Electrochemical Energy Storage
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Module - 06
Sodium ion rechargeable cell
Lecture - 27
Negative Electrodes : Carbonaceous Materials, Alloy based and Other Materials

Welcome to my course Electrochemical Energy Storage and we are now in module number 6 and we are discussing Sodium ion rechargeable cells and this is lecture number 27. In the last lecture, we talked about the positive electrode material, the umbrella of materials for its use in sodium ion batteries.

And here in this particular lecture we will be talking about the Negative Electrodes and which basically includes Carbonaceous Materials, Alloy based materials and some other significant Other Materials. Part of our own research also I will show which is pertinent to this lecture.

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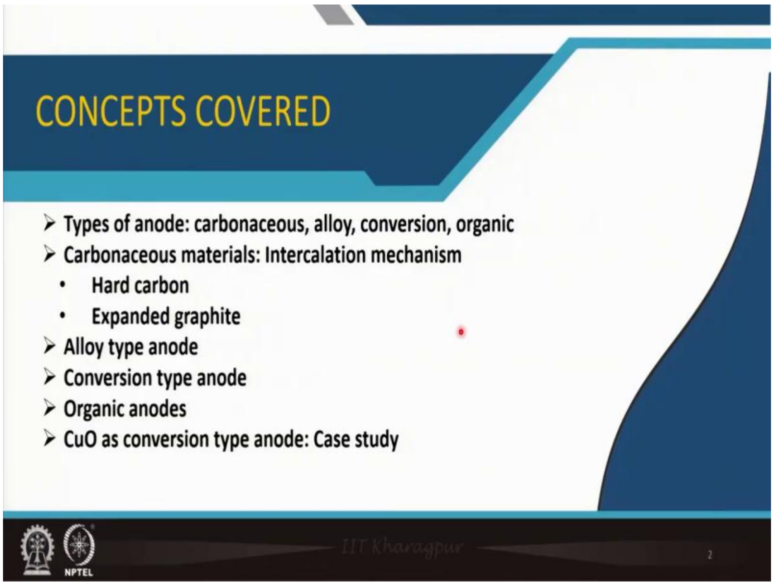

CONCEPTS COVERED

- Types of anode: carbonaceous, alloy, conversion, organic
- Carbonaceous materials: Intercalation mechanism
  - Hard carbon
  - Expanded graphite
- Alloy type anode
- Conversion type anode
- Organic anodes
- CuO as conversion type anode: Case study

Now, if you look at the type of the anodes you will find very very similarity very much similarity of the lithium ion batteries. Here also we will be talking about the carbonaceous material, but not the same type of anode like graphite. It has certain problem. We will discuss that that graphite you can cannot use as anode for sodium ion battery. Certain alloys we will be talking about conversion types of material and organic material.

So, these are the anodes for sodium ion battery. Out of this carbonaceous material they go for this intercalation mechanisms. Only hard carbon, if you pick up any paper on sodium ion battery or any standard text from a monograph you will find that they have only talked about hard carbon or expanded graphite, but less on alloy type of anodes or conversion types of anodes organic anodes.

And certain simple oxide material which is conversion type of anode like copper oxide that we have recently have done some work with promising results. I will just touch to show that this also can be used for sodium ion battery. You can imagine it will be it will be able to produce a very cheap battery.

Copper oxide is a very well known material and if you take Prussian blue for example, on the other side reasonable good sodium ion battery for the renewable energy storage you can easily make using the same facility that you use for coin cell or cylindrical cell or pause cell which already I have described part of my other lectures.

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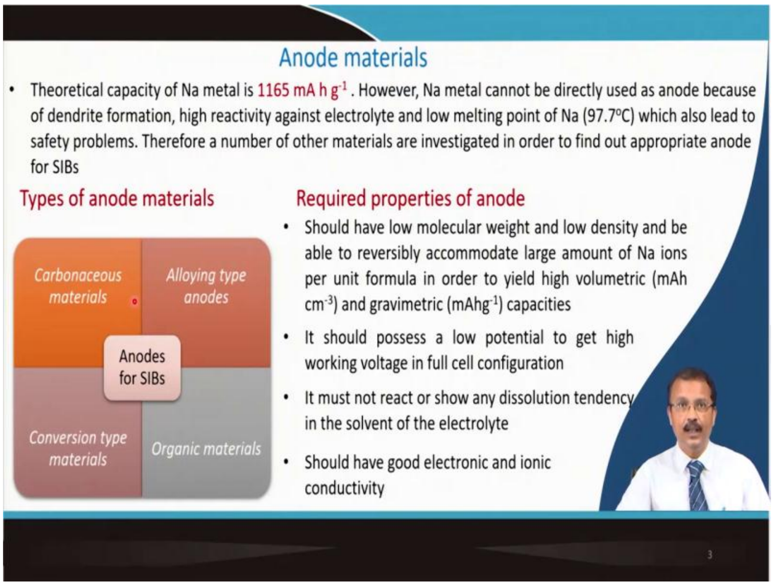

Anode materials

- Theoretical capacity of Na metal is 1165 mA h g^{-1} . However, Na metal cannot be directly used as anode because of dendrite formation, high reactivity against electrolyte and low melting point of Na (97.7°C) which also lead to safety problems. Therefore a number of other materials are investigated in order to find out appropriate anode for SIBs

Types of anode materials

Carbonaceous materials

Alloying type anodes

Anodes for SIBs

Conversion type materials

Organic materials

Required properties of anode

- Should have low molecular weight and low density and be able to reversibly accommodate large amount of Na ions per unit formula in order to yield high volumetric (mAh cm^{-3}) and gravimetric (mAhg^{-1}) capacities
- It should possess a low potential to get high working voltage in full cell configuration
- It must not react or show any dissolution tendency in the solvent of the electrolyte
- Should have good electronic and ionic conductivity

Now, this anode material you can also in half cell configuration you can use sodium metal and you can calculate its estimate its capacity is about 1165 milliampere hour per gram. But, this sodium metal cannot be directly used as anode because of the same problem which is dendrite formation which is much more aggravated in case of sodium metal if you use as anode and this is extremely reacts aggressively with the electrolyte.

And also it is low maintain, in case of if you abuse the battery if there is a hot spot if the temperature is raised it is having a low melting point which I already talked about 97.7 degree Celsius that leads to safety problem. So, therefore, number of other materials they are investigated to find out the appropriate anode for sodium ion battery. So, here you can see we have a four class of material.

One is carbonaceous material you are familiar with it. Alloy type of anodes you are also familiar with it when you have studied the lithium based anode materials for lithium ion batteries. Organic material some of them they are useful and conversion type materials also you know. So, technology wise this is more or less similar type of technology. So, as such it is not very problematic to adopt sodium ion material to lithium ion batteries.

Now, if you look at the required properties of course, it should have low molecular weight and low density and be able to reversibly accommodate large amount of sodium ions per formula unit to yield high volumetric and gravimetric capacity. So, that needs no explanation because from the knowledge of lithium ion battery materials you can appreciate that why it is so.

