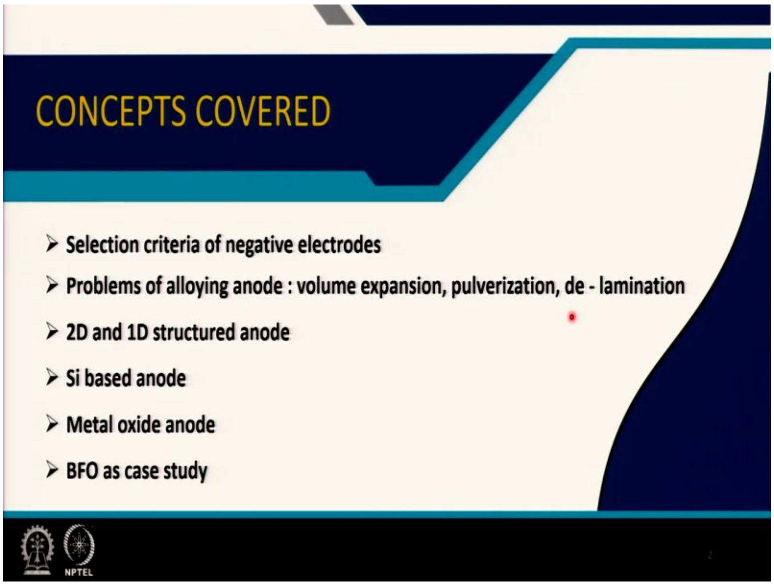
Electrochemical Energy Storage
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 04
Basic components in Li – ion batteries: Electrodes, Electrolytes, and collectors
Lecture - 17
Negative Electrodes: Carbonaceous Materials, Lithium Titanium Oxides etc

Welcome to my course, Electrochemical Energy Storage and this is module number 4 where I am describing the Basic Components in Lithium ion Batteries; including the Electrodes, Electrolytes, and Collectors to be specific. And, in lecture number 17, we will be talking about the Negative Electrodes and particularly Carbonaceous Material, Lithium Titanium Oxides and other relevant materials.

(Refer Slide Time: 00:55)

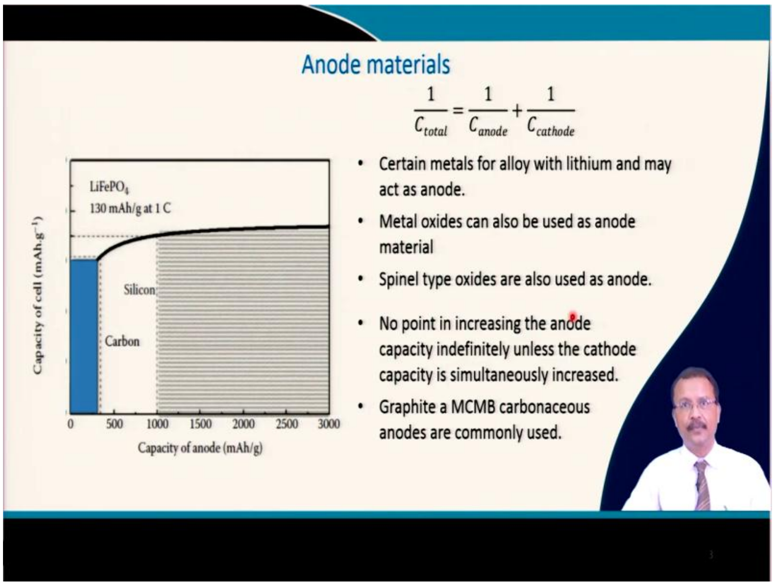


CONCEPTS COVERED

- Selection criteria of negative electrodes
- Problems of alloying anode : volume expansion, pulverization, de - lamination
- 2D and 1D structured anode
- Si based anode
- Metal oxide anode
- BFO as case study

So, the selection criteria of negative electrode that will be covered first, then we will talk about the alloying anode. And, what are their actual difficulties, that we will recapitulate once again. Then how to overcome that in terms of 2 D and 1 D structural anode that we will be talking about, then, silicon based anode, that we will introduce and metal oxide anode also will be introduced. And, at the end a case study of bismuth iron oxide, which I one of my earlier lectures we talked about, so, that we will also introduce.

(Refer Slide Time: 01:45)



Anode materials

$$\frac{1}{C_{total}} = \frac{1}{C_{anode}} + \frac{1}{C_{cathode}}$$

- Certain metals for alloy with lithium and may act as anode.
- Metal oxides can also be used as anode material
- Spinel type oxides are also used as anode.
- No point in increasing the anode capacity indefinitely unless the cathode capacity is simultaneously increased.
- Graphite a MCMB carbonaceous anodes are commonly used.

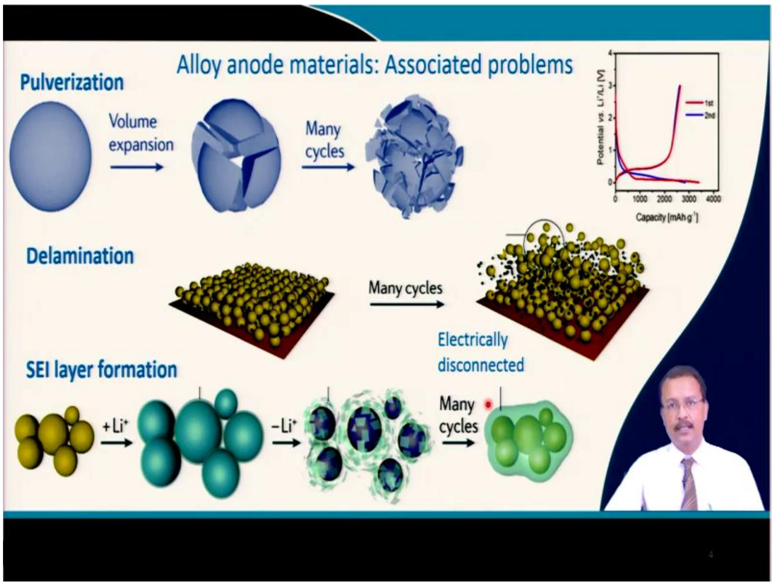
$$\frac{1}{C_{total}} = \frac{1}{C_{anode}} + \frac{1}{C_{cathode}}$$

So, this already you know that there is no point in indefinitely increasing the capacity of the anode, because if you do not increase the capacity of the cathode. Then eventually will not be it will not be beneficial for you. Because it is basically two capacitor, which are connected in series, so it if it is abnormally high and if it is low then the total capacity will be lower than this particular capacity of this particular electrode.

