Electrochemical Energy Storage
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Module - 06
Sodium ion rechargeable cell
Lecture - 26
Positive Electrodes: Layered Oxide, Polyanionic Compounds (Phosphates, Sulphates etc.), Organic Compounds

Welcome to my course Electrochemical Energy Storage. And this is module number-6. And in this module, we will be talking on sodium ion rechargeable batteries. So far we have only talked about lithium-ion batteries, but this is a new chemistry. And this is lecture number-26, where we will be talking about the Positive electrodes which includes Layered oxide, polyanionic compound which includes phosphates sulphates etcetera and also organic compound.

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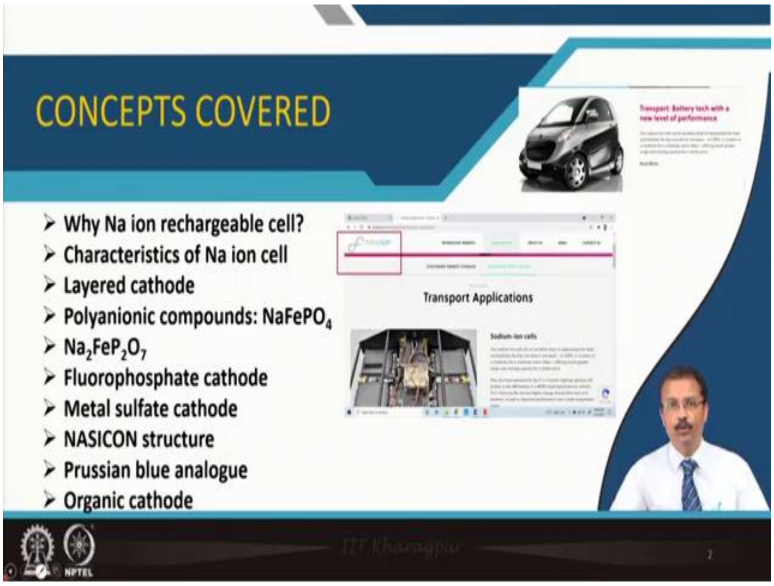

CONCEPTS COVERED

- Why Na ion rechargeable cell?
- Characteristics of Na ion cell
- Layered cathode
- Polyanionic compounds: $NaFePO_4$
- $Na_2FeP_2O_7$
- Fluorophosphate cathode
- Metal sulfate cathode
- NASICON structure
- Prussian blue analogue
- Organic cathode

Now, this is interesting that instead of lithium-ion batteries, now people are also working on sodium ion batteries as well. And this is to my knowledge is the only company Faradion, UK based company. And they are now using sodium ion battery for small cars even. So, I would like you to go through their website for further details.

Although you will not get much as far as the technical properties of this batteries or the chemistries are concerned, but what for their plant to be used that those kind of idea we will be getting.

So, I will talk about why suddenly sodium ion rechargeable cell we are moving away from lithium-ion batteries, then what are their characteristics, and then different types of positive electrode materials. You can see layered cathode, polyanionic compound, then sodium iron phosphate, then fluorophosphate cathode, metal sulfate cathode, NASICON structure already I have introduced in part of my other lecture Prussian blue analog and organic cathodes, a whole lot of material people are studying so that the best fitted one that will be commercially used.

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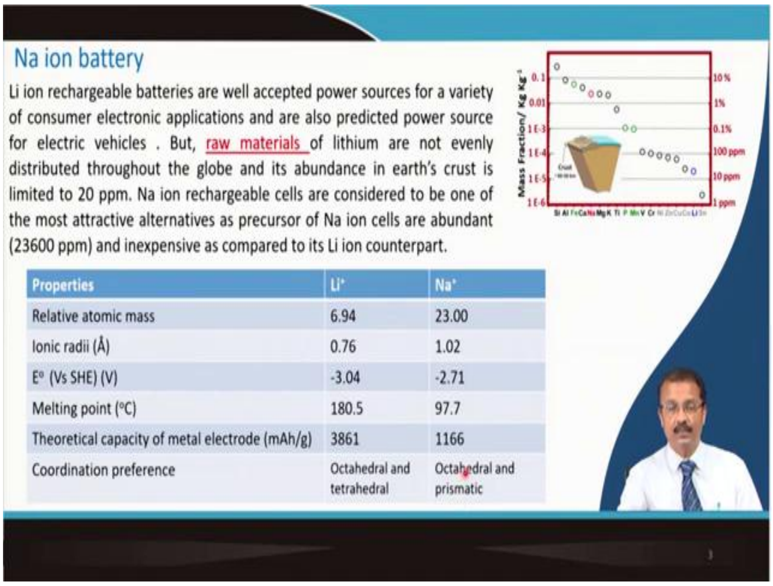

Na ion battery

Li ion rechargeable batteries are well accepted power sources for a variety of consumer electronic applications and are also predicted power source for electric vehicles . But, raw materials of lithium are not evenly distributed throughout the globe and its abundance in earth's crust is limited to 20 ppm. Na ion rechargeable cells are considered to be one of the most attractive alternatives as precursor of Na ion cells are abundant (23600 ppm) and inexpensive as compared to its Li ion counterpart.

Properties	Li^+	Na^+
Relative atomic mass	6.94	23.00
Ionic radii (Å)	0.76	1.02
E° (Vs SHE) (V)	-3.04	-2.71
Melting point (°C)	180.5	97.7
Theoretical capacity of metal electrode (mAh/g)	3861	1166
Coordination preference	Octahedral and tetrahedral	Octahedral and prismatic

So, if you talk about the sodium ion battery as compared to lithium rechargeable batteries, one thing is quite clear that lithium-ion battery is a well accepted power source for a variety of not only consumer electronic applications, but also they are predicted power source for electric vehicles, in certain electric vehicles already people have started to use it.

But the raw material if you see that lithium they are not abundant they are not abundant in earth crust, and very limited amount is available about 20 ppm in the earth crust you will find lithium. Sodium, on the other hand that is most attractive in some sense that it is abundantly available. And it is much much cheaper than lithium. So, sodium precursor materials are abundant. And you can compare their ppm level which is way ahead than 20 ppm, and it is also inexpensive.

So, if you have a brief comparison between these two this – lithium-ion and sodium ion, atomic mass certainly it is heavier, so the batteries will have high energy density in case of lithium-ion battery, but sodium ion battery will have lower energy density because of the weight.

Ionic radius is much larger as compared to lithium in terms of Angstrom you can see. The standard electrode reduction potential this is also a bit lower minus 2.71 volt as compared to 3.04 volt when lithium is measured as compared to standard hydrogen electrode.

Melting point, this is also lower that is another disadvantage that sodium is having lower melting point than lithium. Theoretical capacity also much lower and I guess you will be able to estimate the theoretical capacity of sodium and compare it with lithium from the Faraday law which I taught earlier.