It should possess a low potential to get a high working voltage. So, graphite you remember that works around 0.2 to 0.5 volt versus lithium plus by lithium this redox couple. And most of the sodium ion cathode material positive material what you have seen this lies around 3.8 to 3.3 volt.

So, you need to have an anode material which gives you the potential much lower. So, that the voltage window is at least 3 volt. So, you do not have any 5 volt sodium ion battery cathode material, so, that you will have to keep it in mind that this potential should be low.

It should not react or there should not be any dissolution tendency to the solvent with the electrolyte that is also obvious you do not want to lose the active material and thereby reducing the capacity as the cycles go on.

And of course, they should have both sodium ion conductivity as well as electronic conductivity. So, for many of this material getting a good electronic conductivity is a challenge. So, that is one of the requirements that it should have good electronic and also ionic conductivity.

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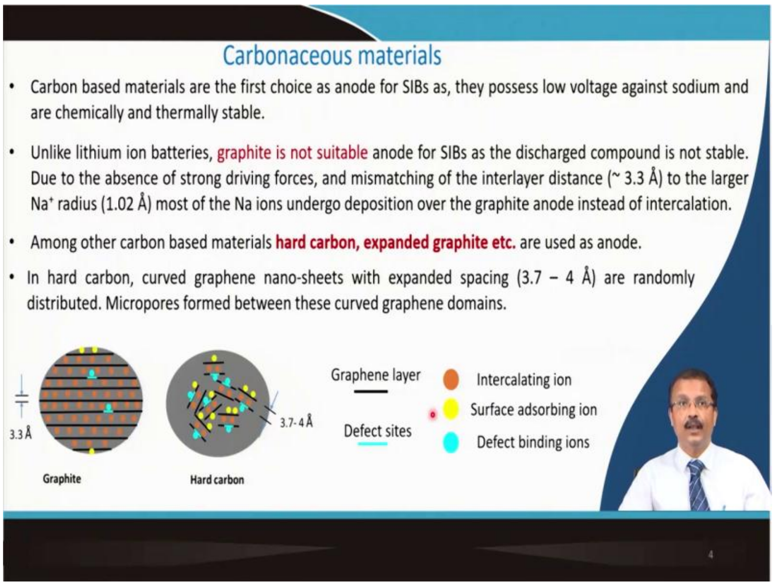

Carbonaceous materials

- Carbon based materials are the first choice as anode for SIBs as, they possess low voltage against sodium and are chemically and thermally stable.
- Unlike lithium ion batteries, graphite is not suitable anode for SIBs as the discharged compound is not stable. Due to the absence of strong driving forces, and mismatching of the interlayer distance (~ 3.3 Å) to the larger Na^+ radius (1.02 Å) most of the Na ions undergo deposition over the graphite anode instead of intercalation.
- Among other carbon based materials **hard carbon, expanded graphite etc.** are used as anode.
- In hard carbon, curved graphene nano-sheets with expanded spacing (3.7 – 4 Å) are randomly distributed. Micropores formed between these curved graphene domains.

So, carbonaceous material if you see the carbon based material is of course, the first choice because it is wide availability and we have the knowledge to use it for lithium ion batteries.

So, the first choice should be graphite, but it is a regular structure as you can see here and this spacing which is 3.3 Angstrom this cannot accommodate this relatively larger sodium ion. So, sodium ion cannot actually intercalate that easily in graphite. So, that is one of the major problem.

So, although this is of our first choice because they possess low voltage against sodium and also chemically and thermally stable, but as I said this is not suitable anode as the discharge compound is not stable. So that means, when it is discharged; that means, when sodium is coming inside the structure then it is not stable.

So, due to the absence of strong driving forces and mismatching interlayer distance 3.3 Angstrom to the larger sodium ion radius which is 1.02 Angstrom, so it find it is difficult to go in. So, most of the sodium ions undergo a deposition over the graphite anode and you know the deposition is something that we do not need.

Because the deposition is not a layer by layer deposition, it will form a dendrite structure, it will start to grow, it will have a floppy structure, part of it will be disintegrated inside the electrolyte or if it starts to grow it will puncture the puncture your separator and there will be short circuit.

So, among other carbon materials hard carbon and expanded graphite they are useful. So, they are used as anode. So, in case of hard carbon, you can see there is a curved graphene nano sheets. So, each single sheet is the graphene sheet. So, this is having a curved graphene nano sheet and the spacing is higher. So, it is from 3.7 to 4 Angstrom which is larger than this and they are randomly distributed right.

And micropores they formed between these curved graphene domains. So, between this curved graphene domains there are micropores I will explain it later. So, you have this color you should follow. So, this is intercalating ions which are orange. This yellow one is the surface adsorbing ions. So, some of the sodium is also surface adsorbed on the graphene sheet and this blue kind of thing is a defect binding ions because it does not have a good crystal structure like this.

So, there are lot of defects here. So, in the defect this sodium ion are bonded. Now, if it is very strongly bonded it is very difficult to take it out and that will create problem. So, one should be little bit careful about it.

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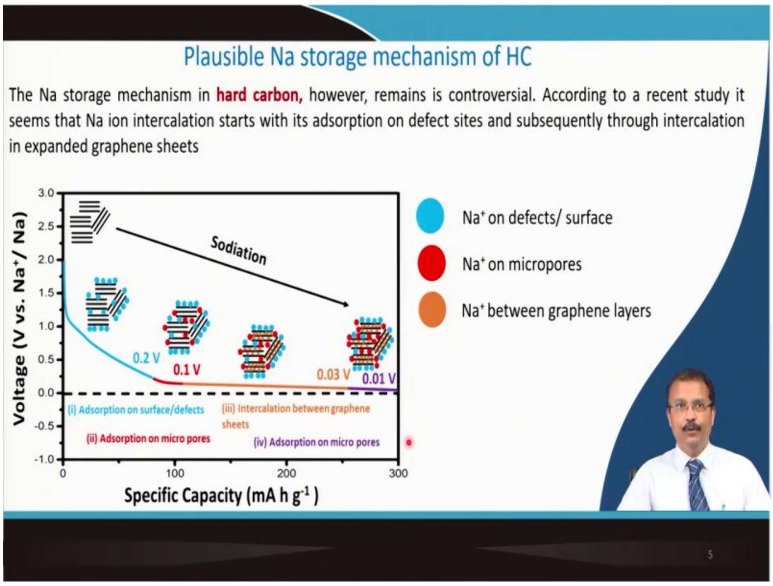

Plausible Na storage mechanism of HC

The Na storage mechanism in **hard carbon,** however, remains is controversial. According to a recent study it seems that Na ion intercalation starts with its adsorption on defect sites and subsequently through intercalation in expanded graphene sheets

So, the mechanism of the sodium storage in hard carbon this is a controversial mechanism. So, in a recent study whatever we could get or we could understand that sodium ion intercalation start first with the adsorption. So, this blue you see that on this hard carbon layers they are just simply adsorbed, right.

It starts with absorption on defect sites here and subsequently through intercalation in expanded graphene sheets. So, here you see that there are four steps and depending on this four steps there is a change in the voltage regime.

