Electrochemical Energy Storage
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Module - 11
Li - Air Batteries
Lecture - 45
State of the art Li-Air Batteries: Case Study

Welcome to my course Electrochemical Energy Storage and this is module number 11 where I am talking about Li- Air batteries. This is the last lecture, lecture number 45 of this module where we are talking about state of the art of Li- Air Batteries and some case study we will be considering.

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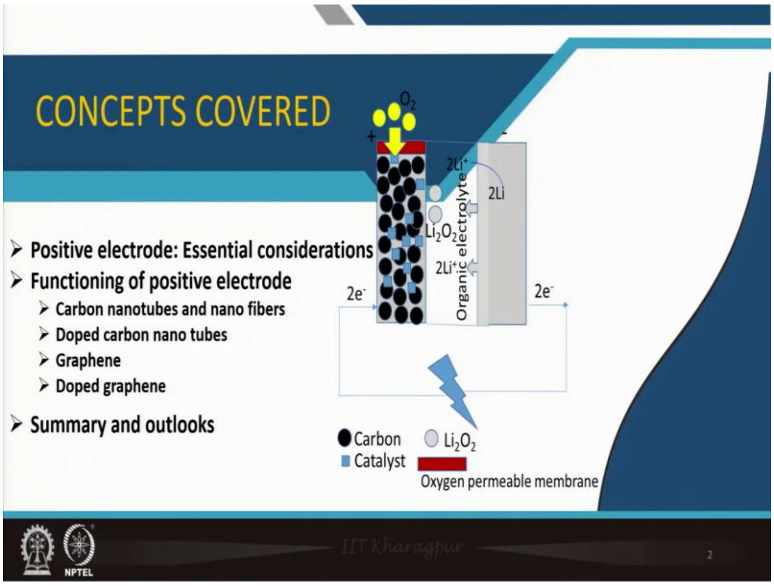

CONCEPTS COVERED

- Positive electrode: Essential considerations
- Functioning of positive electrode
  - Carbon nanotubes and nano fibers
  - Doped carbon nano tubes
  - Graphene
  - Doped graphene
- Summary and outlooks

Case study I think it is important for me to introduce, because so far you know about the operational principle of Li-Air battery very simple operation, what are the limitations and carbonaceous material they are used as positive electrode material. So, how they are made in the last lecture we have talked about it.

So, mostly I will be concentrating on the positive electrode material electrolyte already I have introduced, negative electrode we have introduced we talked about the various types of electrolyte and salts and binders they are used. So, this part we will be considering the positive electrode what are the essential consideration, some of it will be a recapitulation.

Then how this positive electrode actually functions and we will take the case study of carbon nanotube mostly and sometimes nano fibers then doped carbon nanotubes will be talked about. Then graphene they are also been used graphene and doped graphene they have used as positive electrode material and finally what stage we are now in where we stand. So, these are the topics that we will be covered in this particular lecture.

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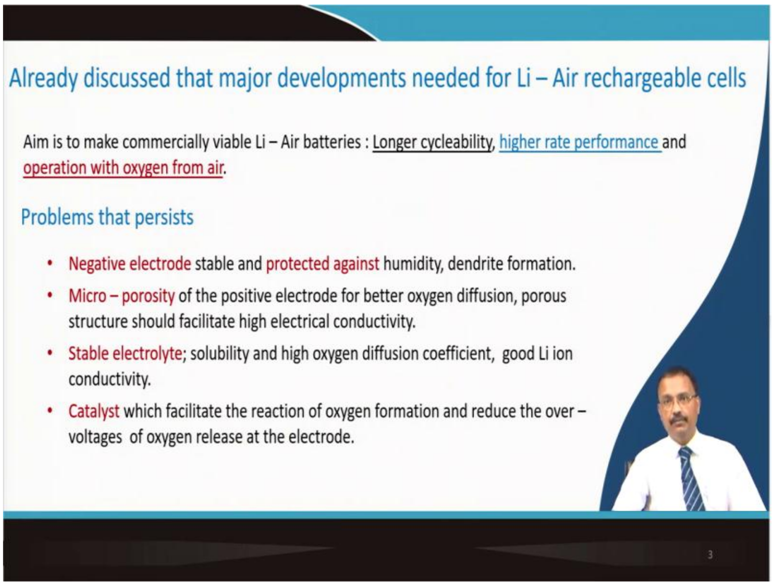

Already discussed that major developments needed for Li – Air rechargeable cells

Aim is to make commercially viable Li – Air batteries : Longer cycleability, higher rate performance and operation with oxygen from air.

Problems that persists

- Negative electrode stable and protected against humidity, dendrite formation.
- Micro – porosity of the positive electrode for better oxygen diffusion, porous structure should facilitate high electrical conductivity.
- Stable electrolyte; solubility and high oxygen diffusion coefficient, good Li ion conductivity.
- Catalyst which facilitate the reaction of oxygen formation and reduce the over – voltages of oxygen release at the electrode.

So, this part already I have described right. So, already discussed the major development of rechargeable cell and the aim is now well defined that we need to make commercial commercially viable Li- Air batteries and cycleability is one of the major issues, because the cycleability is almost not there people are reporting 5, 10, 20, 50 cycles and after that the battery is dead.

So, cycleability is one thing second is the high rate performance it should be charged fast in a shorter time and also you should have the flexibility to have a to get a high power density. You should discharge it also at higher rate, which is very difficult you will be able to see that the data that we have accurate from various literature report they are not very encouraging so far.

And finally, what is more important that I do not want to make lithium oxygen battery because oxygen I will have to carry then in case of electric mobility applications. So, I will have to use air, so the use of air what are the shortcomings very very limited studies that have been done. In fact, I did not include it although I have provided you sufficient literature.

So, that after understanding the basic concept you can always understand these papers and in light of this problems whatever I have listed here. The problems still persist you will be able to understand that what kind of material I should develop, so that to make it commercial.

So, that idea should be very clear to you after listening to this lecture. So, negative electrode as you can understand this is lithium metal foil this should be stable, it should be protected under humidity. So, water droplet or minute quantity of water is also not allowed in Li- Air battery system and formation of dendrite of course it will be there because we are using pure lithium. So, that will have to be impeded how to impede this lithium dendrite formation.

Now, another factor that is important is micro porosity in the positive electrode. So, why micro porosity is required, because you know that the oxygen should diffuse out and oxygen reduction reaction should be taken place. So, porous structure is required and it should be porous, but at the same time it should give you sufficient electrical conductivity, because this porous region is not electronically conducting.

So therefore if you make the structure quite porous, but this interconnection you will have to manipulate, so that the electron conduction path they should not be compromised. Then third problem is your stability of the electrolyte I talked about carbonate based electrolyte, ether based electrolyte, sulfonate based electrolyte.

So, this electrolyte is important because of this solution of this oxygen and their diffusion coefficient, because from my earlier lecture you know that the electrode should be filled up with electrolyte at various type partially or fully apart from being tried enough. So, what are the pros and cons already I have talked about.

And it should have good lithium ion conductivity that is also more important, the use of catalyst is very important the mechanism still I could not understand it well that in what way exactly it works. So, today also we will talk about it the use of catalysts sometimes soluble catalysts they are also used.

So, whatever we understand that it fascilates the reaction of this oxygen formation and reduce the over voltage, over voltage I talked about and when this reduction product after discharge they get dissociated a simple dissociation does not take place. So, lithium Li 2 O 2 does not simply form Li and oxygen. But how to catalyze that? So, the over voltage is reduced capacity is increased. So, those are the burning issues of these Li- Air batteries.

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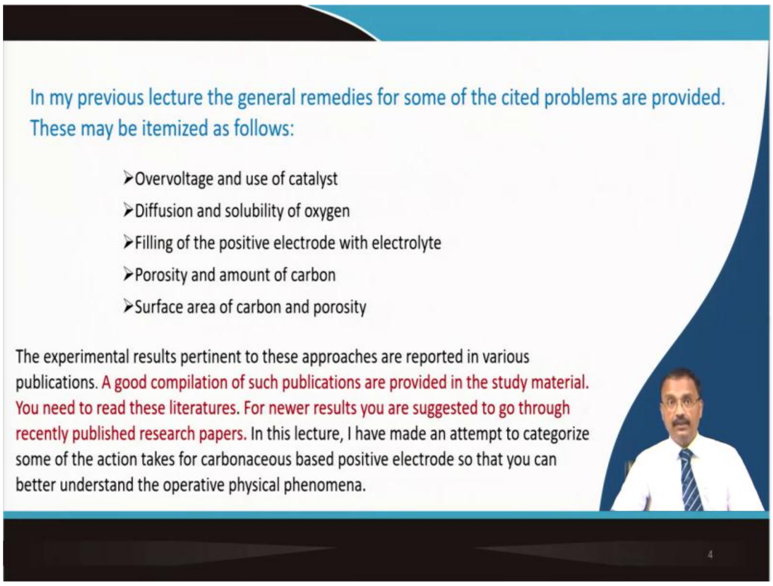

In my previous lecture the general remedies for some of the cited problems are provided. These may be itemized as follows:

- Overvoltage and use of catalyst
- Diffusion and solubility of oxygen
- Filling of the positive electrode with electrolyte
- Porosity and amount of carbon
- Surface area of carbon and porosity

The experimental results pertinent to these approaches are reported in various publications. A good compilation of such publications are provided in the study material. You need to read these literatures. For newer results you are suggested to go through recently published research papers. In this lecture, I have made an attempt to categorize some of the action takes for carbonaceous based positive electrode so that you can better understand the operative physical phenomena.