And coordination preference both are octahedral. And in case of lithium, it prefers to stay in tetrahedral site; and this actually stays in a prismatic site, so that we will be talking about.

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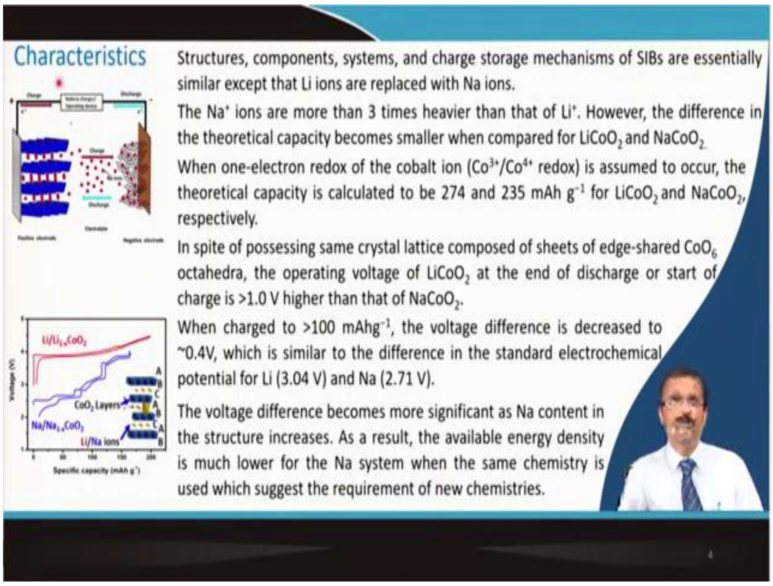

Characteristics

Structures, components, systems, and charge storage mechanisms of SIBs are essentially similar except that Li ions are replaced with Na ions.

The Na^+ ions are more than 3 times heavier than that of Li^+. However, the difference in the theoretical capacity becomes smaller when compared for $LiCoO_2$ and $NaCoO_2$.

When one-electron redox of the cobalt ion (Co^{3+}/Co^{4+} redox) is assumed to occur, the theoretical capacity is calculated to be 274 and 235 mAh g^{-1} for $LiCoO_2$ and $NaCoO_2$, respectively.

In spite of possessing same crystal lattice composed of sheets of edge-shared CoO_6 octahedra, the operating voltage of $LiCoO_2$ at the end of discharge or start of charge is >1.0 V higher than that of $NaCoO_2$.

When charged to >100 $mAhg^{-1}$, the voltage difference is decreased to ~0.4V, which is similar to the difference in the standard electrochemical potential for Li (3.04 V) and Na (2.71 V).

The voltage difference becomes more significant as Na content in the structure increases. As a result, the available energy density is much lower for the Na system when the same chemistry is used which suggest the requirement of new chemistries.

Now, if you look at the characteristics of these two batteries, the structure, component, system, and charge storage mechanism of sodium ion batteries are more or less similar to that of lithium-ion battery.

The same kind of processing that is adopted, and I have talked about the self-application. So, the same equipment that you will be able to use unlike lead acid battery. So, the change in the chemistry from lithium to sodium it is not of a much concern, but as I said it is heavier than lithium.

Now, the theoretical capacity becomes smaller in lithium cobalt oxide and similar structure which is sodium cobalt oxide. So, when one electron redox of the cobalt ion from plus 3 to plus 4 state is assumed to occur, the theoretical capacity if you assume all the lithium can be taken out from lithium cobalt oxide, it is 274 in case of LiCoO2, but in case of sodium cobalt oxide it is 235.

So, the crystal structure is more or less same. It composed sheets of edge-shared transition metal octahedron, operating voltage of lithium cobalt oxide at the end of the discharge or start of the charge that is more than 1 volt as you can see here. So, you are charging it.

So, this is the charging voltage. Then you start to discharge, and discharge ends here. Similarly, sodium you can see several steps are there because of the chemistry. And then when you discharge it, then this difference is quite large.

So, assume that you are using about 100 milliampere hour per gram. This actually this should be milliampere per gram. So, this is the rate; this hour will not be there. The voltage difference is decreased to 0.4 because that is from the standard reduction potential you see that this difference is there.

So, this is coming up. So, in the charge state, this voltage difference is not that much. And there is something to do with the structure of this layered type of cathode material.

And the voltage difference that becomes more significant as sodium content in the structure is increases that means it is in the discharge state you can see that the difference is more. So, the available energy density is relatively lower because you know that the voltage along with the capacity that will give you the energy. So, energy will be lower in case of sodium system as compared to lithium-ion battery systems.

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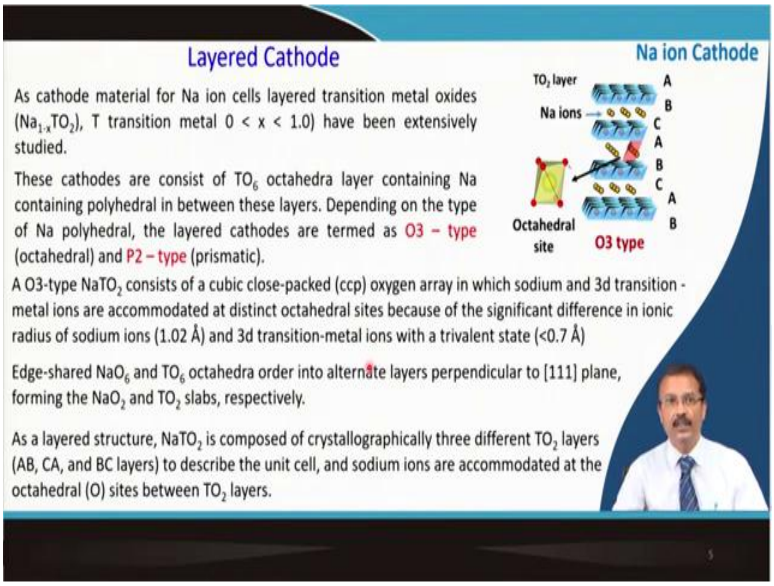

Layered Cathode

As cathode material for Na ion cells layered transition metal oxides ($Na_{1-x}TO_2$), T transition metal $0 < x < 1.0$) have been extensively studied.

These cathodes are consist of TO_6 octahedra layer containing Na containing polyhedral in between these layers. Depending on the type of Na polyhedral, the layered cathodes are termed as O3 – type (octahedral) and P2 – type (prismatic).

A O3-type $NaTO_2$ consists of a cubic close-packed (ccp) oxygen array in which sodium and 3d transition - metal ions are accommodated at distinct octahedral sites because of the significant difference in ionic radius of sodium ions (1.02 Å) and 3d transition-metal ions with a trivalent state (<0.7 Å)

Edge-shared NaO_6 and TO_6 octahedra order into alternate layers perpendicular to [111] plane, forming the NaO_2 and TO_2 slabs, respectively.