So, up to 0.2 volt adsorption of the surface defects, adsorption of the ions on the surface or on the defects that takes place then the voltage is lowered 0.1. So, in 0.1 you can see that this adsorption in micropores takes place. So, the micropore is in between this graphene layer. So, this layer and this layer this small space here it intercalates. Number three is the intercalation between graphene sheets. So, here you can see that it is not really a single layer of graphene.

So, at least if you consider three layers contain that part. So, micropores in case of micropores it goes inside this in between space of this thick graphene layer. And then at lower potential intercalation between the graphene sheets that takes place. And finally, although it is not very well established yet, but some people they think that adsorption on micropores is also possible.

It is not intercalation, but again this green kind of things they come back and they start to adsorb here. So, the color you follow this is surface adsorbs on defect, this is on micropores and this is intercalated inside the layers. So, the voltage is pretty low and this many things occur when this expanded sorry hard carbon they are actually sodiated.

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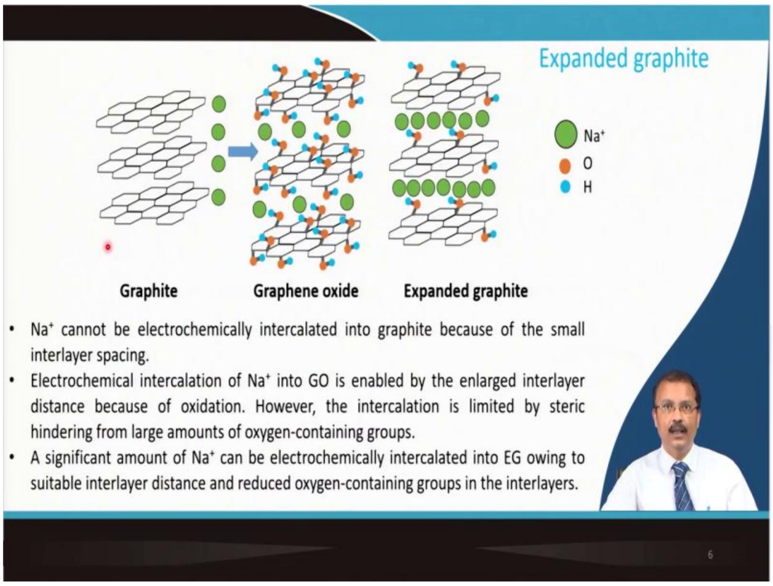

Expanded graphite

- Na^+ cannot be electrochemically intercalated into graphite because of the small interlayer spacing.
- Electrochemical intercalation of Na^+ into GO is enabled by the enlarged interlayer distance because of oxidation. However, the intercalation is limited by steric hindering from large amounts of oxygen-containing groups.
- A significant amount of Na^+ can be electrochemically intercalated into EG owing to suitable interlayer distance and reduced oxygen-containing groups in the interlayers.

In case of expanded graph graphite you can see that this is the layer the space is not enough. So, sodium cannot be in electrochemically intercalated into the graphite because of its small interlayer spacing. So, electrochemical intercalation of sodium can be possible if you change it to graphene oxide. So, when once it transform from here to here then space is little bit enlarged because of the oxidation.

Now, this oxidation when it takes place the sodium ion insertion they are a bit limited because of the steric hindrance of large amount of oxygen containing groups. So, oxygen containing groups are here you see that this one and this one this blue one this is the oxygen containing group O and H hydroxyl could be here. So, due to although this space is increased, but it cannot go in that easily because of the hindrance of this right.

Then what you do? You again do a reduce graphene oxide. So, once you reduce it then many of this things are removed. So, then a significant amount of sodium can be intercalated into this expanded graphite. So, expanded graphite is nothing but graphene oxide.

Once it is gets reduced then its electronic conductivity also increases and apart from that significant amount of sodium can exactly be go in going to the suitable interlayer distance and reduced oxygen containing groups in the interlayer. So, that is the concept of expanded graphite and this can be used as negative electrode material for sodium ion batteries.

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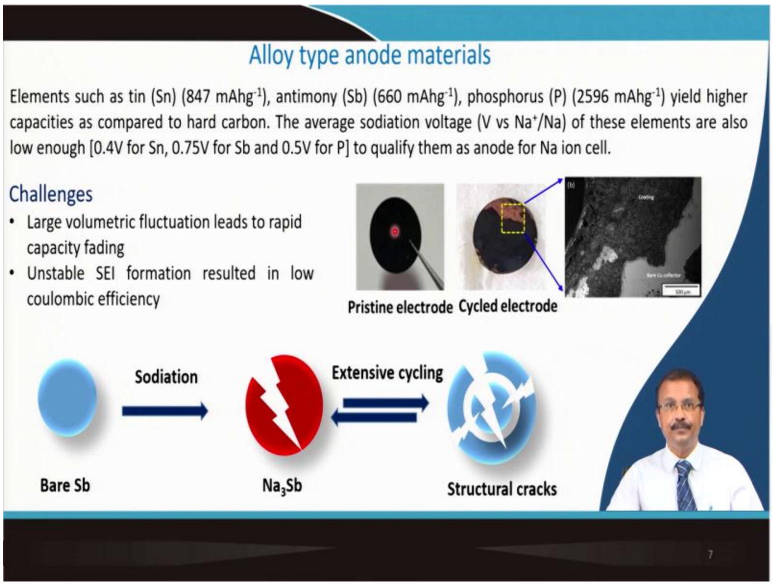

Alloy type anode materials

Elements such as tin (Sn) (847 mAhg^{-1}), antimony (Sb) (660 mAhg^{-1}), phosphorus (P) (2596 mAhg^{-1}) yield higher capacities as compared to hard carbon. The average sodiation voltage (V vs Na$^+$/Na) of these elements are also low enough [0.4V for Sn, 0.75V for Sb and 0.5V for P] to qualify them as anode for Na ion cell.

Challenges

- Large volumetric fluctuation leads to rapid capacity fading
- Unstable SEI formation resulted in low coulombic efficiency

Then we will talk about this alloy type of materials. The same type of material like tin, that also can be used here because you know that it forms an alloy with lithium, it forms an alloy with sodium as well. So, whatever I have described that when alloying takes place depending on the phase diagram you will have to see that what kind of phases form and if there is a two phase mixture with the minimum free energy the free energy remains same.

Then the voltage will also be same. So, you will get a plateau which you need there is not a change in the voltage profile because of a single phase solid solution type of material of alloying. So, this is good.

The same thing happens here. So, you can see the capacity tin, antimony, phosphorus, they yield higher capacity. In fact, from the capacity you can calculate that how much sodium is incorporated in this metals be that tin or so, this antimony or phosphorus.

And this capacity is much much larger than your hard carbon. Although getting too much capacity is of no use because you know that unless you can develop a cathode which is having a very high capacity, it does not make sense to go beyond 1000 milli ampere hour per gram because it will not give a good capacity in your full cell full sodium ion cell.

So, you can limit yourself you do not need this type of very high capacity for this. The average sodiation voltage that is also important. You will have to keep it low and indeed they are low. You see 0.4 volt for tin, 0.74 volt for antimony and 0.5 volt for phosphorus. So, I will prefer of course, tin here because this is having the lowest voltage.