So, as I told in my previous lecture general kind of remedy for some of these problems already I have cited and what remedy we talked about let us itemize it number 1 is over voltage. So, once it is over voltage you do need catalyst in the positive electrode to reduce this over voltage, the diffusion and solubility of oxygen the second term is also very important.

The third one is filling the positive electrode with electrolyte. So, that it comes in close proximity or lithium ion and the reduced oxygen they come in close proximity to form this reduction product Li 2 O 2 that gives you the capacity. So, filling of the positive electrode will only be possible when you have a porous types of electrode material.

So, that is why the porosity is important in carbon and we talked about bimodal kind of porosity, today also we will be talking about it to understand this issues a bit further. And the surface area that means it depends on the particle size of the carbon and it is porosity they are the important factor.

So, all these things are basically related to your positive electrode material. So, there are numerous experiments that is being going on and it is really it was very difficult task for me to review all those literature and categorize the plan of action; whatever people are doing to circumvent some of this burning problems.

So, if you go through the cited literature which I have given at the end of this lecture, you will mostly find that these problems have been addressed by new experimental design. And marginal improvement as far as the electrochemical characteristics that has been achieved.

But some of the results every day you will see the newer papers are being published, because this is a burning topic and you are also suggested to go through good quality papers from reputed journals in American Chemical Society, journal of Electrochemical Society, Power Source Nature Materials.

So, please have a look so that you are at par with the state of the art of the happening whatever is happening in lithium ion batteries. So, as I told that I have made an attempt to categorize some of the action taken for carbonaceous material carbonaceous based positive electrode material and so that you can basically understand the link.

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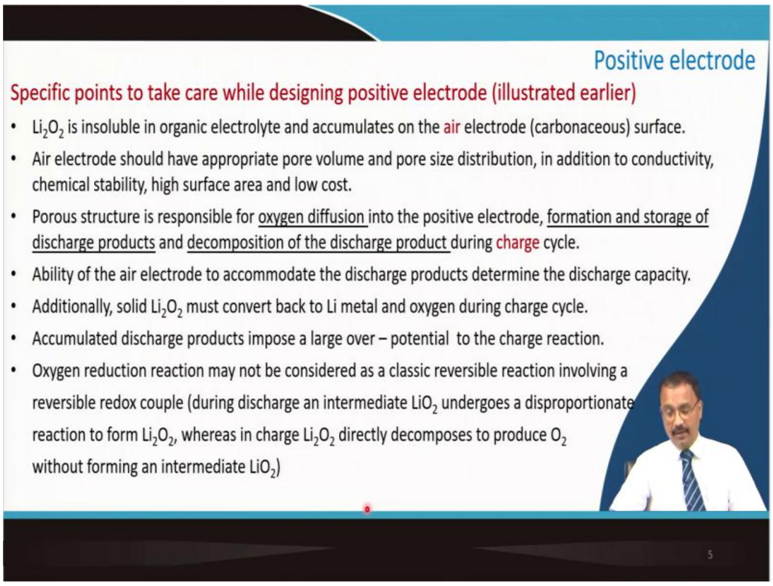

Positive electrode

Specific points to take care while designing positive electrode (illustrated earlier)

- Li_2O_2 is insoluble in organic electrolyte and accumulates on the air electrode (carbonaceous) surface.
- Air electrode should have appropriate pore volume and pore size distribution, in addition to conductivity, chemical stability, high surface area and low cost.
- Porous structure is responsible for oxygen diffusion into the positive electrode, formation and storage of discharge products and decomposition of the discharge product during charge cycle.
- Ability of the air electrode to accommodate the discharge products determine the discharge capacity.
- Additionally, solid Li_2O_2 must convert back to Li metal and oxygen during charge cycle.
- Accumulated discharge products impose a large over – potential to the charge reaction.
- Oxygen reduction reaction may not be considered as a classic reversible reaction involving a reversible redox couple (during discharge an intermediate LiO_2 undergoes a disproportionate reaction to form Li_2O_2, whereas in charge Li_2O_2 directly decomposes to produce O_2 without forming an intermediate LiO_2)

So, the problems whatever I have already illustrated what are the problems lithium oxygen Li 2 O 2 which is the discharge product that is insoluble in organic electrolyte. So, this one is insoluble in organic electrolyte and therefore it accumulates in the air electrode and air electrode is basically carbonaceous surface.

So, you know it should be porous but it should not be the case that this discharge product is completely blocking this pore. So, if it completely blocks then in further cycle oxygen cannot come in and also it will be difficult for it to get dissociated. So, that problem is there.

So, it should have appropriate pore volumes and pore size distribution and more porous material you know the conductivity will be compromised chemical stability also will get compromised. So, these are the factors that you should look into.

Now, porous structure that is responsible for oxygen diffusion, of course formation and storage of the discharge product Li 2 O 2 and finally decomposition of the discharge product during the charge cycle. So, these three are the important criteria for the porous material. And this discharge product should be there inside the positive electrode.

So, that you get the capacity also nicely it should convert back to lithium metal and oxygen, there should not be any intermediate product. And particularly for the carbonate based electrolyte you have seen that this lithium Li 2 O 2 that basically initiate the decomposition of the electrolyte so other products also accumulates, that is the decomposition product of the electrolyte.

Ether based material ether based electrolyte this problem is not that severe, but carbonate based electrolyte this problem is severe. So, once this discharge product is accumulated then you need to have a large over potential is required. So, to decompose that and they are all lithium based product. So, you are losing lithium and your voltage charging voltage is going up and that you must be noticing in my earlier lectures.

Oxygen reduction reaction they may not be considered a classic reversal involving a reversible redox couple. So, as I was saying that Li 2 O 2 not directly form Li and oxygen, but in between LiO 2 forms and then there is a disproportionate reaction to form Li 2 O 2, these all I have already described in my earlier lecture.

So, this is just I am recapitulating so that you can understand or you at least you can remember this problems. So, this is the problem during discharge, but here during charge they actually decompose oxygen and to the best of our knowledge any intermediate product it never forms, but this electrolyte decomposed product that remains.

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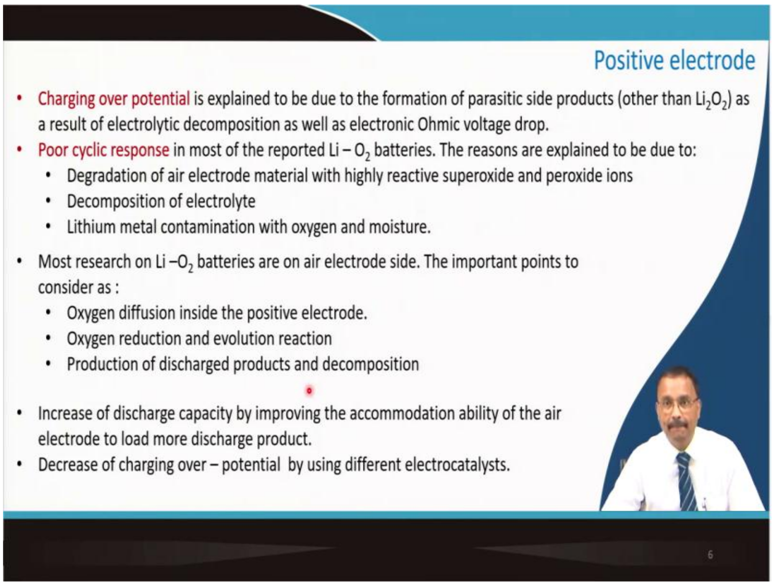

Positive electrode

- Charging over potential is explained to be due to the formation of parasitic side products (other than Li_2O_2) as a result of electrolytic decomposition as well as electronic Ohmic voltage drop.
- Poor cyclic response in most of the reported $Li - O_2$ batteries. The reasons are explained to be due to:
    - Degradation of air electrode material with highly reactive superoxide and peroxide ions
    - Decomposition of electrolyte
    - Lithium metal contamination with oxygen and moisture.
- Most research on $Li - O_2$ batteries are on air electrode side. The important points to consider as :
    - Oxygen diffusion inside the positive electrode.
    - Oxygen reduction and evolution reaction
    - Production of discharged products and decomposition
- Increase of discharge capacity by improving the accommodation ability of the air electrode to load more discharge product.
- Decrease of charging over – potential by using different electrocatalysts.