Now, certain metal metals for alloy that actually forms, that forms alloy with lithium and may act as anode that by this time you suddenly know. Now, metal oxide can also act as an anode material that also I have explained in a form of a case study.

Spinel type oxide that also can be used as anode lithium titanium oxide is another example. And, traditionally graphite and this MCMB carbonaceous material that actually commercially used as anode material, so, we will have a look at different anode material that you are having for lithium ion batteries.

(Refer Slide Time: 03:14)



Alloy anode materials: Associated problems

Pulverization

Delamination

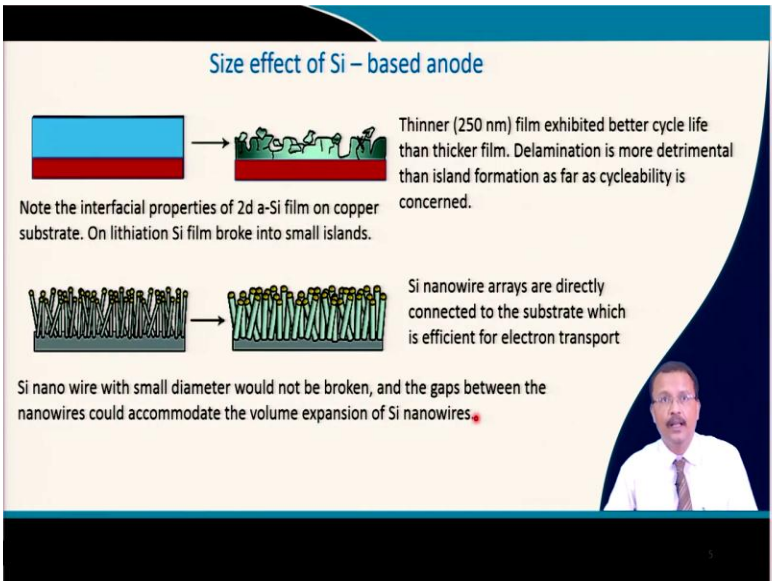
SEI layer formation

Now, as a recapitulation this alloy base anode has a problem of volume expansion, and that leads to pulverization, and after many cycles this will be disintegrated like this. And, the structural integrity with the this current collector will not be there and that is the major problem.

Delamination will take place and once it delaminate after many cycles then that is also detrimental for the performance of the battery. It is unavoidable at lower voltage potential to form this SEI layer on the top of the surface of this active material.

So, this actually forms a disintegrated kind of SEI layer and then after many cycle it forms a some kind of thicker SEI layer. And, if it is impervious to lithium ion, then that is also a problem. And, this is related to as you can understand the lumo band and the Fermi energy level of the anode which I have explained several times in my earlier part, earlier lectures.

(Refer Slide Time: 04:33)



Size effect of Si – based anode

Thinner (250 nm) film exhibited better cycle life than thicker film. Delamination is more detrimental than island formation as far as cycleability is concerned.

Note the interfacial properties of 2d a-Si film on copper substrate. On lithiation Si film broke into small islands.

Si nanowire arrays are directly connected to the substrate which is efficient for electron transport

Si nano wire with small diameter would not be broken, and the gaps between the nanowires could accommodate the volume expansion of Si nanowires.

Now, let us consider another material which is not metal, but semiconducting in nature. So, silicon is one of them, it has a huge potential as negative electrode material. So, one deposited a thinner about 250 nanometer film on copper current collector. And, it actually exhibited a relatively better cycler life than a micron thick film.

But, if a film is thicker than a particular thickness this 2 d dimension film, then delamination takes place which is more detrimental, than the form of island formation. Because there are two types of difficulties that can be there for this type of anode. So, when lithium forms an alloy, then the first it will try to form the island structure, not the continuous structure and that is part of this pulverization.

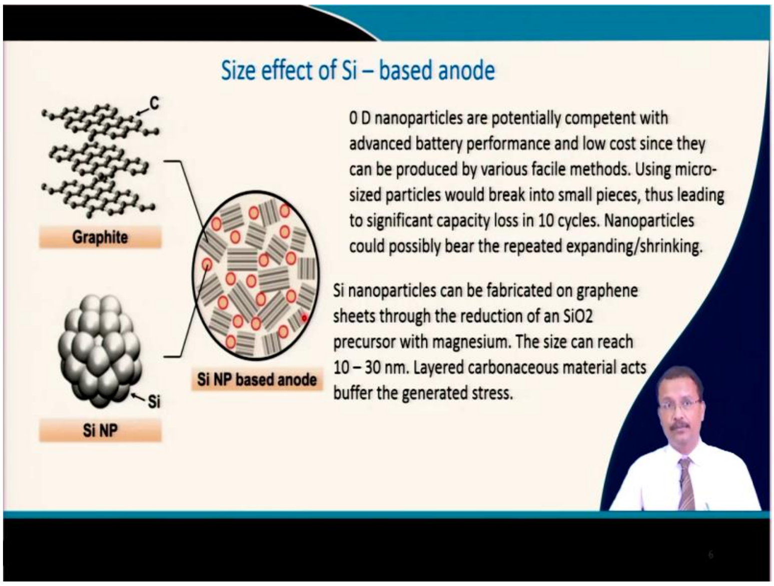
And, then finally, it will be delaminated. So, even if it is pulverized still it is in contact with the current collector. So, capacity fades, but it is not that detrimental, but if it delaminates then it loses contact with the current collector. So, that is more dangerous.