As a layered structure, $NaTO_2$ is composed of crystallographically three different TO_2 layers (AB, CA, and BC layers) to describe the unit cell, and sodium ions are accommodated at the octahedral (O) sites between TO_2 layers.

So, like your sodium like your lithium-ion batteries, sodium ion battery is also have this kind of layered cathode. So, one of the example is sodium transition metal oxide T stands for that O 2. So, there is a typical layer structure as you can see A B C, A B C kind of stacking that is there.

So, it consists this transition metal octahedra here, that contains the sodium containing polyhedra in between these layers. So, this is also in a polyhedral form. So, in this particular case, it is in the octahedral type of polyhedra it is assuming the sodium.

And depending on the type of this sodium ion polyhedral, the layered cathode we term as O 3-type which is octahedral also sometimes it is P 2-type which is prismatic. And when you take out the sodium from the structure, then like your lithium-ion battery there is also structural phase transition takes place from O 3 to P 3 to several other structure it can form.

So, this O 3-type NaTO 2 that consists cubic close pack oxygen array in which sodium and this 3d transition metals ion are accommodated at a distinct octahedral site, as you can see here both are in octahedral coordination.

There is a significant difference of the radius of sodium ion 1.02 Angstrom and 3 d transition metal ions in trivalent state it is less than 0.7 angstrom. So, there is a size difference between sodium site in this octahedral, and transition metal which stays in other type of octahedral in the transition metal layer. So, this Na O 6 and TO 6 this octahedra are etched into alternate layers perpendicular to 111 plane that you cannot visible, it is not visible here along with the 111 plane.

But if you can draw this crystal structure based on its space group using a program like Vesta, if I find time, I will introduce the Vesta program, so that any space group for any crystal structure if it is known to you can have a look of the crystal structure, and at different direction how it looks like it will be easily visible to you. So, that is a wonderful program I will try to part of it to introduce somewhere in this lectures.

So, as a layered structure this NaTO 2 that composed of crystallographically three different TO 2 type layers. One constant A B, or C A, or B C types of layer. And that basically describes the unit cell. And sodium ions they are accommodated at the octahedral site that is in between this TO 2 layer as we have shown in this schematic.

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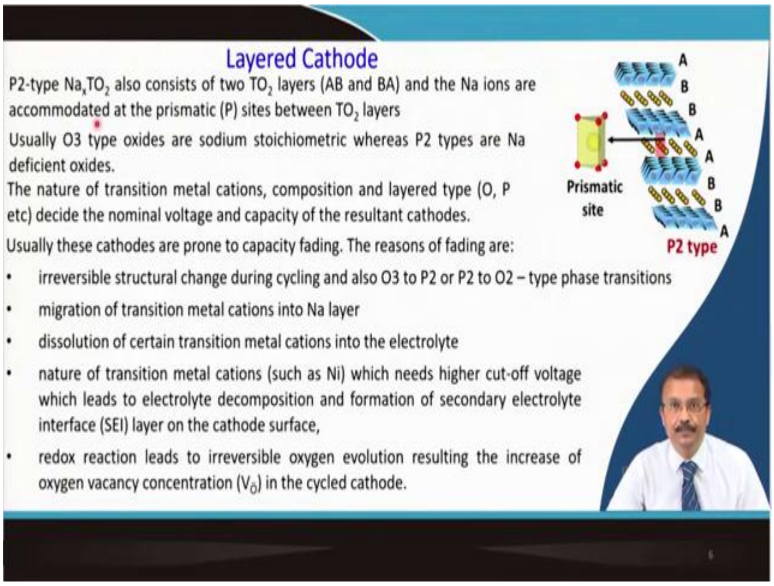

Layered Cathode

P2-type Na_xTO_2 also consists of two TO_2 layers (AB and BA) and the Na ions are accommodated at the prismatic (P) sites between TO_2 layers

Usually O3 type oxides are sodium stoichiometric whereas P2 types are Na deficient oxides.

The nature of transition metal cations, composition and layered type (O, P etc) decide the nominal voltage and capacity of the resultant cathodes.

Usually these cathodes are prone to capacity fading. The reasons of fading are:

- irreversible structural change during cycling and also O3 to P2 or P2 to O2 – type phase transitions
- migration of transition metal cations into Na layer
- dissolution of certain transition metal cations into the electrolyte
- nature of transition metal cations (such as Ni) which needs higher cut-off voltage which leads to electrolyte decomposition and formation of secondary electrolyte interface (SEI) layer on the cathode surface,
- redox reaction leads to irreversible oxygen evolution resulting the increase of oxygen vacancy concentration (V_δ) in the cycled cathode.

Now, this P 2 type structure of the layered material that also consists of two TO 2 layers one is AB and then BA, AB and BA type. And sodium ions are accommodated in a prismatic site between TO 2 layers. So, in between, this it is not octahedral, but prismatic layer.

Now, usually this O 3 type oxides are sodium Stoichiometric, whereas, when it is prismatic type, then it is sodium deficient oxide because of the structural consideration. So, the nature of the transition metal cation which stays here in this layers, composition and layer type O, P, etcetera, I mean this kind of configurations are there that decides the nominal voltage that we will have and as well as the capacity of the resultant cathode.

Usually, these cathodes are prone to capacitive fading. The reason you may be able to appreciate now. First is this irreversible structural change during cycling O 3 to P 2 or P 2 to O 2 – type phase transition.

Another one is the migration of the transition metal cation into the sodium layer that also you can estimate from crystal field stabilization energy concept which I taught earlier followed by octahedral state stabilization energy. So, you will be seeing that in the sodium layer transition metal cation disorder cannot be avoidable, and that leads to capacity fading.

Dissolution of certain transition metal cations into the electrolyte that is another thing that is happening. And you are losing your active material and that will lead to capacitive fading. Nature of transition metal cation, if you use nickel which needs higher cut off voltage because the oxidation potential is higher as compared to cobalt and as compared to manganese which are basically used as transition metal cation.

That can lead to the electrolyte decomposition and formation of the secondary electrolyte interface not on the negative electrode, but on the positive electrode. And you know that this kind of SEI usually dissolves in the electrolyte and that creates problem leads to capacity fading.

Redox reaction leads to irreversible oxygen evolution that is another problem. In lithium cobalt oxide also you have seen that oxygen comes out when the charging voltage is higher. And oxygen vacancy that is introduced in the material in order to maintain the charge balance. And as a result cyclability is deteriorated.