So, charging over potential this basically is explained due to the parasitic side product. So, Li 2 O 2 and electrolytic decomposition so that leads to the ohmic voltage drop. So, you need to put more voltage during charging. Poor cyclic response it is another problem for this type of battery and there could be various problem that there could be various reasons for this problem.

So, first and foremost problem is the degradation of the electrode material with the superoxide whatever is being formed and also the peroxide ions that also I talked about it. Electrolyte decomposition is the second problem and finally this lithium metal that is also contaminated with oxygen and fresh moisture. So, all these three factors they will contribute to poor cyclic responses.

So, most problem of this Li- Air batteries they are concentrated or they are due to the positive electrode part and you must make sure that oxygen diffusion inside the positive electrode unhampered it should come, oxygen reduction water reaction and evolution reaction during the charging OER.

So, this should not get hampered and production of discharged product and their decomposition that should be efficiently it could be efficiently done. So, increase of the discharge capacity is possible if you can accommodate the discharge product. So, it can load more discharge product, so the capacity will increase and usually the over potential during charging that can be manipulate by using electro catalyst.

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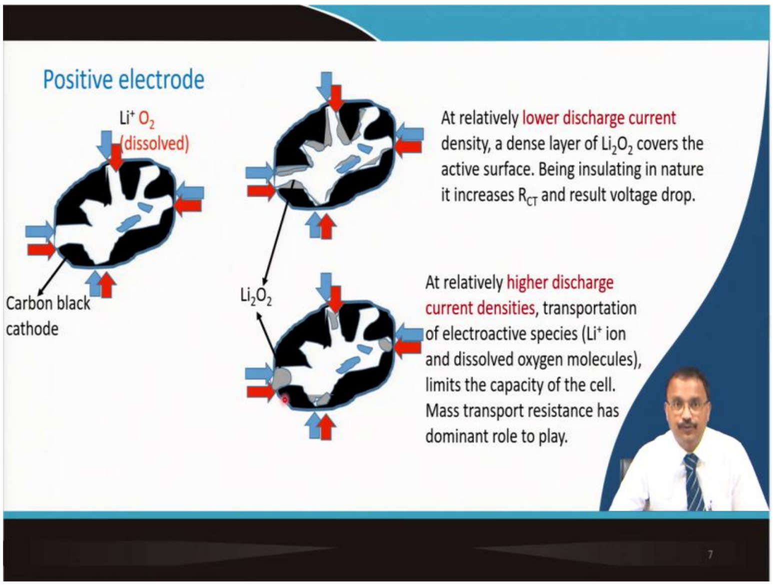

Positive electrode

At relatively lower discharge current density, a dense layer of Li_2O_2 covers the active surface. Being insulating in nature it increases R_{CT} and result voltage drop.

At relatively higher discharge current densities, transportation of electroactive species (Li^+ ion and dissolved oxygen molecules), limits the capacity of the cell. Mass transport resistance has dominant role to play.

So, pictographically if you see you have a porous carbon material any carbonaceous material which are porous in nature. So, oxygen that is the dissolved oxygen the electrolyte that should pass through it and lithium ion also should come and they form during discharge particularly at lower discharge current.

You can see the thin layer of Li 2 O 2 and that basically covers this active surface and you can easily identify if you do a EIS impedance spectroscopy this charge transfer resistance if you monitor you will be able to see that how exactly this things are being accommodated.

Now, if you increase the current density during discharge then what will happen this transportation of this electro active species. That means, the lithium ion and oxygen dissolved molecule that basically will limit the capacity of the cell, because it will form and part of it will get clogged this pores will get clogged. So, it is the mass transport which is important this is a mass transport resistance.

The first one is the charge transfer resistance, so the mass transport resistance will dominate the capacity behavior in higher discharge current lower discharge current we assume that a relatively thin layer of Li 2 O 2 forms. But it is quite thick as you can see at higher discharge current this Li 2 O 2 is forming and that basically the will increase the mass transport resistance for this type of situation.

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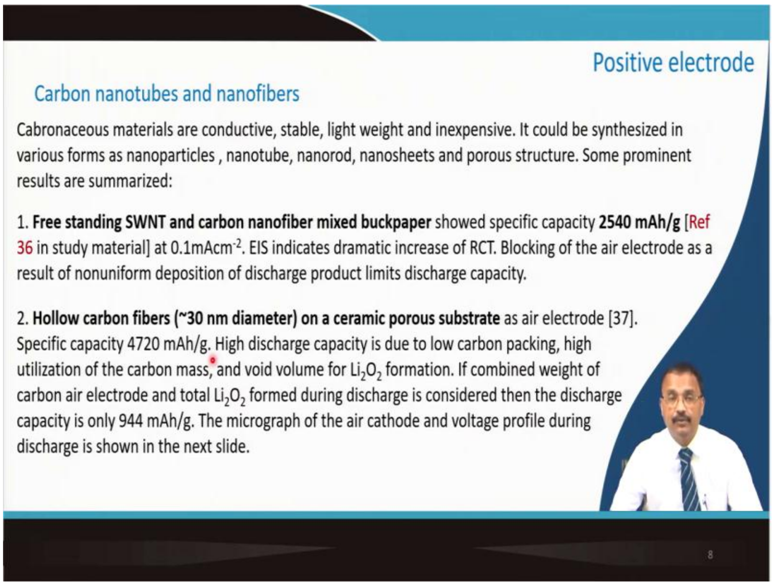

Positive electrode

Carbon nanotubes and nanofibers

Cabronaceous materials are conductive, stable, light weight and inexpensive. It could be synthesized in various forms as nanoparticles , nanotube, nanorod, nanosheets and porous structure. Some prominent results are summarized:

1. **Free standing SWNT and carbon nanofiber mixed buckpaper** showed specific capacity **2540 mAh/g** [Ref 36 in study material] at 0.1mAcm^{-2}. EIS indicates dramatic increase of RCT. Blocking of the air electrode as a result of nonuniform deposition of discharge product limits discharge capacity.

2. **Hollow carbon fibers (~30 nm diameter) on a ceramic porous substrate** as air electrode [37]. Specific capacity 4720 mAh/g. High discharge capacity is due to low carbon packing, high utilization of the carbon mass, and void volume for Li_2O_2 formation. If combined weight of carbon air electrode and total Li_2O_2 formed during discharge is considered then the discharge capacity is only 944 mAh/g. The micrograph of the air cathode and voltage profile during discharge is shown in the next slide.

So, in light of this let us now describe certain carbonaceous material performance. So, this carbonaceous material they are conductive stable they are light weight you know that and it could be prepared in various forms nanoparticles is one of them, nanotube I have already talked about it can be formed in a nanorod structure nanosheet or porous structure.

So, if you take for example a free standing single wall carbon nanotube. So, single wall carbon nanotube is mixed up with carbon nanofiber and mixed a buck paper. So, it showed a typical capacity quite large 2540 milliampere hour per gram. And this is at per as per this reference 36 of the study material which I have provided.

Typical current density was 0.1 milliampere per centimeter square people did the EIS spectroscopy and they saw a dramatic increase of rct. So, they claim that blocking of the air electrode as a result of a non uniform deposition of the discharge product limit the discharge capacity.

See the current density is here 0.1 milliampere per centimeter square and they characterize it through the measurement of charge transfer resistance and the microstructure is somewhere here something like this. So, the holes are blocked so first discharge capacity is quite large, but after all non uniform distribution deposition of the discharge product that will also hamper the effective charging of this battery and it will not work well.

People then tried hollow carbon fiber, because it has more porosity typical diameter is 30 nanometer and they took on a ceramic porous substrate as air electrode, ceramic porous substrate basically is made by anodization and anodization is a technique where from aluminum sheet you can deposit porous alumina.

And hollow carbon fiber was grown on a ceramic porous substrate, you see that this type of battery operation principle is quite straight forward. But getting the ideal electrochemical performance is a nightmare job because of this problem. So, that is why typically I want to highlight what are the problems that people face.

