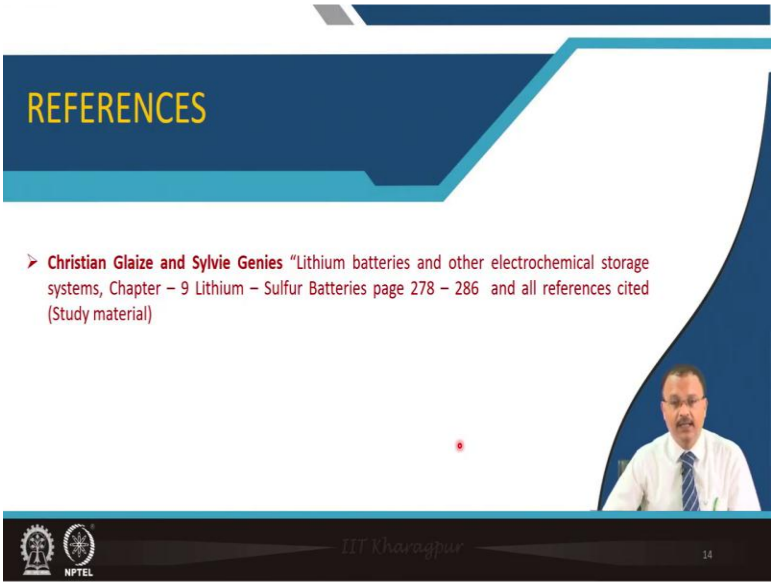

REFERENCES

- **Christian Glaize and Sylvie Genies** "Lithium batteries and other electrochemical storage systems, Chapter – 9 Lithium – Sulfur Batteries page 278 – 286 and all references cited (Study material)

So, this part of the lecture is again the book by Glaze is the text book and again all the references which only talks about the concept which I talked about in this lecture is nicely illustrated in the references, cited there in the book chapters in relevant part and you should read those references as well.

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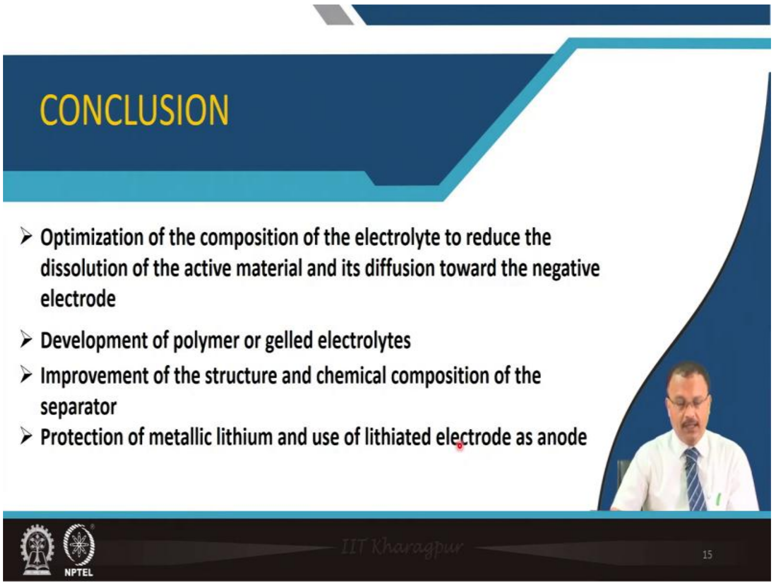

CONCLUSION

- Optimization of the composition of the electrolyte to reduce the dissolution of the active material and its diffusion toward the negative electrode
- Development of polymer or gelled electrolytes
- Improvement of the structure and chemical composition of the separator
- Protection of metallic lithium and use of lithiated electrode as anode

So, in this particular lecture we talked about the optimization of the composition of the electrolyte to reduce the dissolution of the active material and its diffusion towards negative electrode. Then we shed light on polymer or gelled electrolyte and improvement of the structure of and the chemical composition of the separator the two layer separator is found effective. And finally, protection of lithium it is a bit complicated or use of lithiated electrode as anode that is introduced.

Thank you for your attention.