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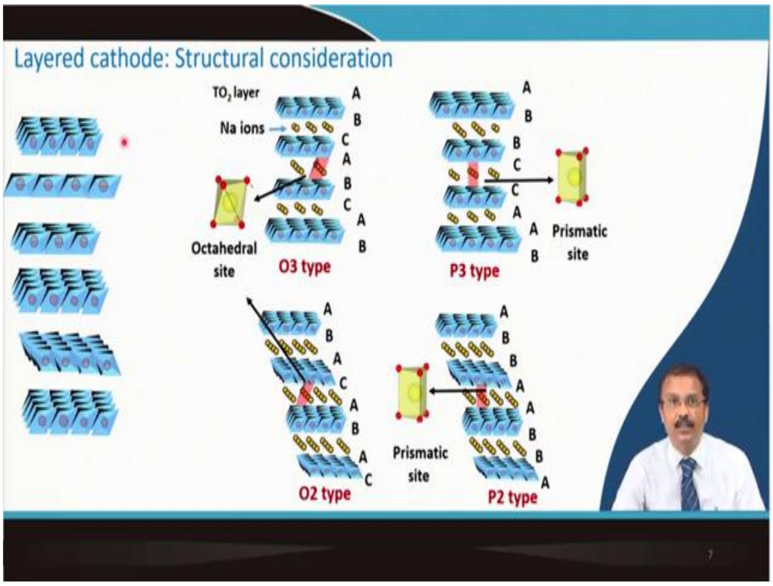

Layered cathode: Structural consideration

So, this is the type of structure that we are talking about. So, you can see now this octahedral site, you can see the prismatic site, and that is the stacking sequence for O 3, for P 3, for O 2, and P 2 type. And depending on the type of the layer structure and depending on the type of transition metal cation, this kind of phase transition from one phase to another which is a slight change in their octahedral configuration, and layered structured configuration that can deteriorate the electrochemical properties.

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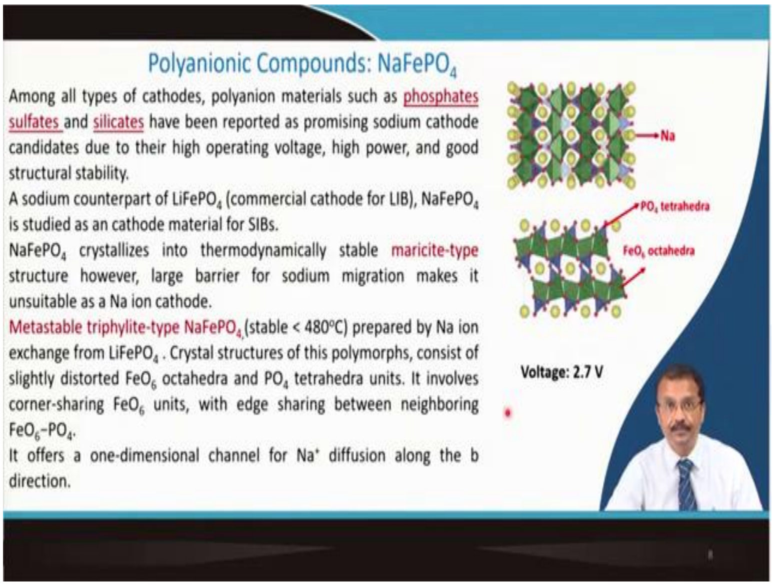

Polyanionic Compounds: $NaFePO_4$

Among all types of cathodes, polyanion materials such as phosphates sulfates and silicates have been reported as promising sodium cathode candidates due to their high operating voltage, high power, and good structural stability.

A sodium counterpart of $LiFePO_4$ (commercial cathode for LIB), $NaFePO_4$ is studied as an cathode material for SIBs.

$NaFePO_4$ crystallizes into thermodynamically stable maricite-type structure however, large barrier for sodium migration makes it unsuitable as a Na ion cathode.

Metastable triphylite-type $NaFePO_4$ (stable < 480°C) prepared by Na ion exchange from $LiFePO_4$. Crystal structures of this polymorphs, consist of slightly distorted FeO_6 octahedra and PO_4 tetrahedra units. It involves corner-sharing FeO_6 units, with edge sharing between neighboring FeO_6-PO_4.

It offers a one-dimensional channel for Na^+ diffusion along the b direction.

Voltage: 2.7 V

With respect to this layered type of cathode material polyanion compound like your lithium-ion phosphate, there is this is sodium iron phosphate something similar to this. People are only picking up those material. So, among all types of cathodes, this polyanion material it could be phosphate, it could be sulfate, it could be silicate, they are reported to be sodium cathode candidate. And mainly that is due to their higher operating voltage higher power, you can drain more power out of it. And of course, the structural stability which we much better than this simple layered structure.

Sodium counter part of lithium phosphate this is a commercial cathode for lithium battery you have seen it, sodium iron phosphate this has been studied extensively. It basically crystallizes into a stable state we call it maricite-type of structure, but there is a large barrier of sodium migration. So, sodium cannot be extracted from this structure that easily. So, this is not very suitable, this sodium iron phosphate unlike lithium iron phosphate, it is not very suitable cathode material.

As compared to that if you take a metastable triphylite-type sodium iron phosphate, this is quite stable at this temperature less than this temperature. And this is basically prepared by sodium ion exchange in lithium iron phosphate. So, lithium that you can do electrochemically, electrochemically you can do that you have already seen it you take a NASICON structure, put lithium salt, extract the sodium first, and there are plenty of lithium sodium is lost somewhere inside the system, and it is lithium that would intercalate.

So, something similar can be done. So, from lithium iron phosphate this kind of structure you can make. And this crystal structures of this type of polymorph, they consist slightly distorted of this Fe O 6 octahedra that you can see, and P O 4 tetrahedra. So, this octahedron tetrahedron is slightly distorted.

So, it involves the corner sharing of Fe O 6 octahedra with each sharing between neighboring Fe O 6 and P O 4. So, structurally it is something like that, so that a one-dimensional one channel for lithium ion diffusing direction that is expedite.

So, what you are doing the same structure which is stable structure which is thermodynamically stable, you are slightly distorting it just to make sure that the sodium ion are properly you can take out and put it back.