So, you see the specific capacity is 4720 milliampere hour per gram I am pretty sure you will be able to estimate the theoretical capacity which I have shown how to do that and you will have to take the weight of carbon by the way otherwise it does not make sense. So, the discharge capacity is due to low carbon packing, so that means the porosity that is improving your higher discharge capacity and Li 2 O 2 form and suddenly they are not blocking the passage.

So, if you take the combined weight of air electrode and total Li 2 O 2 whatever has formed during discharge, if you consider that then you see the difference the capacity in the fall from 4720 milliampere hour per gram to 944 milliampere hour per gram. So, the micrograph of this air cathode and the voltage profile that let us see that.

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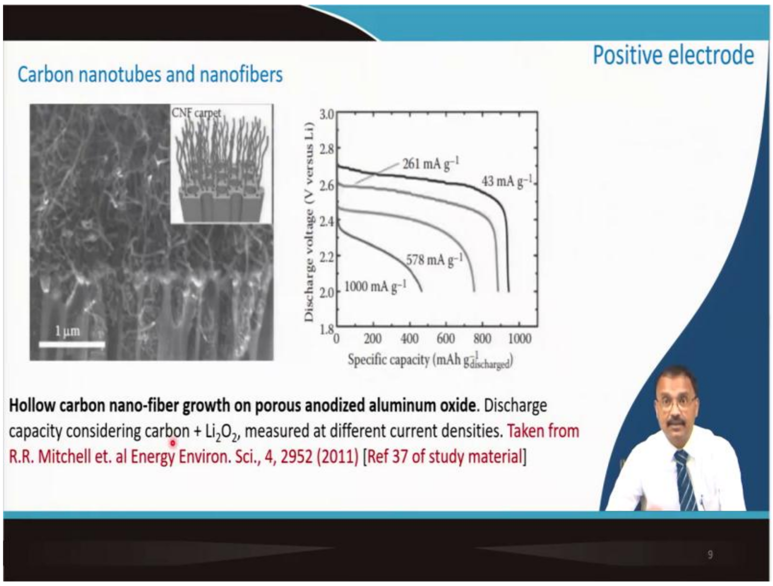

Positive electrode

Carbon nanotubes and nanofibers

Hollow carbon nano-fiber growth on porous anodized aluminum oxide. Discharge capacity considering carbon + Li_2O_2, measured at different current densities. Taken from R.R. Mitchell et. al Energy Environ. Sci., 4, 2952 (2011) [Ref 37 of study material]

So, this is hollow carbon which I was talking about. So, this is a anodized kind of alumina and then carbon nanofiber grown on top of it. So, this is a porous anodized aluminum oxide and carbon grown on top of it. Lot of pores porous space that you can see it is just like a structure of a bristle structure the tooth brush the bristle that you use it is a porous structure.

So, the capacity consider you will have to consider the carbon and Li 2 O 2 together. So, if you see that once you are at lower end lower discharge current it is 43 milli ampere per gram you get a reasonable good proper I mean capacity which is 900 something. And but once you increase the discharge current density the capacity dramatically falls. So, the rate performance of this battery is not yet optimized. So, just have a look of this paper to get more details out of it.

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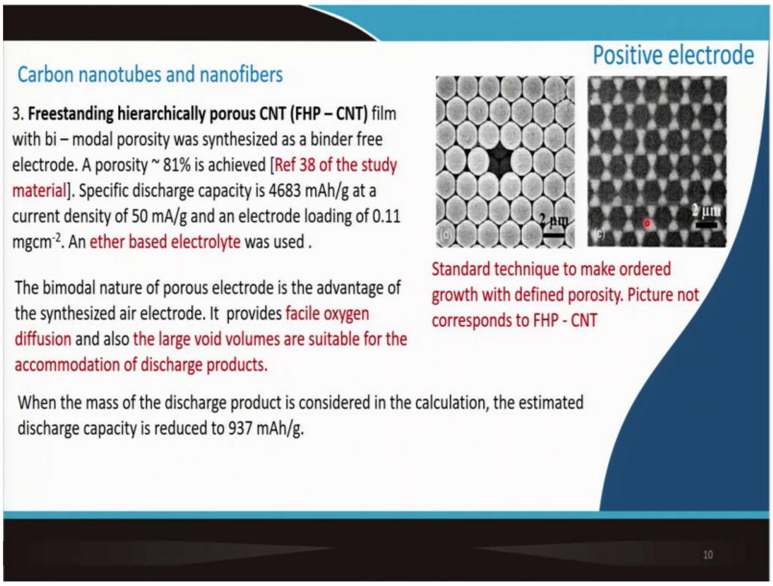

Positive electrode

Carbon nanotubes and nanofibers

3. **Freestanding hierarchically porous CNT (FHP – CNT)** film with bi – modal porosity was synthesized as a binder free electrode. A porosity ~ 81% is achieved [Ref 38 of the study material]. Specific discharge capacity is 4683 mAh/g at a current density of 50 mA/g and an electrode loading of 0.11 mgcm^{-2}. An ether based electrolyte was used .

The bimodal nature of porous electrode is the advantage of the synthesized air electrode. It provides facile oxygen diffusion and also the large void volumes are suitable for the accommodation of discharge products.

Standard technique to make ordered growth with defined porosity. Picture not corresponds to FHP - CNT

When the mass of the discharge product is considered in the calculation, the estimated discharge capacity is reduced to 937 mAh/g.

Now, porosity is important to how to make a bimodal kind of pore size distribution which is important and this is a representative figure. So, this is not exactly related to this free standing hierarchical porous carbon nanotube, so not the similar picture but the concept let me try to make you understand. So, if you take a polystrain this rubber this polystrain polymer balls and on a substrate you deposit is uniformly you will get this kind of structure.

Then usually oxygen plasma can be used so that this balls will get evaporated. Now if you have an active material and if you can infiltrate that active material inside this, then what will happen this active material will go there and form this kind of structure right. And by oxygen plasma if you get rid of this plastic balls then this will be the porous region, the bigger porous region will be those region where those balls were seated and this material has infiltrate to this triangular kind of void. So, this will be something like this.

So, they will also have small porous region. So, you have their bimodal kind of porosity distribution. So, bimodal means you have 2 different types of size of the porosity that you are getting. So, this is one way to make a bimodal kind of porosity. So, for this material carbon nanotube also its free standing ah, so free standing hierarchical porous carbon nanotube which was made by some similar technique and it had a bimodal porosity and it is a binder free electrode. So, you are not using any PVDF kind of or PAA kind of binder in it.

So, porosity is typically 81 percent. So, large porosity is achieved maintaining this electronic conduction, reference 38 you can read this paper. Specific capacity depends on how much Li 2 O 2 is being formed it is 4683 milliampere hour per gram, current density is relatively higher 50 milliampere per gram and electrode loading is important. How much electrode you are putting in this free standing carboniceous positive electrode.

And ether based electrolyte was used so that you do not have not completely eliminated, but lithium carbonate formation is grossly reduced. So, the bimodal nature of the porous electrode which was formed in this material, this gave some kind of advantage it provides facile oxygen diffusion.

There is one and also the discharge product they can be accommodated inside this other types of holes one hole is bigger another hole is smaller. So, the when the mass of the discharge product is considered for the calculation, because the carbon loading is also there. So, if you calculate estimate both this weight then this value was reduced to 937 milliampere hour per gram.

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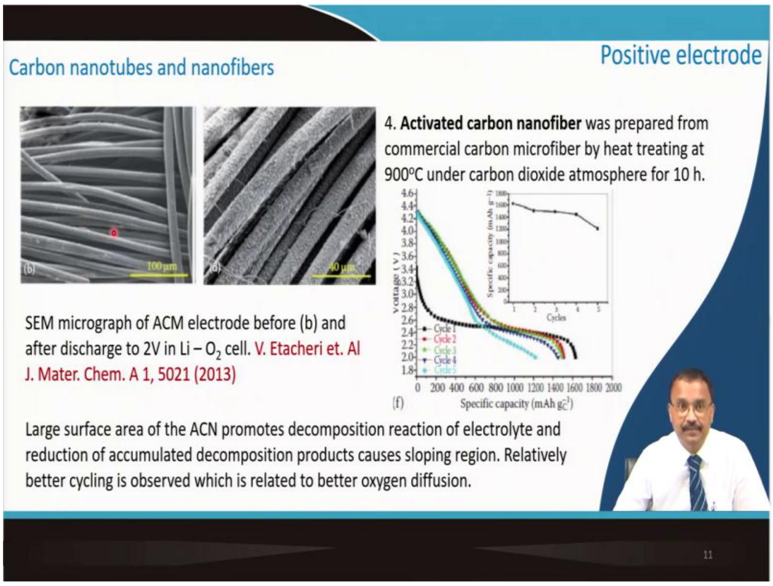

Carbon nanotubes and nanofibers

Positive electrode

4. **Activated carbon nanofiber** was prepared from commercial carbon microfiber by heat treating at 900°C under carbon dioxide atmosphere for 10 h.