Challenge is same that you well know it is well known to you that large volumetric fluctuation takes place when sodiation and desodiation takes place and that leads to very rapid capacity fading. So, during sodiation there is a volume expansion, crack can initiate, structural crack can disintegrate and this things are taken from our own research.

So, after you see that it is a nicely coated pristine electrode anode material and we were testing it with sodium half cell. So, the copper substrate you can see; you can see the copper substrate and you can see it is delaminated the coating is here and the bare copper correct current collector is somewhere here. So, it is coming out.

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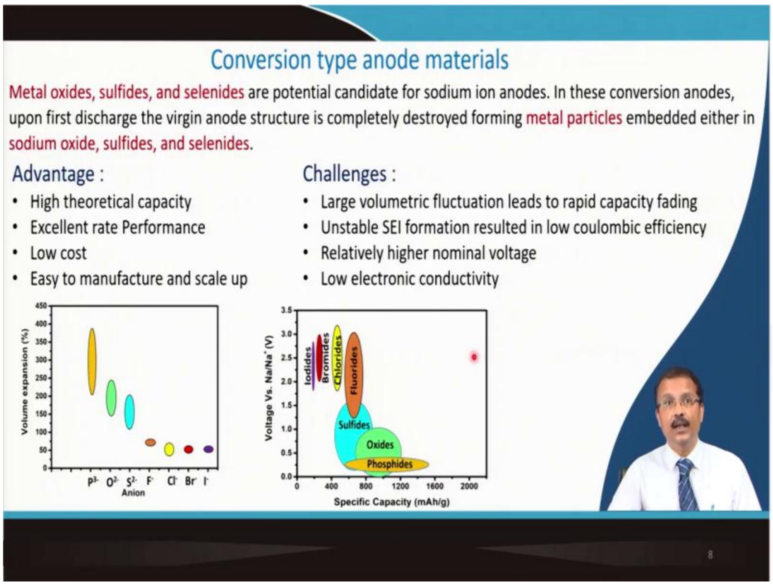

Conversion type anode materials

Metal oxides, sulfides, and selenides are potential candidate for sodium ion anodes. In these conversion anodes, upon first discharge the virgin anode structure is completely destroyed forming metal particles embedded either in sodium oxide, sulfides, and selenides.

Advantage :

- High theoretical capacity
- Excellent rate Performance
- Low cost
- Easy to manufacture and scale up

Challenges :

- Large volumetric fluctuation leads to rapid capacity fading
- Unstable SEI formation resulted in low coulombic efficiency
- Relatively higher nominal voltage
- Low electronic conductivity

So, this problems remain. If you talk about conversion type of anode material it is not only metal oxides, but sulphides and selenides they are also potential candidate for sodium ion anodes.

In this conversion types of anode upon first discharge the virgin anode structure is completely destroyed you know that forming small metal nanoparticles which are embedded in sodium oxide. In case of lithium it was lithium oxide, now apart from oxide you are taking sulphide.

So, sodium sulphide, sodium selenides in that matrix you will have the small metal nanoparticle. Now, there are certain advantages of this and you can see that theoretical capacity is relatively higher, rate performance is quite good, relatively low cost easy to manufacture. Because this oxide sulphides they are easy to manufacture. So, certainly advantages are there, but challenges are also there.

Large volumetric fluctuation leads to rapid capacity fading, unstable SEI formation because you know in negative electrode SEI formation is required, but we do not want thicker SEI impervious to sodium ion diffusion through it and also it should not disintegrate to expose the fresh surface of the negative electrode material. So, that again SEI layer can form.

Relatively higher nominal voltage that is another problem it is not as low as your hard carbon or expanded graphite and it is having lower electronic conductivity. So, you can compare among various types of phosphate, oxide, sulfide, then fluoride, chloride, bromide, iodide this material you can see and volume expansion you see that volume expansion is very large here right.

Now, if you consider the voltage you see the voltage here volume contraction is very high, but the voltage here is very low. Oxide is here, it is slightly lower than this and voltage is also going up. This material they have very nominal about 50 percent, I should not say its nominal it is quite large, but its voltage is very high.

So, this kind of material one cannot use it is makes no sense unless you have a 6 volt sodium ion cathode material developed, but you will have to be satisfied with sulfide, phosphides and oxides with this kind of conversion material for this obvious reasons.

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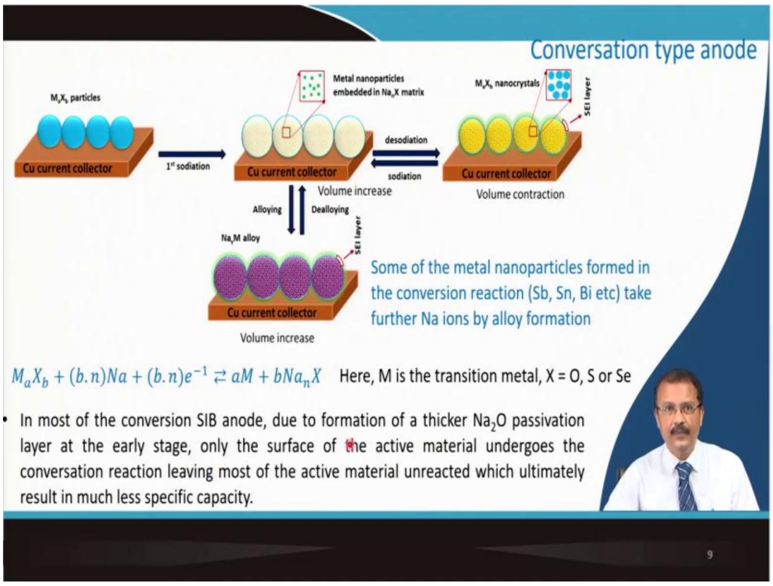

Conversation type anode

Some of the metal nanoparticles formed in the conversion reaction (Sb, Sn, Bi etc) take further Na ions by alloy formation

$M_aX_b + (b.n)Na + (b.n)e^{-1} \rightleftarrows aM + bNa_nX$ Here, M is the transition metal, X = O, S or Se

- In most of the conversion SIB anode, due to formation of a thicker Na_2O passivation layer at the early stage, only the surface of the active material undergoes the conversation reaction leaving most of the active material unreacted which ultimately result in much less specific capacity.

So, this I have already described and this is just a recapitulation. So, on copper current collector you have this type of conversion type of oxide or other types of material. Then what is happening in case of oxide? It is sodium oxide and small metal particles are there. So, this metal particles they also can form oxide and or they can directly form alloy.

So, some of the metal nanoparticles due to this conversion reaction take further sodium ions for alloy formation, but it is not always the case. Not always this metal particle will form alloy they can live there. If there are multiple metal particle which is being produced here. Say one of them they will get this sodiation and volume expansion takes place. The other one that will remain as a metal particle, so, that can act as a buffer.

As I have explained that the stress can be used to move the dislocations and that will buffer this stress. So, the relation is quite straight forward that you can easily understand that what exactly is forming here. And in most of this conversion sodium ion battery anode due to the formation of a thicker passivation layer at the earlier stage. So, this is quite thicker.