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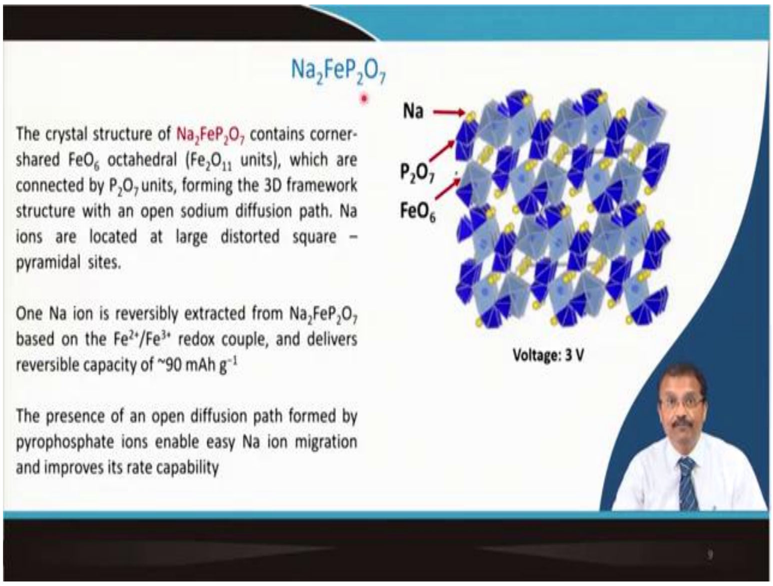

$Na_2FeP_2O_7$

The crystal structure of $Na_2FeP_2O_7$ contains corner-shared FeO_6 octahedral (Fe_2O_{11} units), which are connected by P_2O_7 units, forming the 3D framework structure with an open sodium diffusion path. Na ions are located at large distorted square – pyramidal sites.

One Na ion is reversibly extracted from $Na_2FeP_2O_7$ based on the Fe^{2+}/Fe^{3+} redox couple, and delivers reversible capacity of ~90 mAh g^{-1}

The presence of an open diffusion path formed by pyrophosphate ions enable easy Na ion migration and improves its rate capability

Voltage: 3 V

Na 2 Fe P 2 O 7 that is another crystal structure. And please go through this structure and correlate it with the schematic that we have shown. And if you have access to this program called vesta and you know their space group, then you can actually construct this kind of structure. And you can rotate it along with a axis, b axis, or ab plane you can rotate that. And clearly you can see what are the channels available for the sodium to move.

So, two dimensionally it is very difficult to make you understand that what exactly is going on. But from the text you will get the idea that it contains corner shared Fe O 6. So, this Fe O 6 is corner shared octahedral which are connected to this P 2 O 7 unit and that forms a 3D framework structure with the open sodium ion diffusion path. So, these are the small yellow spheres of the sodium. So, it has a clear cut channel for the sodium ion diffusion.

So, one sodium ion reversibly you can extract, not both of it because this is limited by this redox Fe 2 plus 2 3 plus. And it delivers reversibly about 90 milliampere hour per gram. I will expect that you can calculate the theoretical capacity from its molecular weight. It is 1 electron exchange. And from Faraday law, you can actually get these values. Now, the presence of an open diffusion path formed by the pyrophosphate ions enable easy sodium ion migration, and improve its rate performance. The voltage is in about 3 volt range that also you can calculate from the free energy composition diagram you can estimate that what will be the open circuit voltage under equilibrium condition.

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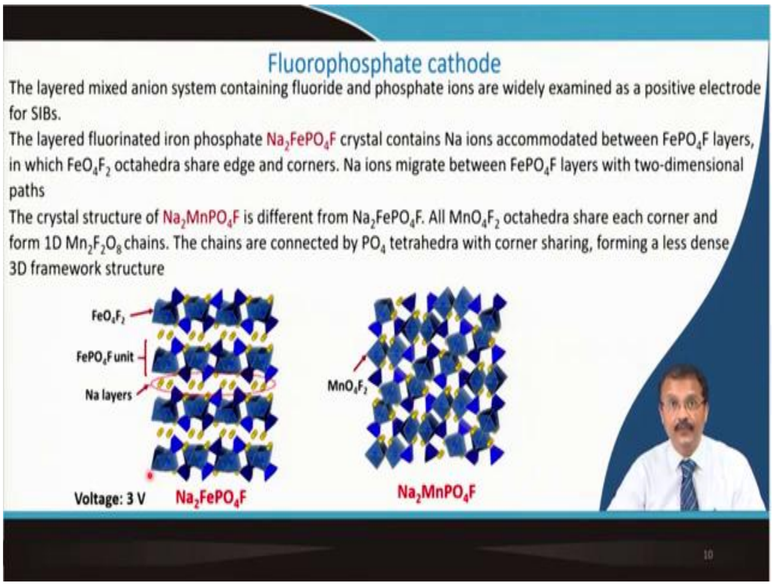

Fluorophosphate cathode

The layered mixed anion system containing fluoride and phosphate ions are widely examined as a positive electrode for SIBs.

The layered fluorinated iron phosphate Na_2FePO_4F crystal contains Na ions accommodated between $FePO_4F$ layers, in which FeO_4F_2 octahedra share edge and corners. Na ions migrate between $FePO_4F$ layers with two-dimensional paths

The crystal structure of Na_2MnPO_4F is different from Na_2FePO_4F. All MnO_4F_2 octahedra share each corner and form 1D $Mn_2F_2O_8$ chains. The chains are connected by PO_4 tetrahedra with corner sharing, forming a less dense 3D framework structure

Fluorophosphate is another cathode that is being talked about. The layered mixed anion system contains fluoride and phosphate ions that are widely examined as positive electrodes for SIBs. Lot of papers have been published. This layered fluorinated iron phosphate that contains sodium ion accommodated between Fe P O 4 F layers.

So, this unit Fe P O 4 F layers in which this Fe O 4 F 2. So, octahedra is there. They are H shared, they share both age and corners. And sodium ion migrates between this layer Fe P O 4 F with two-dimensional path. So, this is the sodium layer, two-dimensional path, you can extract it without disturbing much the structure.

The crystal structure of this when you replace iron with manganese is different from this one. So, this is manganese containing one. So, here all Mn O 4 F 2 octahedra share each corner, and form a 1D type, 1D type Mn 2 Fe 2 O 8 chains. And this chains are connected by P O 4 tetrahedra which are corner shared. This actually form a less dense 3D framework structure. This also can be used as positive electrode material.

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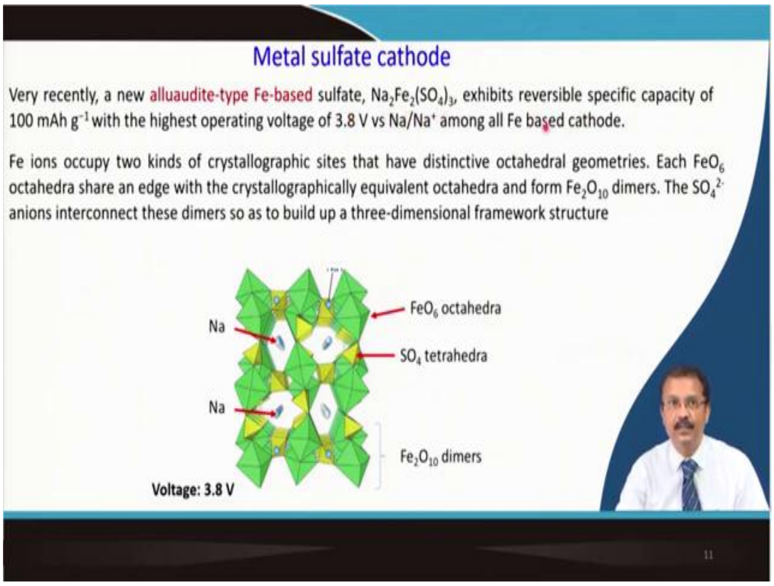

Metal sulfate cathode

Very recently, a new alluaudite-type Fe-based sulfate, $Na_2Fe_2(SO_4)_3$, exhibits reversible specific capacity of 100 mAh g^{-1} with the highest operating voltage of 3.8 V vs Na/Na^+ among all Fe based cathode.