So, in order to overcome people have started to grow different types of structure. So, one of this kind of structure is in the form of a nanowire as you can see. This nanowire is directly connected here with the current collector with the substrate and this is efficient for the electron transport.

And, there is a volume expansion that you cannot avoid, but you know that there is space available in between this is a structure we call it is a bristle structure same like your toothbrush the bristles. So, this structure is effective, if you start to grow the silicon nanowire in smaller dimension with lots of gaps in between and it is firmly adhered with the current collector.

So, this small diameter will not that easily break. Although the volume expansion will be there the space will be filled up, but it will still perform. So, this is one of the structure and this has been experimentally verified. And, there therefore, people have started to think about the size effect, the effect of nanostructure in the size effect in controlling the electrochemical properties of this material.

(Refer Slide Time: 07:33)



Size effect of Si – based anode

0 D nanoparticles are potentially competent with advanced battery performance and low cost since they can be produced by various facile methods. Using micro-sized particles would break into small pieces, thus leading to significant capacity loss in 10 cycles. Nanoparticles could possibly bear the repeated expanding/shrinking.

Si nanoparticles can be fabricated on graphene sheets through the reduction of an SiO2 precursor with magnesium. The size can reach 10 – 30 nm. Layered carbonaceous material acts buffer the generated stress.

So, if a nanoparticle is synthesized if the size is reduced considerably, almost a 0 dimension nanoparticles. They are potentially competent with advanced battery performance at low cost. Since, they can be actually produced by various facile methods. So, it is not that cumbersome to grow the bristle like structure on a current collector.

So, the use of a micron size particle. So, that has a problem, that will break into various small pieces and that basically will lead to the capacity loss. Now, if you have a very small particle, then it is good for you, because it will not have this kind of severe pulverization effect. So, breaking a smaller particle is very difficult.

So, you take a piece of chalk you can easily break it take the broken part try to break it is also you will have to put more effort, but once it is very small it is very difficult to break.

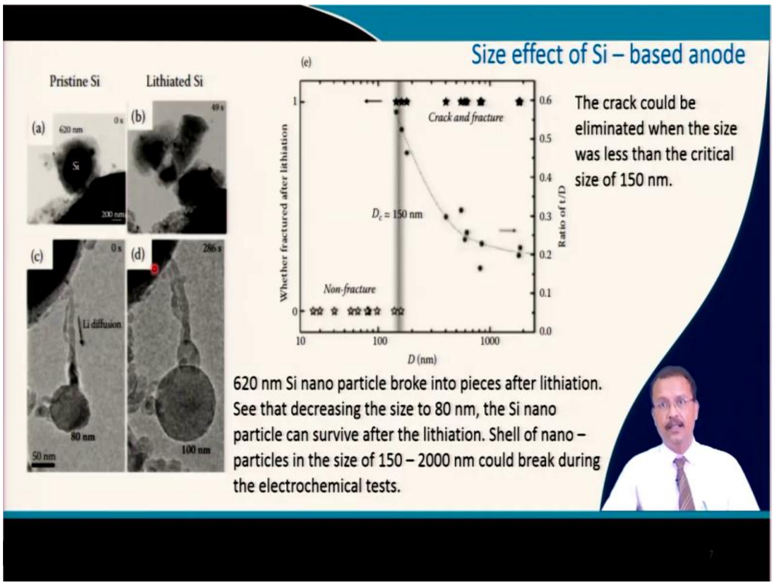
But, at the same time your specific surface area will start to increase and then there will be interaction with the electrolyte and that will form SEI layer, which is usually will be deposited on the surface. And, this SEI layer if it is disintegrate, if it is not mechanically very strong or if it is impervious to lithium, then that is of no use right.

So, silicon nanoparticle can be fabricated on graphene sheet. So, this is the graphite and this graphite each part the flake you take a single part it is graphene and in fact, the single sheet is very difficult to get. So, there are multiple of this sheets and then is the silicon nanoparticle, they can be fabricated on this graphene sheet, through the reduction of silicon dioxide particle with magnesium.

So, if you reduce silicon dioxide with magnesium to form silicon nanoparticle and then embed it to the graphene sheet, and the size of this nanoparticle is in the range of 10 to 30 nanometer so, quite small. Then even if there is a volume expansion takes place the stress will actually be buffered by this graphene layers which are very strong.

So, it is one of the configuration that you can think of, but the challenge is that such a small nanoparticle usually because of their high surface energy, they always try to form this kind of agglomerate. So, if it forms the agglomerate, then this is not this is something like a bigger particle, although the individual particle is in the nano range. So, disperse of this in this kind of situation in the in between the graphene sheet, that is indeed challenging.

(Refer Slide Time: 10:52)



Size effect of Si – based anode

The crack could be eliminated when the size was less than the critical size of 150 nm.

620 nm Si nano particle broke into pieces after lithiation. See that decreasing the size to 80 nm, the Si nano particle can survive after the lithiation. Shell of nano – particles in the size of 150 – 2000 nm could break during the electrochemical tests.

So, this is one of the experimental evidence that has been taken from literature, just to show that what exactly happens, when the particle size is reduced. So, this is as you can see a pristine silicon which is 620 nanometer size. And, then once you Lithiate it will form alloy with this silicon, but it will start to disintegrate you see that it has been disintegrated to smaller size.