SEM micrograph of ACM electrode before (b) and after discharge to 2V in Li – O_2 cell. V. Etacheri et. Al J. Mater. Chem. A 1, 5021 (2013)

Large surface area of the ACN promotes decomposition reaction of electrolyte and reduction of accumulated decomposition products causes sloping region. Relatively better cycling is observed which is related to better oxygen diffusion.

Carbon Nano fibers that is also used and this is one of the examples and you can see the SEM Scanning Electron Micrograph of the activated carbon Nano fiber, activated carbon we used I have talked about it while I was talking about the super capacitor. So, if you compare before and after discharge then you can see that some kind of deposition you can notice. So, this activated nano carbon, carbon nanofiber they were made by heat treating at this temperature under carbon dioxide atmosphere for 10 hours.

So, this large surface area of this carbon nanofiber that basically promotes the decomposition reaction of the electrolyte and reduction of accumulated decomposition product and that gives you this sloping region. So, this sloping region in the discharge profile is due to this fact. And very few cycles it survived about 5 charge discharge cycle it survived. And this is not very successful attempt because of the problem of this electrolyte decomposition.

So, suddenly the charge cycle it will be difficult for lithium oxygen to get efficiently dissociated, because of the presence of this electrolyte and decomposed product and the charge profile also you can see that will also reflect that cycleability is not as good as expected.

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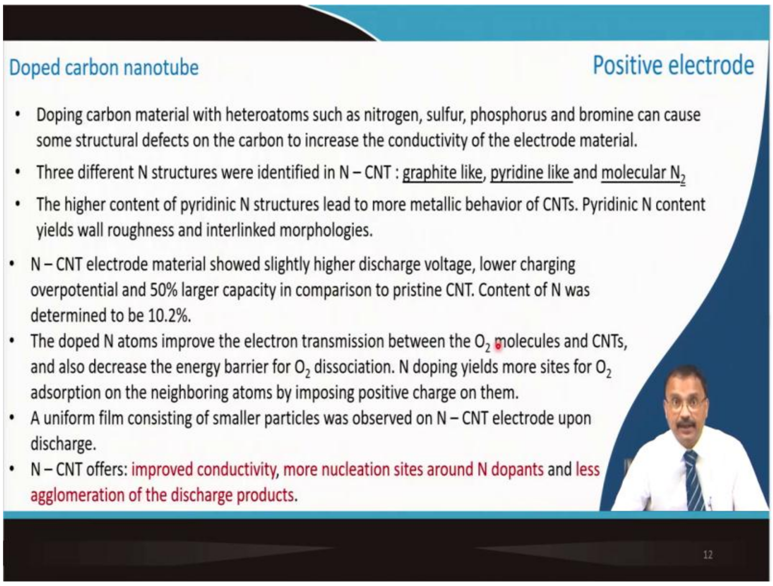

Doped carbon nanotube

Positive electrode

- Doping carbon material with heteroatoms such as nitrogen, sulfur, phosphorus and bromine can cause some structural defects on the carbon to increase the conductivity of the electrode material.
- Three different N structures were identified in N – CNT : graphite like, pyridine like and molecular N_2
- The higher content of pyridinic N structures lead to more metallic behavior of CNTs. Pyridinic N content yields wall roughness and interlinked morphologies.
- N – CNT electrode material showed slightly higher discharge voltage, lower charging overpotential and 50% larger capacity in comparison to pristine CNT. Content of N was determined to be 10.2%.
- The doped N atoms improve the electron transmission between the O_2 molecules and CNTs, and also decrease the energy barrier for O_2 dissociation. N doping yields more sites for O_2 adsorption on the neighboring atoms by imposing positive charge on them.
- A uniform film consisting of smaller particles was observed on N – CNT electrode upon discharge.
- N – CNT offers: improved conductivity, more nucleation sites around N dopants and less agglomeration of the discharge products.

Doped carbon nanotube that is giving a better data. So, three different types of nitrogen doped structure that was identified and you remember we talked about in case of graphene pyridine type, pyrolytic type, graphite type, nitrogen doping was there. So, various types of this heteroatoms it was tried with carbon nano material and that includes nitrogen, sulfur, phosphorus, bromine. So, they basically introduce structural defect in the carbon nanotube structure.

So, it is observed that if you have the pyridinic type of nitrogen doped structure that basically gives a metallic behavior in CNT and also the roughness of the carbon nanotube that is also influenced with a interlinked kind of morphology. So, this type of nitrogen doped carbon nanotube it exhibited slightly higher discharge voltage. So, that is good and charging potential is also relatively reduced a bit relative as compared to the pristine CNT.

And the nitrogen content was measured to be 10.2 percent. So, this doped nitrogen they basically improve the electron transmission between the oxygen molecules and the CNT something to do with the adhesion of this oxygen and the barrier for oxygen dissociation that is also decreased.

So, this nitrogen doping they provide more active sites for this efficient oxygen reduction reaction. And basically in this work people have found that the carbon nanotube they have a uniform film and because of this factors the conductivity is improved and they give little bit better electrochemical properties as compared to pure carbon nanotube structure.

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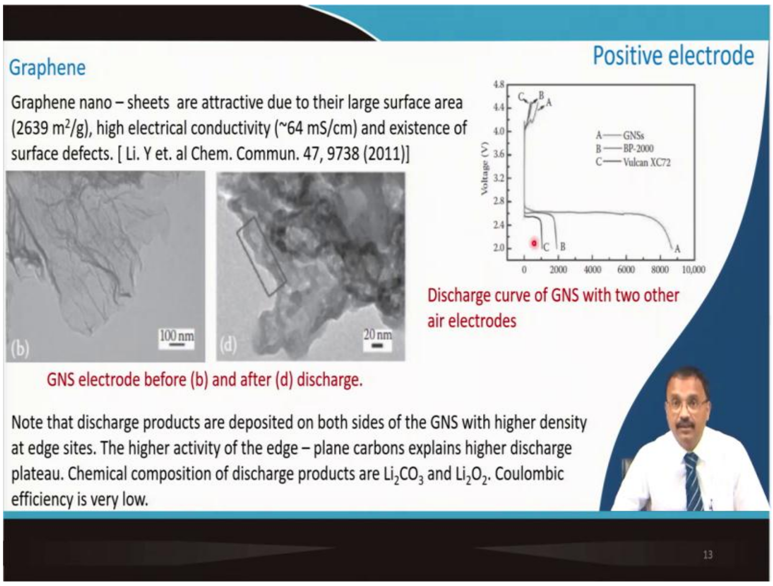
Positive electrode

Graphene

Graphene nano – sheets are attractive due to their large surface area (2639 m^2/g), high electrical conductivity (~64 mS/cm) and existence of surface defects. [Li. Y et. al Chem. Commun. 47, 9738 (2011)]

GNS electrode before (b) and after (d) discharge.

Discharge curve of GNS with two other air electrodes

Note that discharge products are deposited on both sides of the GNS with higher density at edge sites. The higher activity of the edge – plane carbons explains higher discharge plateau. Chemical composition of discharge products are Li_2CO_3 and Li_2O_2. Coulombic efficiency is very low.

Graphene Nano sheet which is abbreviated as GNS that is also used it is having extremely high surface area that you can understand we already talked about Graphene Nano sheet, electrical conductivity is also quite large. But as you can see that this is a pristine graphene and then this type of discharge product they are deposited in both sides of this graphene nanosheet.

And therefore, it gives a very large discharge capacity as compared to other types of electrode, but during charge you are not getting it back, so the coulombic efficiency never improved. So, discharged product is formed in this particular study and it is suspected that this discharge product is lithium carbonate, because they have used carbonate based electrolyte. So, this is not very encouraging result one could get when they used graphene.