Only the surface of the active material undergoes the conversion reaction leaving most of the active material unreacted which ultimately results much less specific capacity. So, in order to these things happen you will have to complete this reactions right, but if it is surface only reaction then most of the part will still remain like this then it is of no use and that is one of the major problems for conversion type of anode material for sodium ion batteries.

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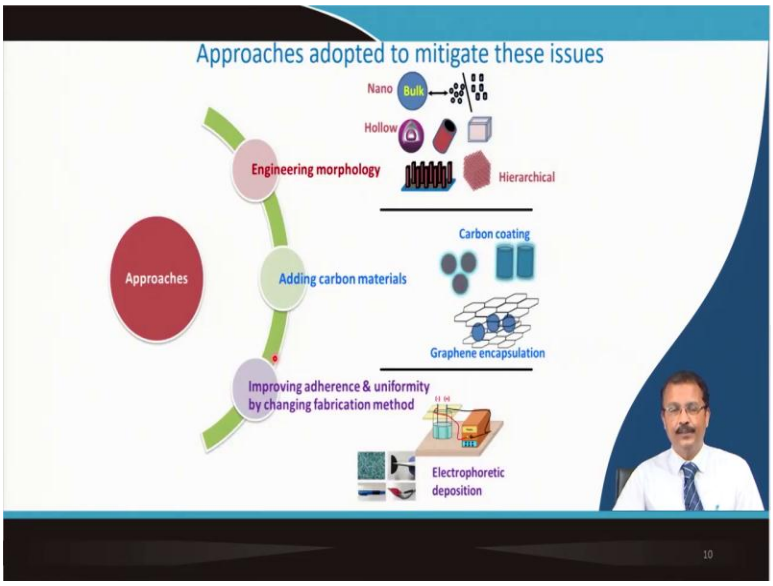
Approaches adopted to mitigate these issues

Approaches

Engineering morphology

Adding carbon materials

Improving adherence & uniformity by changing fabrication method

So, the approaches are very similar to lithium ion battery. One is the engineering morphology. You go for the nano scale synthesis, you can have nano structured material not a solid nano sphere but a hollow sphere or tubular kind of thing. You can have a bristle kind of structure or you can have a hierarchical structure to mitigate the volumetric expansion or you can add carbonaceous material which acts as a buffer. So, here you can see it is encapsulated. It serves two purpose.

One purpose is that it can buffer the stress and number two being conducting, it will improve the rate performance individual particle can be coated with carbon and third one is to do some kind of engineering when you are preparing the electrode material. In many cases we have found that electrophoretic deposition is an excellent process of deposition and you can see here a very good quality electrode. And if you see this picture you can even bent it across a small pin.

So, the stress it can withstand that shows that between the current collector and the anode material there is a good adhesion.

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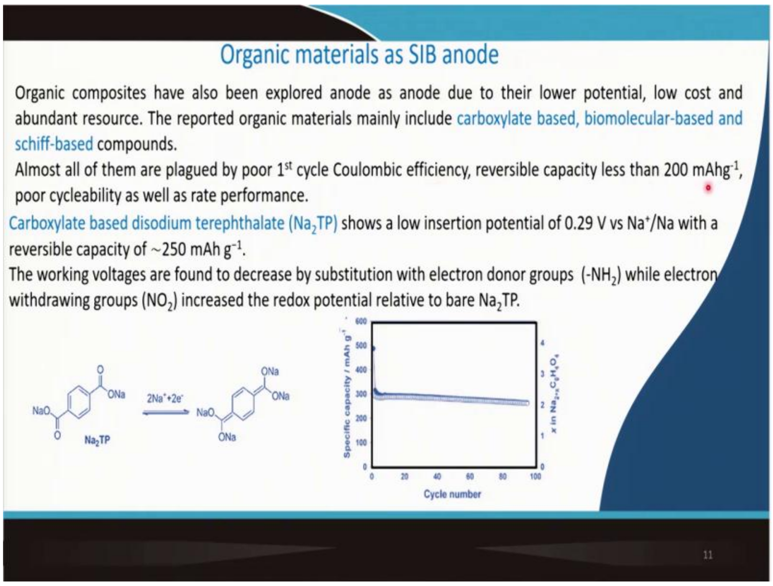

Organic materials as SIB anode

Organic composites have also been explored anode as anode due to their lower potential, low cost and abundant resource. The reported organic materials mainly include carboxylate based, biomolecular-based and schiff-based compounds.

Almost all of them are plagued by poor 1st cycle Coulombic efficiency, reversible capacity less than 200 mAhg^{-1}, poor cycleability as well as rate performance.

Carboxylate based disodium terephthalate (Na_2TP) shows a low insertion potential of 0.29 V vs Na^+/Na with a reversible capacity of ~250 mAh g^{-1}.

The working voltages are found to decrease by substitution with electron donor groups ($-NH_2$) while electron withdrawing groups (NO_2) increased the redox potential relative to bare Na_2TP.

So, organic material as sodium ion battery anode their organic composite also explode because of their low potential, low cost and abundant research. The reported organic materials they mainly include carboxylate based, biomolecular based and schiff based compounds. Almost all of them they are plagued by first cycle coulombic efficiency.

That means, during discharge you can have the discharge profile and this discharge profile after that the charge profile is smaller in capacity as compared to the discharge profile that leads to poor Coulombic efficiency. Reversible capacity is quite low less than 200 milliampere hour per gram. Cyclability is not that good.

Rate performance is also not that good, but one thing you will have to remember that this organic material has just been introduced and there are lot of scope for further research. So, one such material this carboxylate based disodium terephthalate, it is abbreviated as Na2TP that show a low insertion potential about 0.9 volt versus sodium redox couple.

And a redox reversible capacity is reasonably good 250 milliampere hour per gram, not excellent, but comparing considering that the positive electrode capacity is around 100, 115. So, it is quite good. The working voltage is found to decrease by substitution of electron donor like amine while electron withdrawing group like nitrous oxide increase the redox potential relative to this.

So, you have the provision to manipulate their composition and play with their insertion voltage according to your need. And you can see that around 300 milliampere hour per gram that kind of capacity you can get and by changing the composition. And the high coulombic loss the first discharge capacity and second discharge capacity there is some kind of problem probably because of the SEI layer formation which is almost unavoidable.