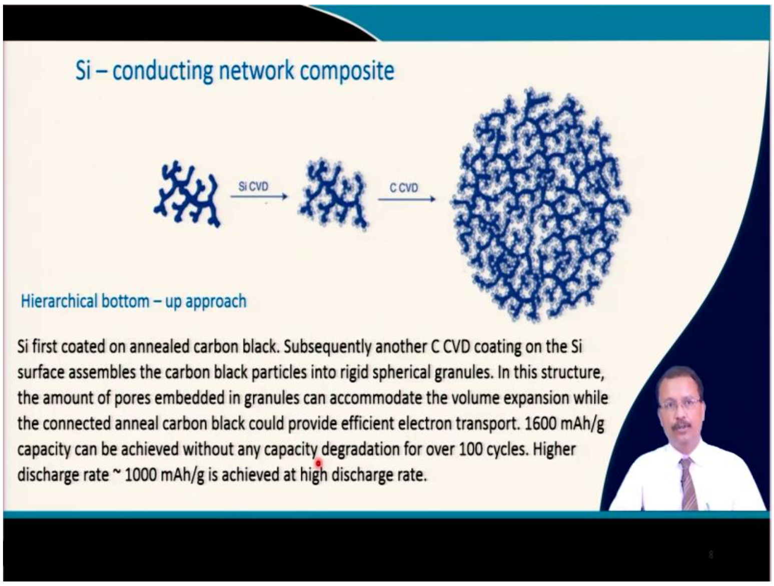
But, once you reduce the size to this level 80 nanometer. Then, as you can see, that it increases with lithiation the size indeed increases, but it is not that detrimental, that it is completely pulverized and it is away delaminated from the current collector. So, that phase is not there, if the size is reduced.

So, if you just pictographically want to see that, then there is a size range here, below that say around 120 nanometer. Actually, we do not find any fracture it will have a volume expansion from here to here, but there will be no fracture like you can see the larger particle size. So, fracture will not be there in this size range the fracture will not be there in this size range, but if it is beyond a critical size, then crack will form and it will be disintegrated.

So, the thickness to diameter ratio is important. So, as you can see that if the diameter is increased here considerably, then this fracture is I mean you cannot avoid it. So, this is one of the reason that, this type of material one should have the process to grow, a facile process to grow, in small dimension.

And, usually if the shell of this nano particle is in the size of in between 150 to 2,000 usually they break during electrochemical test. By shell I means if you see the earlier picture that nanoparticles will be slightly agglomerated. So, the size will grow like this although the individual particle size is that low that is also of no good, because this eventually will disintegrate and that will not serve the purpose of a good anode.

(Refer Slide Time: 13:32)



Si – conducting network composite

Hierarchical bottom – up approach

Si first coated on annealed carbon black. Subsequently another C CVD coating on the Si surface assembles the carbon black particles into rigid spherical granules. In this structure, the amount of pores embedded in granules can accommodate the volume expansion while the connected anneal carbon black could provide efficient electron transport. 1600 mAh/g capacity can be achieved without any capacity degradation for over 100 cycles. Higher discharge rate ~ 1000 mAh/g is achieved at high discharge rate.

Another process that is called hierarchical bottom up approach, where you can have the silicon although this process is a bit complicated for practical implication. But as a laboratory study academic interest one can do that, that this silicon is first coated on this kind of carbon black structure.

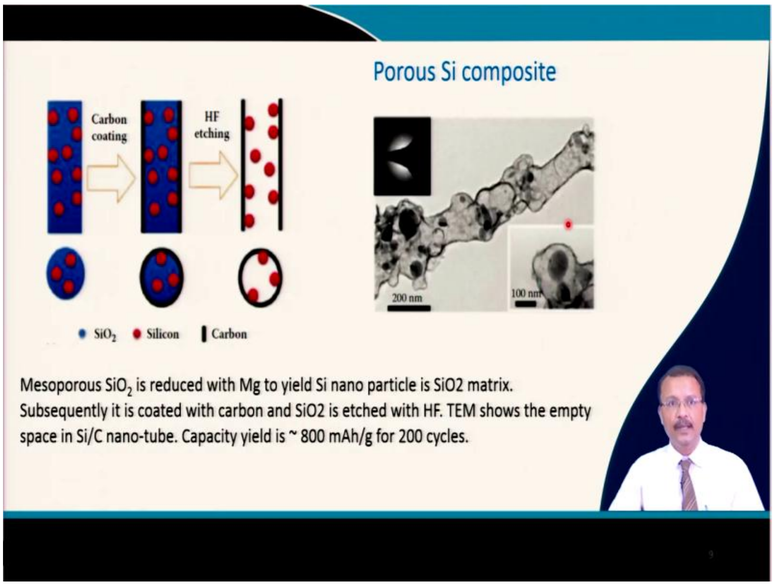
So, as you can see by CVD it is coated. So, it forms this kind of CVD silicon coated on this structure. And, subsequently another carbon CVD coating is done on the silicon surface. On top of the surface you grow carbon layer film which is amorphous in nature on the silicon surface. So, this carbon black particles forms a rigid spherical type of granules.

So, in this type of structure the amount of pore which is embedded in the structure, that can accommodate the volume expansion, while the connected annealed carbon black could provide the efficient electron transport. So, here if the volume is expands then this space, which is there in between that will accommodate this volume expansion. And, this continuous growth of this carbon pathway, that will lead to the electron transport.

So, people have done it and you can see that about 1600 milliampere hour per grand capacity can be achieved without any capacity degradation up to 100 cycles and also you can drain more current. So, the rate performance is also quite good. So, at high discharge rate this 1600 as you know that if I increase the rate then usually the capacity reduces.

So, at higher rate also the capacity reduced, but it is still 1000 milliampere hour per gram.