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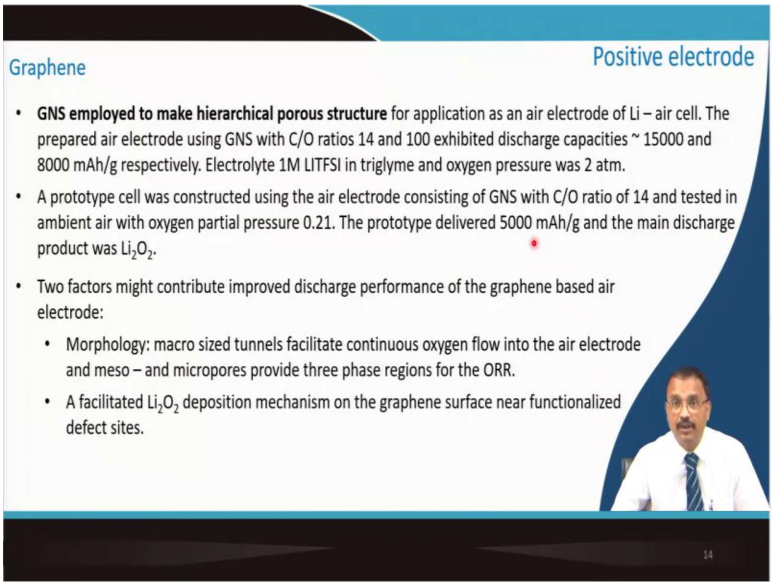

Graphene

Positive electrode

- **GNS employed to make hierarchical porous structure** for application as an air electrode of Li – air cell. The prepared air electrode using GNS with C/O ratios 14 and 100 exhibited discharge capacities ~ 15000 and 8000 mAh/g respectively. Electrolyte 1M LITFSI in triglyme and oxygen pressure was 2 atm.
- A prototype cell was constructed using the air electrode consisting of GNS with C/O ratio of 14 and tested in ambient air with oxygen partial pressure 0.21. The prototype delivered 5000 mAh/g and the main discharge product was Li_2O_2.
- Two factors might contribute improved discharge performance of the graphene based air electrode:
  - Morphology: macro sized tunnels facilitate continuous oxygen flow into the air electrode and meso – and micropores provide three phase regions for the ORR.
  - A facilitated Li_2O_2 deposition mechanism on the graphene surface near functionalized defect sites.

14

So, graphene nanosheet they are also used to make hierarchical porous structure. So, this is the cell configuration electrode with GNS with carbon oxygen ratio is 14 and 100. They actually exhibited quite large capacity and electrolyte is used standard 1 M LITFSI in a solvent triglyme and oxygen pressure was 2 atmosphere. So, in this particular work a prototype cell was constructed and it was tested and it delivered more or less encouraging capacity and the main discharge product was Li 2 O 2.

So, the electrolyte decomposition problem was partially removed. So, it is identified that the discharge performance of the graphene is due to the morphology, the macro size channel porosity which I was talking about which gives the efficient oxygen reduction reaction and also the discharge product deposition mechanism that is also effective. So, it fascilates the Li 2 O 2 deposition mechanism on this graphitic structure.

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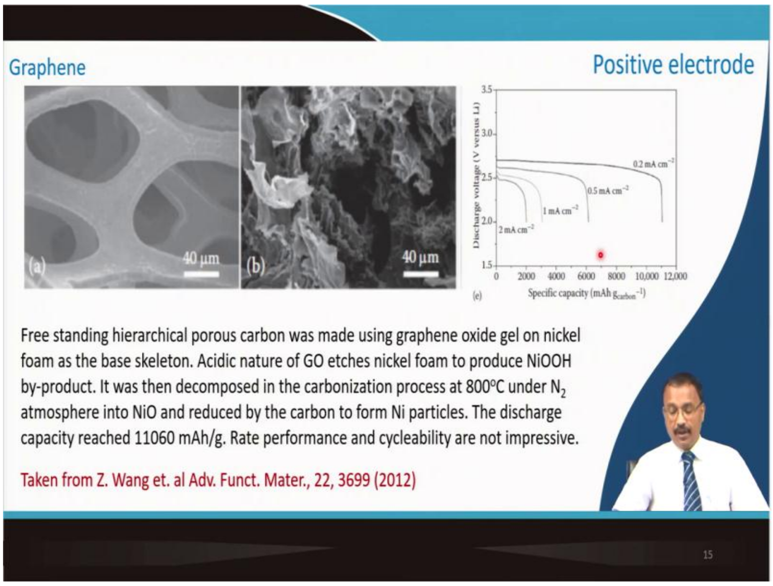

Graphene

Positive electrode

Free standing hierarchical porous carbon was made using graphene oxide gel on nickel foam as the base skeleton. Acidic nature of GO etches nickel foam to produce NiOOH by-product. It was then decomposed in the carbonization process at 800°C under N_2 atmosphere into NiO and reduced by the carbon to form Ni particles. The discharge capacity reached 11060 mAh/g. Rate performance and cycleability are not impressive.

Taken from Z. Wang et. al Adv. Funct. Mater., 22, 3699 (2012)

So, this structure proved to be better as compared to the other carbonaceous material. So, this is a free standing porous structure. So now, in this case this reference used this graphene oxide on a nickel foam as a base skeleton. Now, this graphene oxide they basically etch the nickel form on which they are deposited to form this NiOOH then heat treated at 800 in nitrogen atmosphere.

Then this nickel oxide which was produced that was reduced by this carbon and it form nickel particle. Discharge capacity as you can see for this kind of structure is reasonably good, but at relatively lower current density. But as you increase the current density then the discharge capacity is grossly reduced.

So, in other words the case studies whatever I am presenting you see they are trying to improve the properties, but it is not possible yet to improve the properties all at a once. So, sometimes the rate performance always remain a problem, but coulombic efficiency then the first discharge capacity little bit cycleability they have improved.

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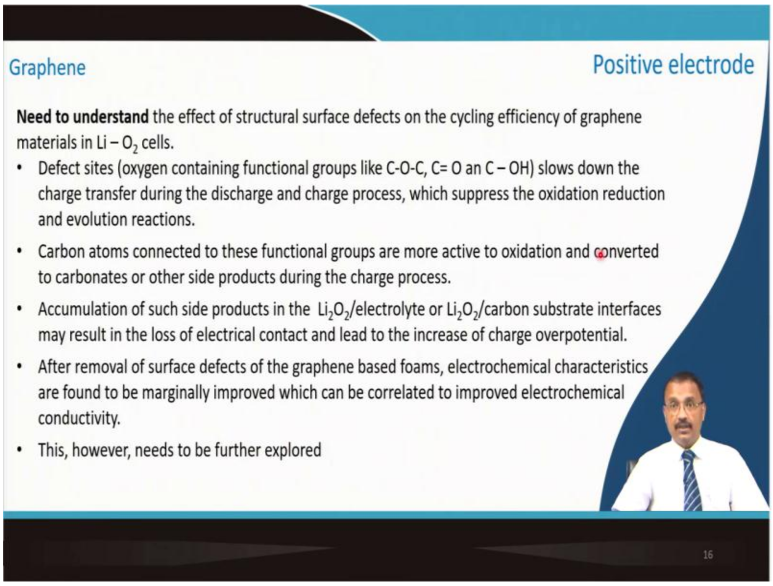

Graphene

Positive electrode

Need to understand the effect of structural surface defects on the cycling efficiency of graphene materials in Li – O_2 cells.

- Defect sites (oxygen containing functional groups like C-O-C, C= O an C – OH) slows down the charge transfer during the discharge and charge process, which suppress the oxidation reduction and evolution reactions.
- Carbon atoms connected to these functional groups are more active to oxidation and converted to carbonates or other side products during the charge process.
- Accumulation of such side products in the Li_2O_2/electrolyte or Li_2O_2/carbon substrate interfaces may result in the loss of electrical contact and lead to the increase of charge overpotential.
- After removal of surface defects of the graphene based foams, electrochemical characteristics are found to be marginally improved which can be correlated to improved electrochemical conductivity.
- This, however, needs to be further explored

But not a material has been developed a battery has been developed which is optimized in terms of its desirable electrochemical properties. So, in case of graphene lot of things we need to understand this structural surface that should be properly characterized. So, particularly the defect size oxygen containing functional group it is having carbon oxygen carbon or carbon double bind oxygen, they actually slow down the charge transfer during the charge discharge process.

And this is basically your this oxygen reduction reaction and OER reactions. So, this will have to be controlled. Second point is the carbon atom which is connected to this functional group are more active to the oxidation and there is a strong tendency that it forms carbonate or other side product not Li 2 O 2.

Then third is this accumulation of the side product in the surface either Li 2 O 2 electrolyte surface or Li 2 O 2 carbon substrate interface that eventually can lose the electrical contact and therefore it increases the over potential. Now, if you can remove this surface defect of this graphene based material, then marginally electrochemical characteristics are improved, but as I said it needs to be further improved.