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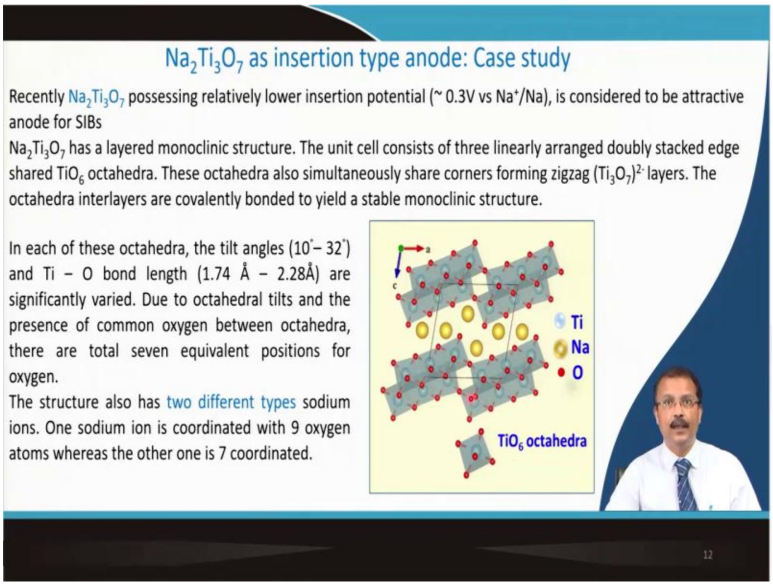

$Na_2Ti_3O_7$ as insertion type anode: Case study

Recently $Na_2Ti_3O_7$ possessing relatively lower insertion potential (~ 0.3V vs Na^+/Na), is considered to be attractive anode for SIBs

$Na_2Ti_3O_7$ has a layered monoclinic structure. The unit cell consists of three linearly arranged doubly stacked edge shared TiO_6 octahedra. These octahedra also simultaneously share corners forming zigzag $(Ti_3O_7)^{2-}$ layers. The octahedra interlayers are covalently bonded to yield a stable monoclinic structure.

In each of these octahedra, the tilt angles (10° – 32°) and Ti – O bond length (1.74 Å – 2.28Å) are significantly varied. Due to octahedral tilts and the presence of common oxygen between octahedra, there are total seven equivalent positions for oxygen.

The structure also has two different types sodium ions. One sodium ion is coordinated with 9 oxygen atoms whereas the other one is 7 coordinated.

So, Na2TiO7 this is also an insertion types of anode and we have started working on this. So, it has a very low insertion potential. That is why we picked it is 0.3 volt and this is considered to be very attractive. So, this is having a monoclinic structure and unit cell consists of three linearly arranged double stacked edge shared TiO6 octahedra that you can see here.

And this octahedra also simultaneously share the corners forming a so called zigzag pattern of this structure. Each of this octahedra there is a small tilt which is about 10 to 32 degree and this titanium and oxygen this bond length are significantly varied. So, due to this octahedral tilt and presence of common oxygen between this octahedra which is apparent from this structure there are total seven equivalent position for the oxygen.

And the structure usually have two different types of sodium ions. And one sodium is coordinated with 9 oxygen and another sodium is coordinated with 7 oxygen.

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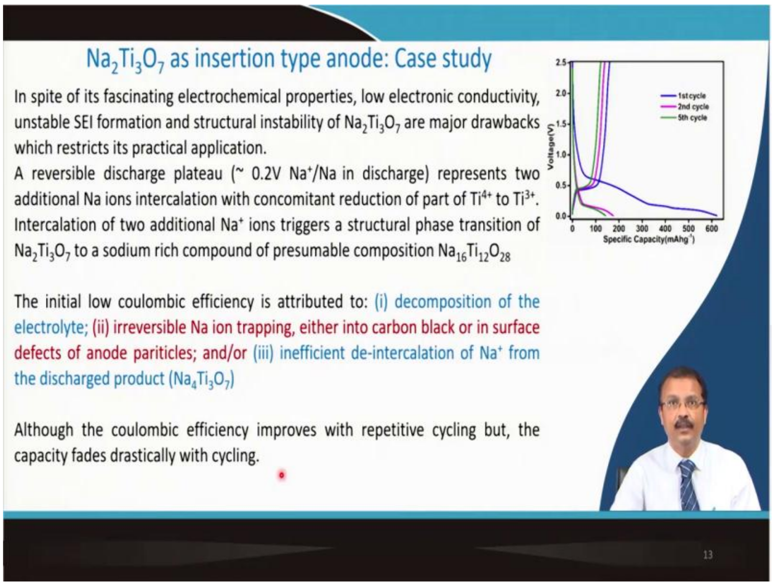

$Na_2Ti_3O_7$ as insertion type anode: Case study

In spite of its fascinating electrochemical properties, low electronic conductivity, unstable SEI formation and structural instability of $Na_2Ti_3O_7$ are major drawbacks which restricts its practical application.

A reversible discharge plateau (~ 0.2V Na^+/Na in discharge) represents two additional Na ions intercalation with concomitant reduction of part of Ti^{4+} to Ti^{3+}. Intercalation of two additional Na^+ ions triggers a structural phase transition of $Na_2Ti_3O_7$ to a sodium rich compound of presumable composition $Na_{16}Ti_{12}O_{28}$

The initial low coulombic efficiency is attributed to: (i) decomposition of the electrolyte; (ii) irreversible Na ion trapping, either into carbon black or in surface defects of anode pariticles; and/or (iii) inefficient de-intercalation of Na^+ from the discharged product ($Na_4Ti_3O_7$)

Although the coulombic efficiency improves with repetitive cycling but, the capacity fades drastically with cycling.

So, in spite of this fascinating electrochemical properties I mean it should be electronic conductivity is very low for this material. So, as you can see in the first discharge there is a plateau which is at quite low voltage, but there is a very huge fall in capacity within the second cycle.

And two sodium ion intercalation actually takes place and there is a concomitant reduction of titanium 4 to titanium plus 3. So, this intercalation again when it takes place that triggers a structural phase transition in this material. So, it is quite complicated. So, this Coulombic efficiency one should actually tackle.

So, that is attributed to decomposition of the electrolyte that is possible on the surface of the anode. Irreversible sodium ion trapping either into the carbon black or in the surface defect, so, they are not coming out during charging of the during discharging of the batteries. And insufficient de intercalation of sodium ion from the discharge product which is now Na4Ti3O7.

So, this Coulombic efficiency improve with repeated cycling. You will see that here. If you compare here then after second cycle the Coulombic efficiency is quite good as compared to the first cycle the difference from here to here, second cycle from here to here, but still capacity fading is there.

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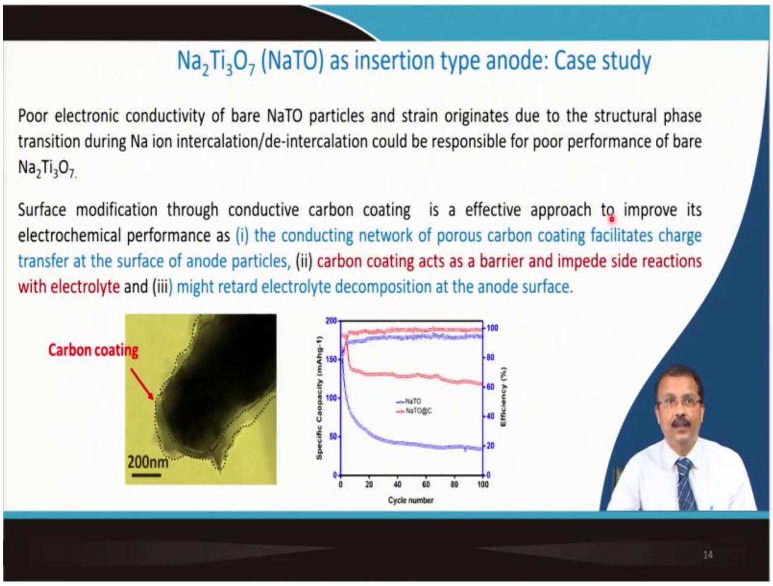

$Na_2Ti_3O_7$ (NaTO) as insertion type anode: Case study

Poor electronic conductivity of bare NaTO particles and strain originates due to the structural phase transition during Na ion intercalation/de-intercalation could be responsible for poor performance of bare $Na_2Ti_3O_7$.