Fe ions occupy two kinds of crystallographic sites that have distinctive octahedral geometries. Each FeO_6 octahedra share an edge with the crystallographically equivalent octahedra and form Fe_2O_{10} dimers. The SO_4^{2-} anions interconnect these dimers so as to build up a three-dimensional framework structure

Voltage: 3.8 V

Then let us talk about metal sulfate cathodes. And this is very recent type of work alluaudite-type Fe-based sulfate sodium 2 Fe 2 SO 4 whole 3 that exhibits a reversible capacity about 100 milliampere hour per gram with the highest operating voltage is quite large here 3.8 volt versus sodium.

So, here this Fe ion that occupies two kind of crystallographic sites that have different types of octahedral geometry. So, Fe O 6 octahedra share and edge with the crystallographically equivalent octahedra which is Fe 2 O 10 type of dimers. And the sulfate ions they interconnect this dimer, so that it is built a three dimensional framework structure. The voltage is pretty large, 38 volt, and you get a theoretical capacity about 100 milliampere hour per gram.

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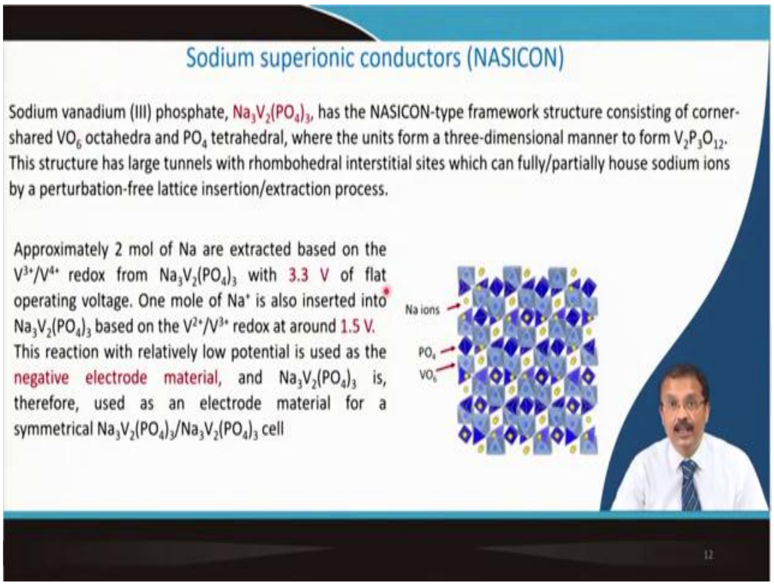

Sodium superionic conductors (NASICON)

Sodium vanadium (III) phosphate, $Na_3V_2(PO_4)_3$, has the NASICON-type framework structure consisting of corner-shared VO_6 octahedra and PO_4 tetrahedral, where the units form a three-dimensional manner to form $V_2P_3O_{12}$. This structure has large tunnels with rhombohedral interstitial sites which can fully/partially house sodium ions by a perturbation-free lattice insertion/extraction process.

Approximately 2 mol of Na are extracted based on the V^{3+}/V^{4+} redox from $Na_3V_2(PO_4)_3$ with 3.3 V of flat operating voltage. One mole of Na^+ is also inserted into $Na_3V_2(PO_4)_3$ based on the V^{2+}/V^{3+} redox at around 1.5 V. This reaction with relatively low potential is used as the negative electrode material, and $Na_3V_2(PO_4)_3$ is, therefore, used as an electrode material for a symmetrical $Na_3V_2(PO_4)_3/Na_3V_2(PO_4)_3$ cell

This already I have talked about sodium super ionic conductor NASICON type of structure, sodium vanadium phosphate is one of them. And this structure you remember the lantern type of structure we talked about, a corner shared V O 6, and P O 4 tetrahedra, this units form a three-dimensional manner to form this so called V 2, P 3 O 12 kind of formulation. And this structure has a large tunnel of rhombohedral interstitial sites which can be fully or partially house sodium ion by a perturbation-free lattice insertion extraction process.

But not all the sodium can be taken out. Approximately 2 moles of sodium ion can be extracted. One is very stubborn, it will not come out during charging, so that is due to the change in the redox of vanadium from plus 3 to plus 4. And it yields a very flat voltage around 3.3 volts. And 1 mole of sodium can also be inserted into this structure at relatively lower voltage about 1.5, then the structure changes to Na 4 instead of Na 3, so one more sodium you can insert it.

And this reaction as you can see is at lower voltage. So, this part can also be used as negative electrode material. So, 1.5 and 3.3, so you can get around a 2 volt battery. So, you can construct a symmetric N VP cell, and one acts as anode another acts as positive electrode.

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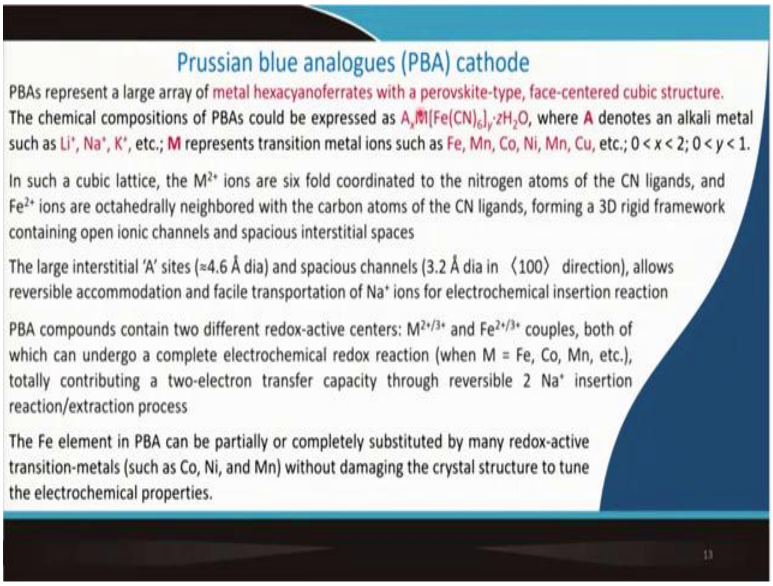

Prussian blue analogues (PBA) cathode

PBAs represent a large array of metal hexacyanoferrates with a perovskite-type, face-centered cubic structure. The chemical compositions of PBAs could be expressed as $A_xM[Fe(CN)_6]_y \cdot zH_2O$, where **A** denotes an alkali metal such as Li^+, Na^+, K^+, etc.; **M** represents transition metal ions such as Fe, Mn, Co, Ni, Mn, Cu, etc.; $0 < x < 2$; $0 < y < 1$.