(Refer Slide Time: 15:50)



Porous Si composite

Mesoporous SiO_2 is reduced with Mg to yield Si nano particle is SiO2 matrix. Subsequently it is coated with carbon and SiO2 is etched with HF. TEM shows the empty space in Si/C nano-tube. Capacity yield is ~ 800 mAh/g for 200 cycles.

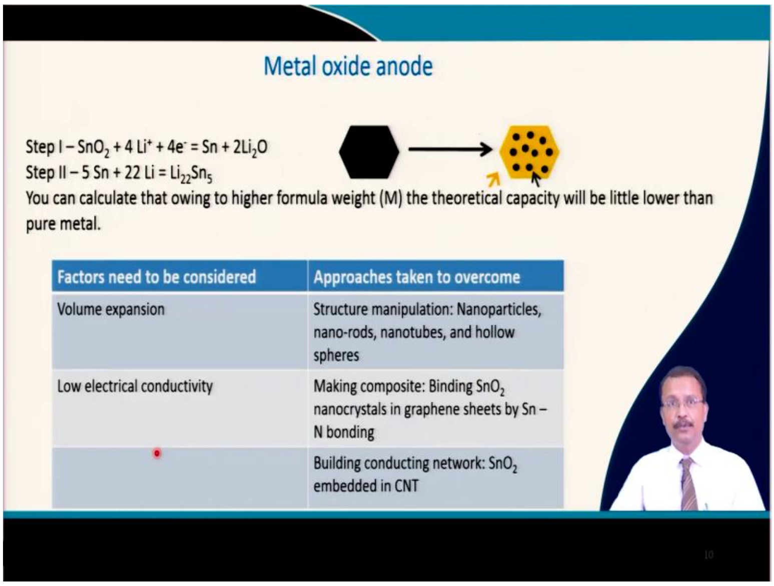
Another interesting structure is a Porous silicon composite. So, here what is done a Mesoporous silicon dioxide, that is first reduced with manganese to form this silicon, this red balls, they are of silicon and this is formed in S i O 2 matrix.

And, then, finally, this matrix and this silicon they are coated with carbon layer. You can see this is coated with carbon layer with a carbon coating, and then with hydrofluoric acid this S i O 2 is eaten up they are etched this part the blue part is etched. So, you get the carbon and this silicon nanoparticles.

So, lot of space is there for the lithiation and the porous carbon layer is there for lithium to go in. So, this is one typical experimental T M picture where you can see this black particles they are embedded in this so, called carbon nano-tube. And, TEM is showing that this structure is feasible.

So, this is a silicon carbon nano-tube structure the capacity is quite high because of the same principle that you have sufficient volume. So, that the volume expansion can be taken care of and simultaneously you have a carbon path. So, that the electron can be transported, but because silicon itself is not electronically conducting it is a semiconducting material. So, that also serves the purpose.

(Refer Slide Time: 17:34)



Metal oxide anode

Step I – $SnO_2 + 4Li^+ + 4e^- = Sn + 2Li_2O$
Step II – $5Sn + 22Li = Li_{22}Sn_5$
You can calculate that owing to higher formula weight (M) the theoretical capacity will be little lower than pure metal.

Factors need to be considered	Approaches taken to overcome
Volume expansion	Structure manipulation: Nanoparticles, nano-rods, nanotubes, and hollow spheres
Low electrical conductivity	Making composite: Binding SnO_2 nanocrystals in graphene sheets by Sn – N bonding
	Building conducting network: SnO_2 embedded in CNT

Then, you know about the metal oxide anode where there are two step reaction; the first step if you take tin oxide, then the first step lithium forms the tin particle in L i 2 O matrix. And, in the second step this tin forms alloy with lithium and this is embedded in the matrix of L i 2 O.

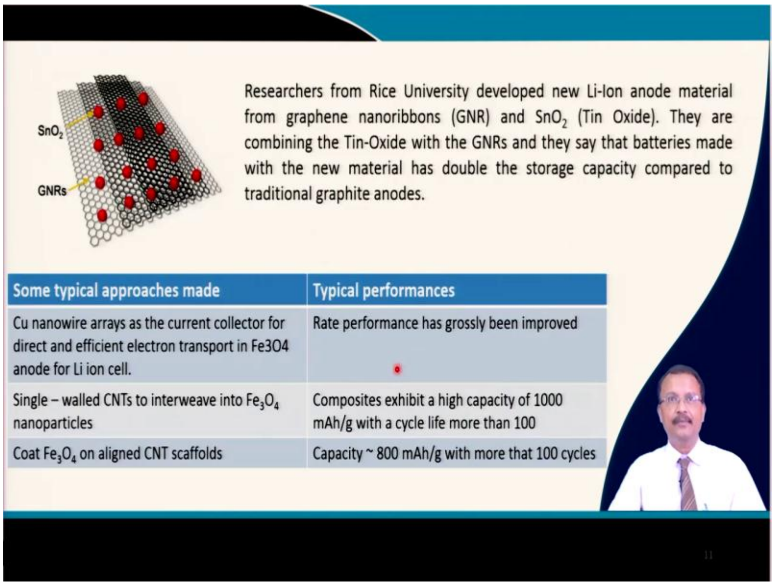
So, you can calculate that owing to higher formula weight, the theoretical capacity will be little lower than pure metal. So, because additionally this oxide is having more molecular weight so, capacity will be a bit reduced.

So, the factor that is needed to be considered for volume expansion, you need to do structural manipulation nanoparticle formation. Because of the size effect that I showed nanorods is one another structure nano-tube, hollow spheres this kind of structure if you grow, then the volume expansion will be taken care of.

Low electrical conductivity that can be overcome by making composite binding tin oxide nanocrystal in graphene sheet by tin and this nitrogen bonding, in the graphene sheet that is beneficial, or building conducting network tin oxide embedded in CNT that is also helpful.