Surface modification through conductive carbon coating is a effective approach to improve its electrochemical performance as (i) the conducting network of porous carbon coating facilitates charge transfer at the surface of anode particles, (ii) carbon coating acts as a barrier and impede side reactions with electrolyte and (iii) might retard electrolyte decomposition at the anode surface.

Then this electronic conductivity this originates due to the structural phase transition during sodium ion intercalation. So, surface modification is our weapon. So, we can deposit a carbon coating here conductive carbon. So, that basically a porous carbon network as you can see here.

So, this carbon network is quite porous and that facilitates the charge transfer of the surface of the anode in line to the mitigating the problem. This is one of the solutions. And also this carbon acts as a barrier to impede the side reaction with the electrolyte particularly at the low potential and it might retard electrolyte decomposition on the anode surface.

So, as compared to the previous plot whatever I showed you can see here the bare one there is a huge drop in capacity within 100 cycles, but once you coat it with carbon this is reasonably good. I will not say that it is fade free initial this large fading takes place because of the SEI formation, but then more or less it gets stabilized.

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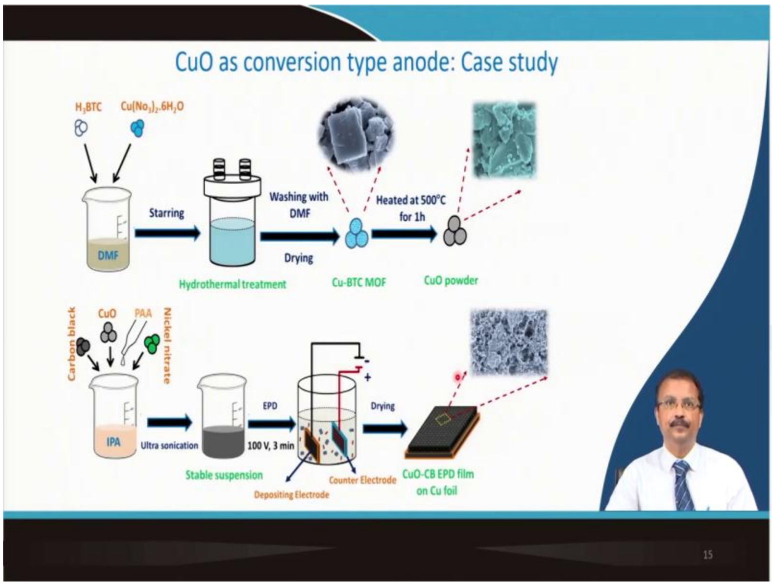

CuO as conversion type anode: Case study

H_3BTC

$Cu(No_3)_2.6H_2O$

DMF

Starring

Hydrothermal treatment

Washing with DMF

Drying

Cu-BTC MOF

Heated at 500°C for 1h

CuO powder

Carbon black

CuO

PAA

Nickel nitrate

IPA

Ultra sonication

Stable suspension

EPD

100 V, 3 min

Depositing Electrode

Counter Electrode

Drying

CuO-CB EPD film on Cu foil

This is a very cheap material copper oxide and this is very close to my heart so that whether this copper oxide can be used and it is a conversion type of material. So, we can prepare it by hydrothermal method. I am not going into the integrate detail of this metal organic framework structure which purposefully we did for the betterment of the powder that we are getting.

But, we did deposit it by electrophoretic deposition and you can see a porous layer is formed out of this powders which were prepared by hydrothermal synthesis.

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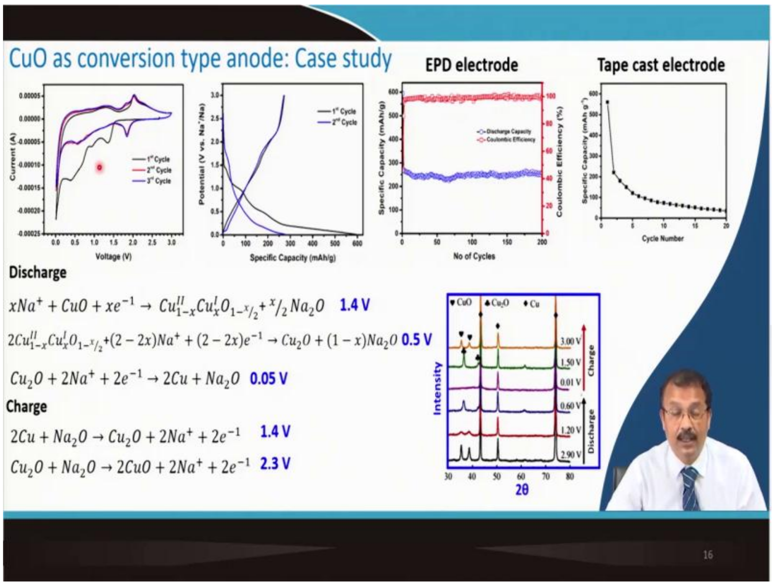

CuO as conversion type anode: Case study

Discharge

$xNa^+ + CuO + xe^{-1} \rightarrow Cu^{II}_{1-x}Cu^{I}_{x}O_{1-x/2} + x/2\,Na_2O$ **1.4 V**

$2Cu^{II}_{1-x}Cu^{I}_{x}O_{1-x/2} + (2-2x)Na^+ + (2-2x)e^{-1} \rightarrow Cu_2O + (1-x)Na_2O$ **0.5 V**

$Cu_2O + 2Na^+ + 2e^{-1} \rightarrow 2Cu + Na_2O$ **0.05 V**

Charge

$2Cu + Na_2O \rightarrow Cu_2O + 2Na^+ + 2e^{-1}$ **1.4 V**

$Cu_2O + Na_2O \rightarrow 2CuO + 2Na^+ + 2e^{-1}$ **2.3 V**

Discharge:

$xNa^{+} + CuO + xe^{-1} \rightarrow \ Cu^{II}_{1-x}Cu^{I}_{x}O_{1-x/2} + x/2\, Na_2O$

$2Cu^{II}_{1-x}Cu^{I}_{x}O_{1-x/2} + (2-2x)Na^{+} + (2-2x)e^{-1} \rightarrow Cu_2O + (1-x)Na_2O$

$Cu_2O + 2Na^{+} + 2e^{-1} \rightarrow 2Cu + Na_2O$

Charge:

$$2Cu + Na_2O \rightarrow Cu_2O + 2Na^{+} + 2e^{-1}$$

$$Cu_2O + Na_2O \rightarrow 2CuO + 2Na^{+} + 2e^{-1}$$

Now, you can have progressively this characterization. For example, during charge and discharge whatever is happening at different voltage stage, you can stop the measurement and do the X-ray diffraction. And from the phase analysis you know exactly what are the phases that you are getting when it gets reduced and eventually get oxidized.