In such a cubic lattice, the M^{2+} ions are six fold coordinated to the nitrogen atoms of the CN ligands, and Fe^{2+} ions are octahedrally neighbored with the carbon atoms of the CN ligands, forming a 3D rigid framework containing open ionic channels and spacious interstitial spaces

The large interstitial 'A' sites (≈4.6 Å dia) and spacious channels (3.2 Å dia in 〈100〉 direction), allows reversible accommodation and facile transportation of Na^+ ions for electrochemical insertion reaction

PBA compounds contain two different redox-active centers: $M^{2+/3+}$ and $Fe^{2+/3+}$ couples, both of which can undergo a complete electrochemical redox reaction (when M = Fe, Co, Mn, etc.), totally contributing a two-electron transfer capacity through reversible 2 Na^+ insertion reaction/extraction process

The Fe element in PBA can be partially or completely substituted by many redox-active transition-metals (such as Co, Ni, and Mn) without damaging the crystal structure to tune the electrochemical properties.

Prussian blue analogues that cathode also is very easy to make. And this basically represents a array of metal hexacyanoferrates. This is having a perovskite structure with face centered cubic lattice. Chemical composition of PBAs you can express like this. So, z molecule of water is also embedded here.

And A denotes this alkali metal, it could be lithium, it could be sodium. And M that represents a transition metal ions, and it could be iron, manganese, cobalt, copper, etcetera. And the range of the sodium is between 0 to 2, and range of this is from 0 to 1.

So, in the cubic lattice with M 2 plus ions they are having a six fold coordinated to the nitrogen atom of this cyanide ligands. And Fe 2 plus that is octahedrally neighbored. I will show you the structure in the next slide with the carbon atom of this cyanide ligand. So, this also forms a 3D rigid framework structure containing some open channel for that gives you a spacious interstitial space.

So, this large interstitial A site which is about 4.6 Angstrom in diameter, and spacious channel it measures about 3.2 Angstrom if you look at 100 direction that allows a reversible accommodation and facile transport of sodium ions. So, this compound contains two different redox active center.

One is this M cation and iron. So, both are possible so which can undergo a complete electrochemical redox reaction. So, this metal could be iron, metal you can replace part of it with cobalt. So, this can be replaced. So, two different types of transition metal cation you can use.

So, what you are doing a two electron transfer process is possible, and two sodium insertion and reaction extraction process can be operative. So, this Fe element in this Prussian, Prussian blue analogue, this can be partially or completely substituted as I said by many redox active transition metal cations without damaging the crystal structure. So, this could be another good material which is very easy to synthesize.

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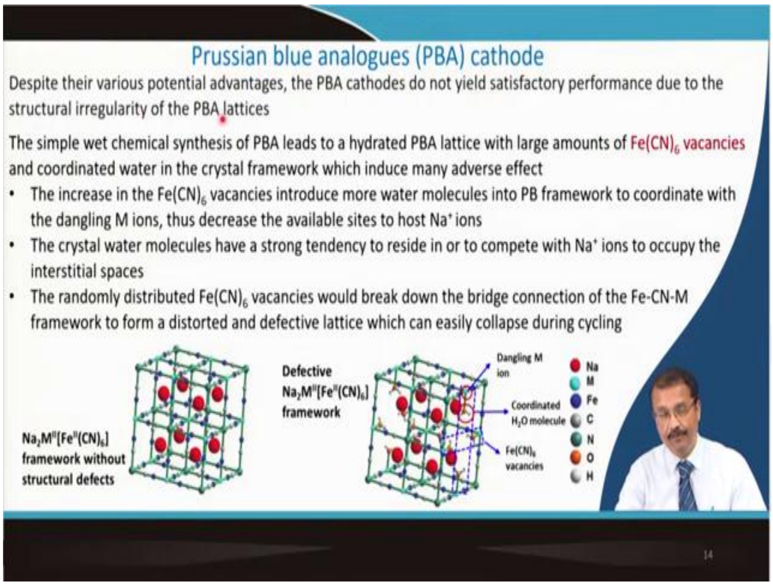

Prussian blue analogues (PBA) cathode

Despite their various potential advantages, the PBA cathodes do not yield satisfactory performance due to the structural irregularity of the PBA lattices

The simple wet chemical synthesis of PBA leads to a hydrated PBA lattice with large amounts of $Fe(CN)_6$ vacancies and coordinated water in the crystal framework which induce many adverse effect

- The increase in the $Fe(CN)_6$ vacancies introduce more water molecules into PB framework to coordinate with the dangling M ions, thus decrease the available sites to host Na^+ ions
- The crystal water molecules have a strong tendency to reside in or to compete with Na^+ ions to occupy the interstitial spaces
- The randomly distributed $Fe(CN)_6$ vacancies would break down the bridge connection of the Fe-CN-M framework to form a distorted and defective lattice which can easily collapse during cycling

But there is a problem they have very potential advantage, but these cathodes they usually do not yield satisfactory performance due to the structured irregularity in the Prussian blue analogue lattice. So, usually, we prepare it we have prepared it in our laboratory by wet chemical synthesis, and that leads to this hydrated PBA lattice. So, two molecular water is embedded in the structure, and that leads to lot of Fe CN 6 vacancy.

So, you can see here as compared to this one when it is a defective structure, lot of vacancies are there, and lot of dangling bonds you can see. All the cations are marked here. Sodium is the bigger one, then transition metal cation is also there iron is there, the cyanide, carbon, nitrogen, oxygen, and hydrogen, so they are all marked in this type of defect structure.

So, this vacancy introduce more water into this Prussian blue framework to coordinate the dangling M bond because now M bond is actually dangling. So, water is absorbed here. This actually decrease the available site for this sodium ion to host because this is replaced by the water molecule.

So, this crystal water is a problem. They have a strong tendency to reside or to compete with this sodium. So, they are enemy to this sodium ions to occupy this interstitial space. Now, this randomly distributed Fe CN 6 vacancy that could break down the bridge connection of Fe cyanide and metal cation framework to form a distorted and defective lattice which can collapse during cycling. So, this is one of the major problem for Prussian blue analog to be used as positive material.