So, as such the this kind of approaches they are conceptually it is ok, but for making a practical battery still you have the choice of LTO and you have the choice for graphite. Rather than this fancy structures, because it is in small scale it is ok. It is easy to publish paper by making this kind of structures, but if you want to make a commercial battery, then this type of fancy structure making in bulk quantity that is indeed challenging.

(Refer Slide Time: 19:46)



Researchers from Rice University developed new Li-Ion anode material from graphene nanoribbons (GNR) and SnO_2 (Tin Oxide). They are combining the Tin-Oxide with the GNRs and they say that batteries made with the new material has double the storage capacity compared to traditional graphite anodes.

Some typical approaches made	Typical performances
Cu nanowire arrays as the current collector for direct and efficient electron transport in Fe3O4 anode for Li ion cell.	Rate performance has grossly been improved
Single – walled CNTs to interweave into Fe_3O_4 nanoparticles	Composites exhibit a high capacity of 1000 mAh/g with a cycle life more than 100
Coat Fe_3O_4 on aligned CNT scaffolds	Capacity ~ 800 mAh/g with more that 100 cycles

So, another such challenge that was reported very recently from Rice University. They developed a new lithium anode material and the concept remains same the graphene nano ribbons and tin oxide. So, they are combining the tin oxide with graphene nano ribbon and they claim that the batteries made with this new material has double storage capacity compared to the conventional graphite anode.

So, they have increased the capacity due to obvious reason you are introducing Tin Oxide and Tin Oxide we know that it will form L i 2 O and metallic tin particle. And, Tin particle will form alloy with lithium and the volume expansion will be grossly retarded, because of the fact that you can see there are lot of space there in between and very small particle.

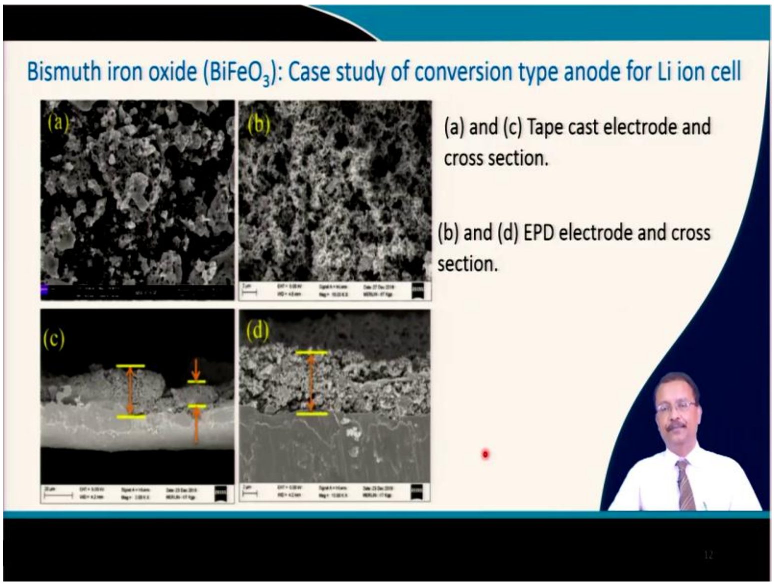
And, even if there is volume expansion then graphene sheet that will actually take care of that. So, this is another approach and there are lot of hue and cry for this type of new cathode nano material, but again scaly scaling it up and use it in commercial battery that remains challenging.

So, some typical approaches that is made copper nanowire arrays as collectors, for direct, and efficient electron transport of F e 3 O 4 anode for lithium ion cell. And, you can see that the type of approaches, that I have explained. That, what is exactly needed to increase the performance that remains same. So, single volt carbon nanotube to and interweave with iron oxide F e 3 O 4 or coat F e 3 O 4 on aligned CNT scaffold.

So, if you do that then in the first case as you can see rate performance is grossly increased. Then this composite, this type of composite, exhibit a very high capacity about 1000 milliampere hour per gram with cycling effect more than 100 for commercial purpose we need at least 500 or more, charge discharge capability before the capacity fades up to 85 percent.

But, it is no way around 100, but people are limiting you might have noticed people are limiting the capacity around 1000, because they know that they do not have the cathode material, which is actually compatible with this kind of anode. So, they have limited this. For this type of thing F e 3 O 4 in aligned CNT the capacity is 800 milliampere hour per gram with more than 100 cycles.

(Refer Slide Time: 22:53)



Bismuth iron oxide ($BiFeO_3$): Case study of conversion type anode for Li ion cell

(a) and (c) Tape cast electrode and cross section.

(b) and (d) EPD electrode and cross section.

So, now we thought that let us work on another oxide material. So, already we have worked on zinc ferrite, which I in the last to last class as a case study we introduced this thing.

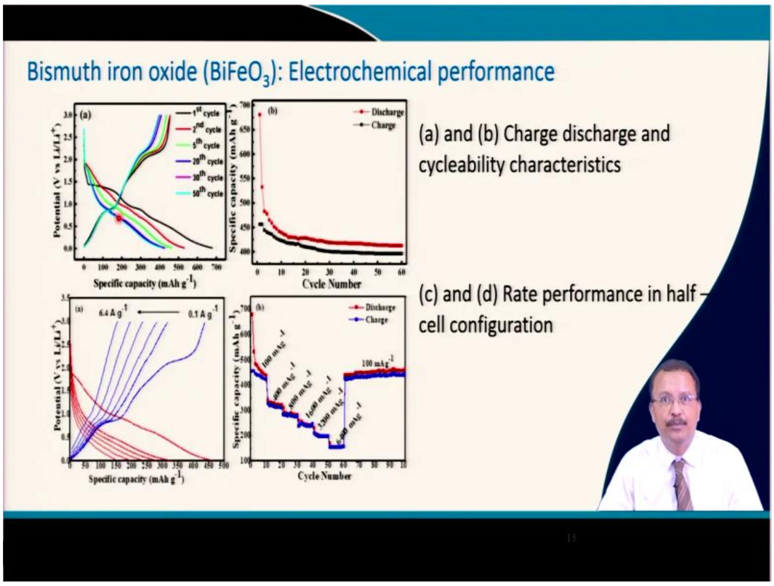
So, bismuth iron oxide this is a multicomponent system, multifunctional system. So, it is a multiferroic material. So, it exhibits both polarization ordering and magnetization ordering is a good photo catalytic material. Of course, it is a good dielectric material. So, we thought that why not to try it, if it qualifies for the negative electrode material for lithium as well as sodium ion batteries.