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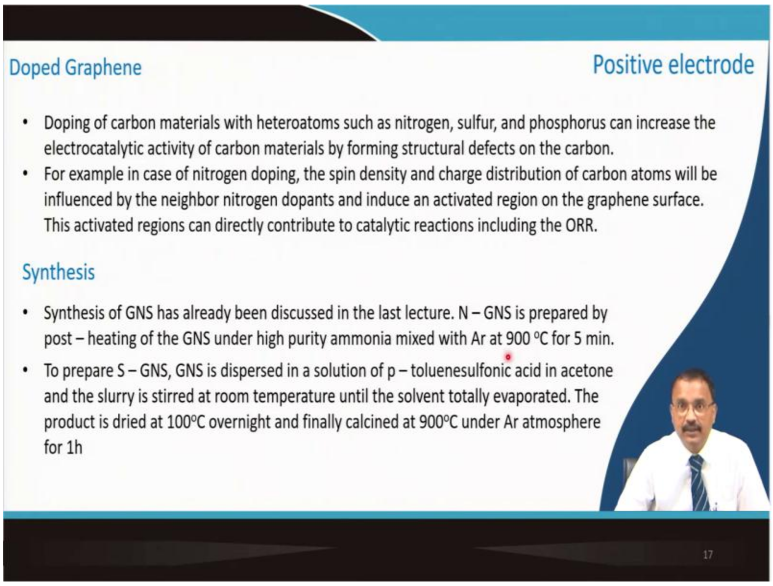

Doped Graphene

Positive electrode

- Doping of carbon materials with heteroatoms such as nitrogen, sulfur, and phosphorus can increase the electrocatalytic activity of carbon materials by forming structural defects on the carbon.
- For example in case of nitrogen doping, the spin density and charge distribution of carbon atoms will be influenced by the neighbor nitrogen dopants and induce an activated region on the graphene surface. This activated regions can directly contribute to catalytic reactions including the ORR.

Synthesis

- Synthesis of GNS has already been discussed in the last lecture. N – GNS is prepared by post – heating of the GNS under high purity ammonia mixed with Ar at 900 °C for 5 min.
- To prepare S – GNS, GNS is dispersed in a solution of p – toluenesulfonic acid in acetone and the slurry is stirred at room temperature until the solvent totally evaporated. The product is dried at 100°C overnight and finally calcined at 900°C under Ar atmosphere for 1h

Finally, Graphene also is doped 2 types of dopants are used one is nitrogen doping and another one is sulfur doping. So, doping with nitrogen is advantages and basically in case of nitrogen doping the charge distribution the spin density of the charge distribution of the carbon atom they will be influenced by the dopant atom which is nitrogen.

And basically that will induce the active sites on the graphene surface and this active sites they basically act as a catalyst to improve the oxygen reduction reaction. So, that is the mechanism which is understood by this literature reports. Now, graphene nanosheet you know how to make it and in order to make nitrogen doping it is basically done by high purity ammonia which is mixed with argon and heat treat it the whole structure at 900 degree Celsius for 5 minutes.

If you want to make sulfur dopant sulfur doped on graphene nanosheet, then this graphene nanosheet is dispersed in a solution of this toluenesulfonic acid and acetone. So, that introduce the sulfur then the solvent is evaporated and the final product is initially dried and calcined at nine hundred in argon ambient for the sulfur doping.

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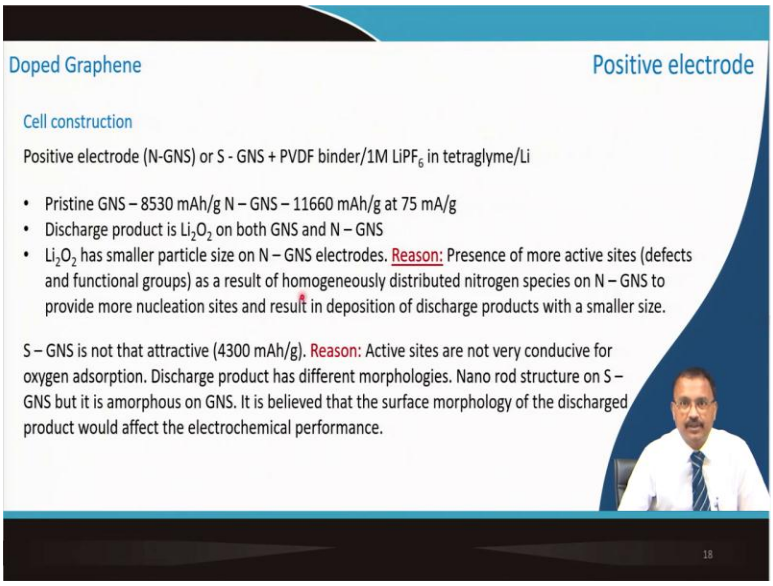

Doped Graphene

Positive electrode

Cell construction

Positive electrode (N-GNS) or S - GNS + PVDF binder/1M $LiPF_6$ in tetraglyme/Li

- Pristine GNS – 8530 mAh/g N – GNS – 11660 mAh/g at 75 mA/g
- Discharge product is Li_2O_2 on both GNS and N – GNS
- Li_2O_2 has smaller particle size on N – GNS electrodes. Reason: Presence of more active sites (defects and functional groups) as a result of homogeneously distributed nitrogen species on N – GNS to provide more nucleation sites and result in deposition of discharge products with a smaller size.

S – GNS is not that attractive (4300 mAh/g). Reason: Active sites are not very conducive for oxygen adsorption. Discharge product has different morphologies. Nano rod structure on S – GNS but it is amorphous on GNS. It is believed that the surface morphology of the discharged product would affect the electrochemical performance.

So, the cell is something like that you have nitrogen or sulfur doped graphene nano sheet we have PVDF binder that is there, so that forms the positive electrode. Then 1 molar LiPF 6 in tetraglyme. So, that is the solvent that is the electrolyte which reduce the formation of this lithium carbonate or other side product or decomposition of the electrolyte is grossly retarded and you have metallic lithium.

So, if you compare pristine graphene which gives you this much of capacity nitrogen gives you much larger capacity, even if you keep the current constant at 75 milliampere per gram. Discharge product is Li 2 O 2 in both this both in GNS and nitrogen dope GNS and this is due to the fact because you are using non carbonate based solvent.

Now the formation of this Li 2 O 2 that is having relatively smaller particle size which is actually required, you know why because the porous region if it is a very large chunk is formed it will block the structure. So, as I said either thin deposition or a smaller particle size is welcome.

So, it basically produce more active sites both defects and functional groups and this is due to the fact that nitrogen is homogeneously doped into the graphene nanosheet and it provides more nucleation site and the discharge product is also of smaller size. So, therefore, the capacity is increased. As compared to this nitrogen doped GNS sulfur doped GNS is not very attractive as you can see it only yields very small capacity as compared to nitrogen doped GNS.

The reason for this is that the active site is not very conducive for oxygen adsorption and also this discharge product they are having a different morphology. So, the microstructure shows the nanorod structure forms it is not a particulate structure, but a nanorod structure forms on sulfur doped Grapheme Nano sheet.

If you compare it with pure graphene nanosheet usually the structure is amorphous in nature. So, electrical performance that is related to this kind of morphology, so if it is small particle size does not clog the porous nature or the surface active site in case of graphene then you can expect a better electrochemical performance.

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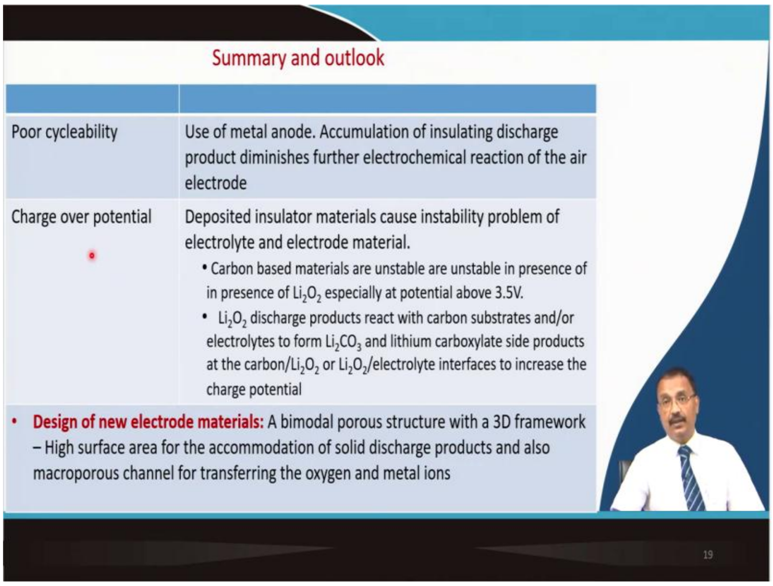

Summary and outlook

Poor cycleability	Use of metal anode. Accumulation of insulating discharge product diminishes further electrochemical reaction of the air electrode
Charge over potential	Deposited insulator materials cause instability problem of electrolyte and electrode material. • Carbon based materials are unstable are unstable in presence of in presence of Li_2O_2 especially at potential above 3.5V. • Li_2O_2 discharge products react with carbon substrates and/or electrolytes to form Li_2CO_3 and lithium carboxylate side products at the carbon/Li_2O_2 or Li_2O_2/electrolyte interfaces to increase the charge potential

- **Design of new electrode materials:** A bimodal porous structure with a 3D framework – High surface area for the accommodation of solid discharge products and also macroporous channel for transferring the oxygen and metal ions

So, finally, this poor cycleability use of metal anode poor cycleability is always there. So, that we have seen and we have discussed time and again, accumulation of insulating discharge product they basically diminishes the further electrochemical reaction of the air electrode.