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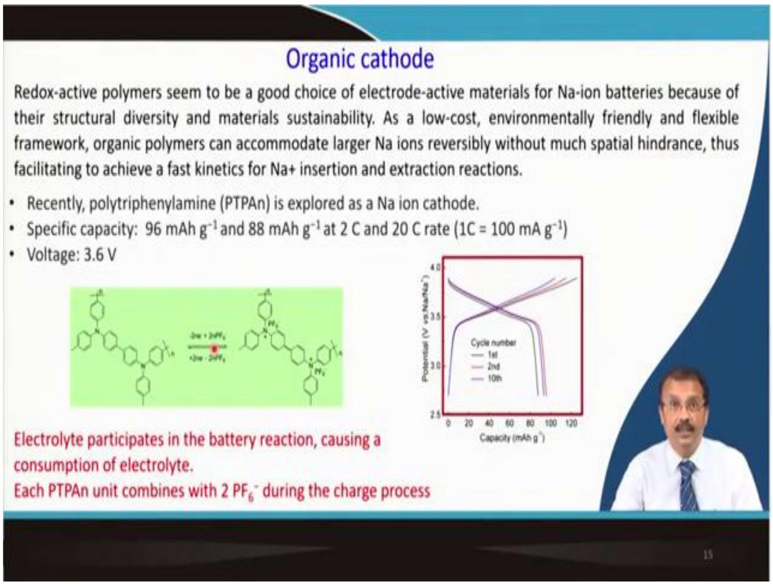

Organic cathode

Redox-active polymers seem to be a good choice of electrode-active materials for Na-ion batteries because of their structural diversity and materials sustainability. As a low-cost, environmentally friendly and flexible framework, organic polymers can accommodate larger Na ions reversibly without much spatial hindrance, thus facilitating to achieve a fast kinetics for Na+ insertion and extraction reactions.

- Recently, polytriphenylamine (PTPAn) is explored as a Na ion cathode.
- Specific capacity: 96 mAh g^{-1} and 88 mAh g^{-1} at 2 C and 20 C rate (1C = 100 mA g^{-1})
- Voltage: 3.6 V

Electrolyte participates in the battery reaction, causing a consumption of electrolyte.
Each PTPAn unit combines with 2 PF_6^- during the charge process

There are certain organic cathode, they are basically redox active polymers. This also could be a good choice for electro active materials for sodium ion batteries because mainly of their structural diversity and they are also sustainable. Of course, they are having low cost, environmental friendly, it is a flexible framework. So, you can make in future flexible batteries as well. And it can accommodate lot of sodium ions reversibly without much special hindrance like the crystalline material.

So, this is one example which is polytriphenylamine that has been explored as sodium ion cathode. One can get a specific capacity about 96 milliampere hour per gram. So, descent discharge capacity that you will get. And of course, it can also perform at 20 C rate. So, 20 C rate you can see it gives 88 milliampere hour per gram. And this is the structural part of this particular polymer.

So, here electrolyte participates in the battery reaction, and consumes the electrolyte. So, each of this so called PTPAn unit combines with the salt anion LIP sodium PF 6 it is combining with that. And that creates some problem as far as the cyclability is concerned because your electrolyte concentration is progressively reducing.

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So, basically the study material for this sodium ion battery, you will not find in a standard textbook because this is relatively new type of technology. So, you will have to actually depend on various review articles. And recently we have written a review article on the Electrode Materials which not only consists of the anode cathode material, but also consists of the anode materials. This is the book is Oxide Electronics by Wiley. So, this publisher's name I forgot to write, it is John Wiley is the publishers, so that is the study material.

And apart from this; this also you can consider which is also another review article in this channel. And for Prussian Blue, the vacancy, the defect size one this is a reasonably good article that you can consider. So, you will have to read for further details about the structure, about their properties, you will have to go through this literature carefully.

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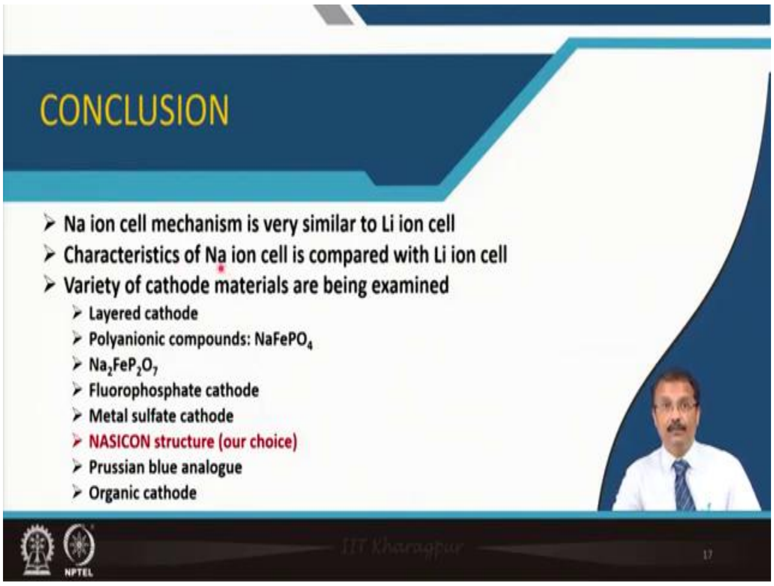

CONCLUSION

- Na ion cell mechanism is very similar to Li ion cell
- Characteristics of Na ion cell is compared with Li ion cell
- Variety of cathode materials are being examined
  - Layered cathode
  - Polyanionic compounds: $NaFePO_4$
  - $Na_2FeP_2O_7$
  - Fluorophosphate cathode
  - Metal sulfate cathode
  - NASICON structure (our choice)
  - Prussian blue analogue
  - Organic cathode

So, we have learnt that sodium ion cell mechanism is very similar to lithium-ions. Characteristics of sodium ion cell is compared with the lithium-ion cells as far as the voltage during charge and discharge, fully charged condition, fully discharged condition, that has been compared for a particular type of lithium-ion based cathode and sodium ion based cathode.

And we have introduced all types of positive electrode material, they are being now actively studied. Layered cathode which has been extensively studied till date. Polyanionic compounds this also few literatures are there.

This is relatively new material. Fluorophosphate is a new material. Metal sulfate cathodes has not yet been researched that rigorously. NASICON structure is of our choice. We are doing lot of work involving NASICON type of structure not only for sodium ion battery, but I have shown you that this material also you can utilize for lithium-ion intercalation. So, for dual ion batteries, this is a very, very good material.

Prussian blue analogue personally I see lot of if you can control the structure well, if you are a good chemist, then it is so simple to make and cost effective. So, there is a good prospect of Prussian blue analog. And organic cathode, they are coming up very few reports are there. So that also I have introduced.

Thank you for your interest.