So, we tried both and eventually we found that both lithium and sodium can be intercalated, it is not intercalation like, because you know the reaction what goes on it forms Bismuth and iron particles separated in L i 2 O matrix, and then it forms alloy with Bismuth. So, that was our effort in the laboratory part of one of the PhD students work.

And, you can see that a and c they are the tape cast layer. So, we do it the tape casting, the surface of the tape cast layer of bismuth iron oxide, carbon blacks are there and it is bonded with a P B D F and then we coated, it on copper substrate. So, this is not that good, because lot of disintegration is even in the virgin state.

Now, porous layer was found by electrophoretic deposition. This also you have seen in case of zinc ferrite this E P D electrophoretic deposition was found quite effective. So, that was coated and you can see almost very uniform structure that we could get.

(Refer Slide Time: 24:57)



Bismuth iron oxide ($BiFeO_3$): Electrochemical performance

(a) and (b) Charge discharge and cycleability characteristics

(c) and (d) Rate performance in half – cell configuration

Then, we did the charge discharge measurement and you can see here that this is basically a 2 phase mixture is forming. So, there are lot of plateaus here, which is which you can see. And, first this material as you can understand that lithium will come inside and form this alloy material.

So, first the discharge operation will be there followed by the charge operation. So, the coulombic efficiency is not that great, discharge capacity was much higher as compared to the charge capacity. So, the coulombic efficiency was not that great, but once you try to cycle it more and more, then initial this coulombic capacity, coulombic deficiency what was there that was grossly reduced.

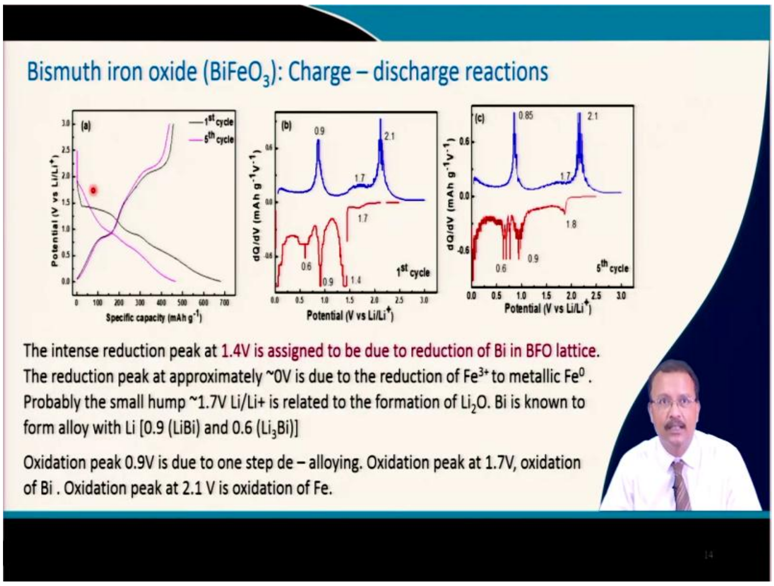
And, then finally, around 450 which is not that bad capacity, if you consider the cathode capacity maximum even if in LMR type of cathode is 300 milliampere hour per gram. So, it is higher than your graphite and this will also solve the purpose we thought.

And, this is the rate performance. So, starting from a very low level of current, it will progressively go to very high level of current, then many of the reaction as you can understand that this is not it is too fast for this reaction to take place. Because, it is a bulky reaction, you can imagine, it is not like the layered material and lithium is going in and coming out.

But, this is a quite complicated reactions because initially it forms a metal nanoparticle and then it forms an alloy. So, if it you can do it very fast so, rate performance is not that great, and that has been shown here that, if you have a capacity around 450. So, the drain current is about 100 milliampere hour per gram, the capacity is higher and then it progressively, but still it performs; progressively drop down to about 150. And, again you go back to lower current; then again you get a quite stable capacity.

So, the performance of course, it was published, but performance is not that great, but I was tempted to introduce our own data, in this part of the lecture just to show you. And, in fact, as a part of your homework you can start to correlate the type of reaction that is going on in this each case and I have shown certain example, if you take this discharge capacity.

(Refer Slide Time: 27:49)



Bismuth iron oxide ($BiFeO_3$): Charge – discharge reactions

The intense reduction peak at 1.4V is assigned to be due to reduction of Bi in BFO lattice. The reduction peak at approximately ~0V is due to the reduction of Fe^{3+} to metallic Fe^0. Probably the small hump ~1.7V Li/Li+ is related to the formation of Li_2O. Bi is known to form alloy with Li [0.9 (LiBi) and 0.6 (Li_3Bi)]

Oxidation peak 0.9V is due to one step de – alloying. Oxidation peak at 1.7V, oxidation of Bi . Oxidation peak at 2.1 V is oxidation of Fe.

And, then basically you do a differential capacity plot. And, this differential capacity plot from first cycle and fifth cycle, you see that there is some change. So, the intense reduction peak, that you can see at 1.4 volt that is probably due to the reduction of bismuth in BFO lattice. So, it is the formation of Bismuth.