Charge over potential that is a major problem and this is related to the formation of the various side product other than lithium oxide. So, that basically gives you this charge over potential, to get the good performance as far as your rate performance is concerned it still we are not very sure that what exactly is needed.

Of course, reduction of the diffusion part will help and in that way a 3D structure might be helpful, but if you want to make a good structure for LiO 2 battery then it is understood that a bimodal porous structure with a 3D framework. So, that the electron can transport efficiently that will be helpful. And of course, high surface area is required and for the accommodation of this discharge product Li 2 O 2, macro porous channel is required for oxygen transport and lithium transport. So, in other word designing of the electrode is important.

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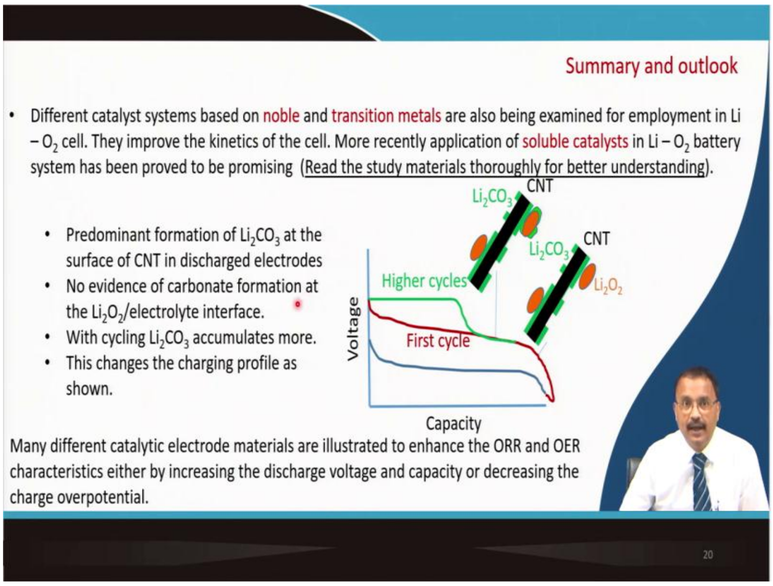

Summary and outlook

- Different catalyst systems based on noble and transition metals are also being examined for employment in Li – O_2 cell. They improve the kinetics of the cell. More recently application of soluble catalysts in Li – O_2 battery system has been proved to be promising (Read the study materials thoroughly for better understanding).
  - Predominant formation of Li_2CO_3 at the surface of CNT in discharged electrodes
  - No evidence of carbonate formation at the Li_2O_2/electrolyte interface.
  - With cycling Li_2CO_3 accumulates more.
  - This changes the charging profile as shown.

Many different catalytic electrode materials are illustrated to enhance the ORR and OER characteristics either by increasing the discharge voltage and capacity or decreasing the charge overpotential.

So, various types of catalyst is used to reduce the over potential and to improve the kinetics of this reactions. So, this kind of electro catalyst they could be noble metal they could be transition metal oxide and in very recent time people have used soluble catalyst also.

So, I have given sufficient references and please go through that and their performance you will be able to see that individual catalyst what exactly they are doing. So, formation of this Li 2 CO 3 and other side product that is a disadvantage for lithium air batteries and carbonate formation exactly on the discharge product we do not have this kind of evidence yet and once you cycle it more than actually this lithium carbonate they forms and this is not shown here.

So, when the discharge just starts and if I consider a carbonate based solvent or ether based solvent is used, it is almost inevitable that lithium carbonate this green material is forming and this is a carbon nanotube material. So, it forms and on top of that Li 2 O 2 this is form this Li 2 O 2 is also forming now as you increase the charge cycle then basically it will get discharged. But eventually this will this formation of lithium carbonate it is not very easy to discharge, so it will basically cover this.

So, as you can see that initially the over potential is little bit low, but at higher cycles this will start to increase and eventually after a few cycles the battery will fail because of this over potential. So, the use of catalyst is almost inevitable to enhance the oxygen reduction reaction and oxygen evaluation reaction and that will decide the final characteristics of this lithium oxygen batteries.

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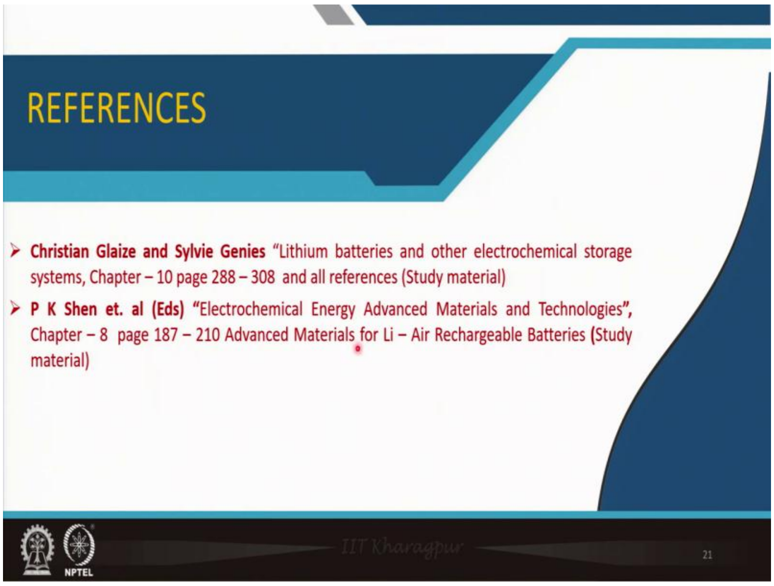

REFERENCES

- **Christian Glaize and Sylvie Genies** "Lithium batteries and other electrochemical storage systems, Chapter – 10 page 288 – 308 and all references (Study material)
- **P K Shen et. al (Eds)** "Electrochemical Energy Advanced Materials and Technologies", Chapter – 8 page 187 – 210 Advanced Materials for Li – Air Rechargeable Batteries (Study material)

The reference for this particular work is by both these books and please look at the literature and the references that is cited in the second reference.

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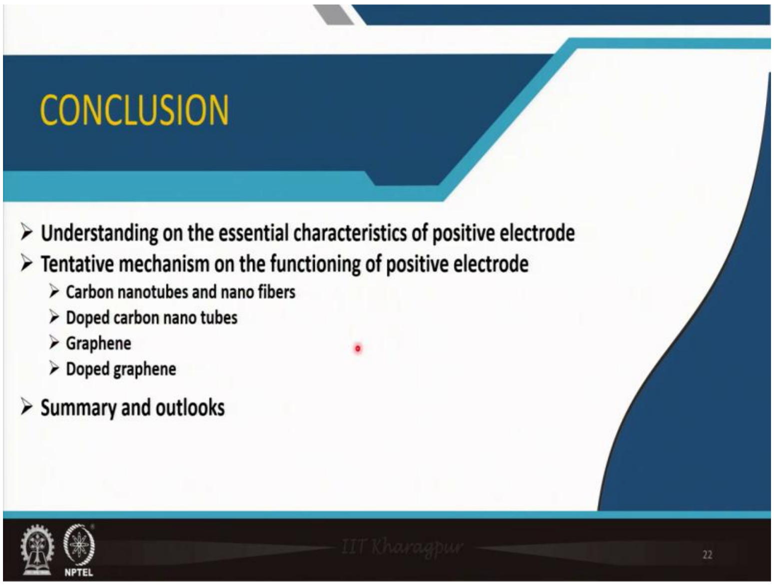

CONCLUSION

- Understanding on the essential characteristics of positive electrode
- Tentative mechanism on the functioning of positive electrode
  - Carbon nanotubes and nano fibers
  - Doped carbon nano tubes
  - Graphene
  - Doped graphene
- Summary and outlooks

So, in this particular lecture we try to understand the essential characteristics of positive electrode and the tentative mechanism of the functioning of the positive electrode and in terms of carbon nanotubes and nanofibers then doped carbon nanotubes, then graphene and doped graphene. And finally I tried to summarize the state of the art of lithium oxygen batteries and certainly more research is needed to make it a commercially viable product.

Thank you for your interest.