So, this CV is important. Alternatively you can do differential capacity plot of your discharge and charge profile to get a better idea about the voltage. So, based on this X-ray diffraction study and also the cyclic voltammetry we can have this discharge and charge reactions what is going on at different voltages. So, I am leaving it on you to understand this.

So, you know that it is not a direct conversion of sodium ion and copper right. So, you can have different phases here and we could identify this phase through the X-ray diffraction analysis. So, at which voltage what reaction is going on if you do this simple set of measurement CV this one and this one then you can actually write this equations.

So, try to redo it because you know that what are the phases, that is being formed at different charge and discharge cycles you can easily see that what are the voltage shows the signature of this reaction. So, only thing you will have to predict that what is exactly being formed. Now, if it is crystalline it is very easy for you to identify through X-ray diffraction, but if it is not crystalline then your that will make your life little bit complicated.

So, finally, you see that again this copper reacts with sodium to form copper 2 oxide and copper 2 oxide and sodium oxide they forms again back this CO. So, this is a bit different types of mechanism that you can see. It is not directly forming any alloy, but it is the oxide that is forming. I will ask you to go through this reaction and try to understand from the CV plot.

But, eventually what you are seeing that this discharge capacity is quite good up to 200 cycles as compared to the other sodium ion data that we see. And the coulombic efficiency is also quite good. And if you compare this with your tape cast electrode, you see the it almost fade within twenty cycles. So, indeed this processing has a strong influence on the electrochemical properties.

The adhesion is very important. Because you know the volumetric expansion etcetera is going on. So, you should have a very strong adherence between the current collector and the active material of your anode.

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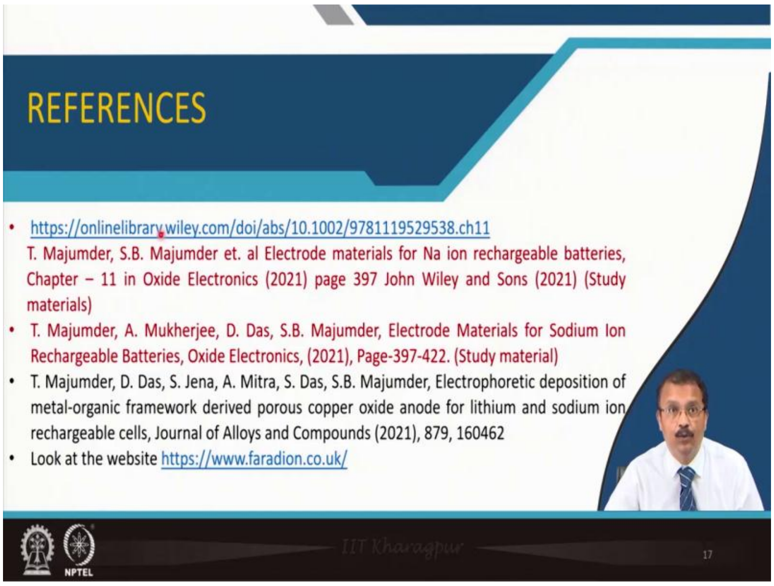

REFERENCES

- https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119529538.ch11
  T. Majumder, S.B. Majumder et. al Electrode materials for Na ion rechargeable batteries, Chapter – 11 in Oxide Electronics (2021) page 397 John Wiley and Sons (2021) (Study materials)
- T. Majumder, A. Mukherjee, D. Das, S.B. Majumder, Electrode Materials for Sodium Ion Rechargeable Batteries, Oxide Electronics, (2021), Page-397-422. (Study material)
- T. Majumder, D. Das, S. Jena, A. Mitra, S. Das, S.B. Majumder, Electrophoretic deposition of metal-organic framework derived porous copper oxide anode for lithium and sodium ion rechargeable cells, Journal of Alloys and Compounds (2021), 879, 160462
- Look at the website https://www.faradion.co.uk/

So, I would like you to go through this book which very recently we have published and many new types of material we have proposed along with that we have reviewed all the anode and cathode materials and also the electrolyte material which I will cover in my next lecture. And there are certain publication. So, this book is important. This paper is important and I think it is downloadable, you can try that.

Apart from our own paper there are many other carbonaceous material and other materials pertinent to this type of electro ceramics that will be quite interesting for you to study and this copper oxide it is quite good. So, that recently also published. So, materials are quite new.

So, in the textbook you will not find a very exhaustive details about this type of material for sodium ion battery. And there is to my best of my knowledge there is only one company unlike there are several companies I talked about for lithium ion batteries. But there is only one company in UK, Faradion. So, I would like you to go through this.

This their website that what exactly their news, what they are planning to do, what they have already achieved and that will give you a fairly good idea about the technological aspect of sodium ion batteries.

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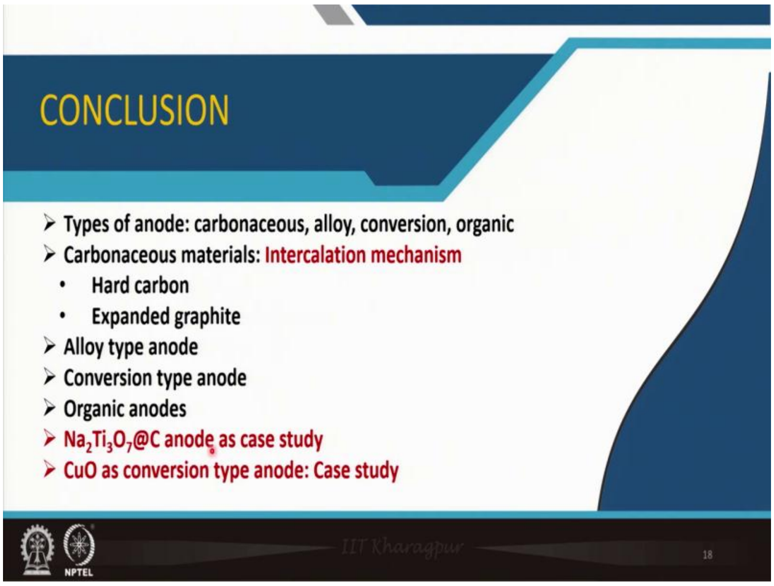

CONCLUSION

- Types of anode: carbonaceous, alloy, conversion, organic
- Carbonaceous materials: Intercalation mechanism
  - Hard carbon
  - Expanded graphite
- Alloy type anode
- Conversion type anode
- Organic anodes
- $Na_2Ti_3O_7$@C anode as case study
- CuO as conversion type anode: Case study

So, we have talked about types of anode: carbonaceous material, alloy, conversion type and organic. Carbonaceous material, it is intercalation type. We considered hard carbon and expanded graphite. Alloy type of anode its more or less same the features like lithium ion battery. Conversion types of anode we have talked about. Organic anodes we have just touched and these two material as a case study.

Very recently we have done some work on these materials and I thought that I should share with you. So, that you can from the knowledge that you are gaining through the lecture you can just correlate that experimentally laboratory based research what exactly you are getting.

Thank you for your attention.