And, what we did we stop the reaction here and then we test it, and it is barely crystalline. If it is not very crystalline, then it is difficult to identify whether it is really bismuth, but it shows some signature and also it is in the nano range. So, you will not get a very sharp peak out of it, but the peak position of bismuth that fairly matches with this formation. So, we assign this peak at 1.4 volt is due to the reduction of bismuth

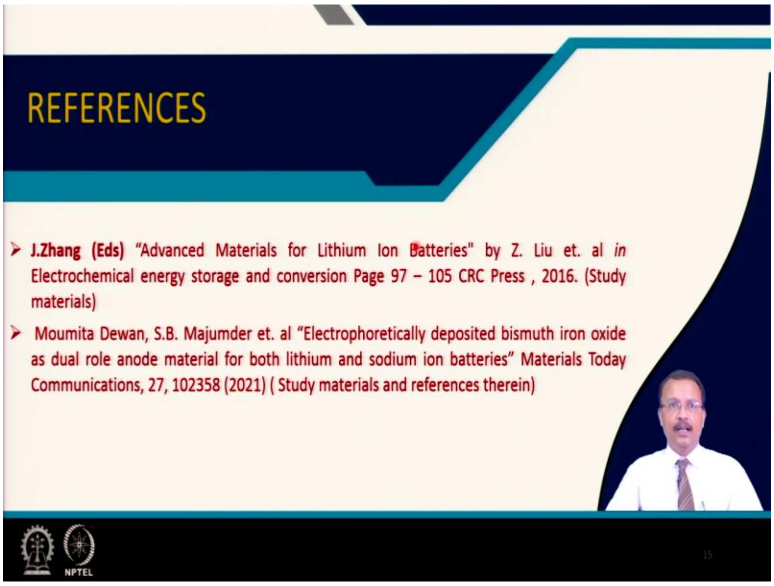
Reduction peak approximately which is at 0 volt, that is due to the reduction of iron to metallic iron, because in bismuth iron oxide, it is not a single element like bismuth, like tin oxide, it is bismuth is there, iron is there. So, that is transformed into metallic iron. And, this small hump which you will see about 1.7 probably that indicates the formation of lithium oxide.

And, bismuth as we know that it forms an alloy with lithium. So, this 0.9 volt and 0.6 volt, this 2 peak 0.6 and 0.9 it will form, the alloy with bismuth material it forms the alloy. And, the rough composition is lithium bismuth and L i 3 B i and the oxidation peak is the d alloying.

So, oxidation peak at 1.7 volt and oxidation peak that is due to bismuth and 2.1 is the oxidation of iron oxide and this oxidation peak at 0.9 is actually a one step delithiation. So, this will be delithiated in 1 step, or even if it is in 2 step, it is very difficult to identify it.

Now, if you keep on cycling this material then all these reactions are occurring although at reduced intensity. So, that tells that these are reversible in nature. So, this actually follows our own understanding about this conversion type of anode material.

(Refer Slide Time: 30:42)

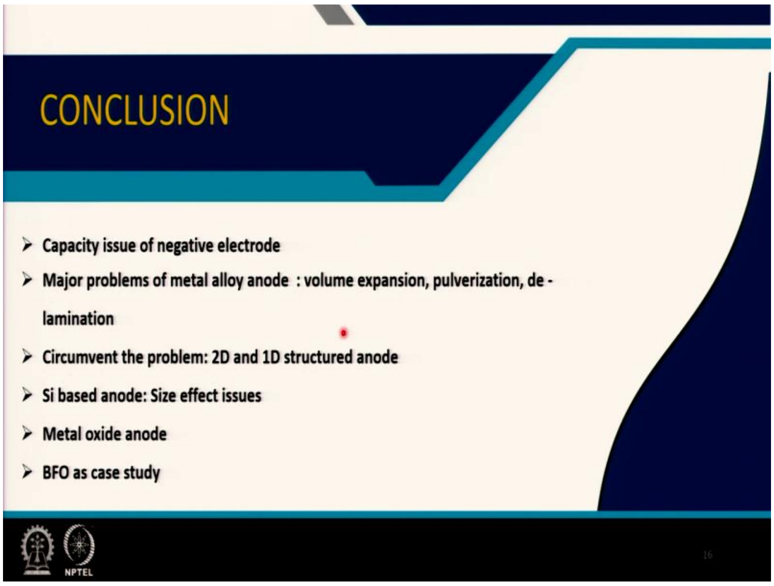


REFERENCES

- **J.Zhang (Eds)** "Advanced Materials for Lithium Ion Batteries" by Z. Liu et. al *in* Electrochemical energy storage and conversion Page 97 – 105 CRC Press , 2016. (Study materials)
- Moumita Dewan, S.B. Majumder et. al "Electrophoretically deposited bismuth iron oxide as dual role anode material for both lithium and sodium ion batteries" Materials Today Communications, 27, 102358 (2021) (Study materials and references therein)

So, the book edited by Zhang, this is important page number 97 to 105 you can get sufficient examples and some of the things that I have covered in my lectures you will find it, and for this bismuth oxide we as I told that already we published the paper. So, if you are interested to know more about bismuth iron oxide. Then please have a look read this paper as well, which is published in materials today communication.

(Refer Slide Time: 31:20)



CONCLUSION

- Capacity issue of negative electrode
- Major problems of metal alloy anode : volume expansion, pulverization, de - lamination
- Circumvent the problem: 2D and 1D structured anode
- Si based anode: Size effect issues
- Metal oxide anode
- BFO as case study

So, in this particular lecture we talked about capacity issues of negative electrodes, then major problem of metal alloy anode, including the volume expansion, the pulverization, the delamination, then to circumvent this problem 2 D and 1 D structured anode, and what are their implications, how they work? And, why they are helping to improve the properties that have been talked about.

And, then we talked about silicon based anode the size effect issue that I have described. Metal oxide anode we have introduced and what is their actual mechanism of this operation. And, finally, BFO as a case study that we have talked about in this lecture.

Thank you for your attention.