# Electrochemical Energy Storage

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## Module - 04
## Basic components in Li – ion batteries: Electrodes, Electrolytes, and collectors
## Lecture - 20
## Novel Materials for Lithium Ion Rechargeable Cells

Welcome to my course, Electrochemical Energy Storage. And, we are now in module 4 where we are talking about the Basic Components of Lithium Ion batteries, we talked about positive Electrode, negative Electrode, separator, Electrolyte, tab, binder, and other components, which are required for lithium ion cell. And, this lecture that is to introduce the Novel Materials for Lithium Ion Rechargeable Cells.

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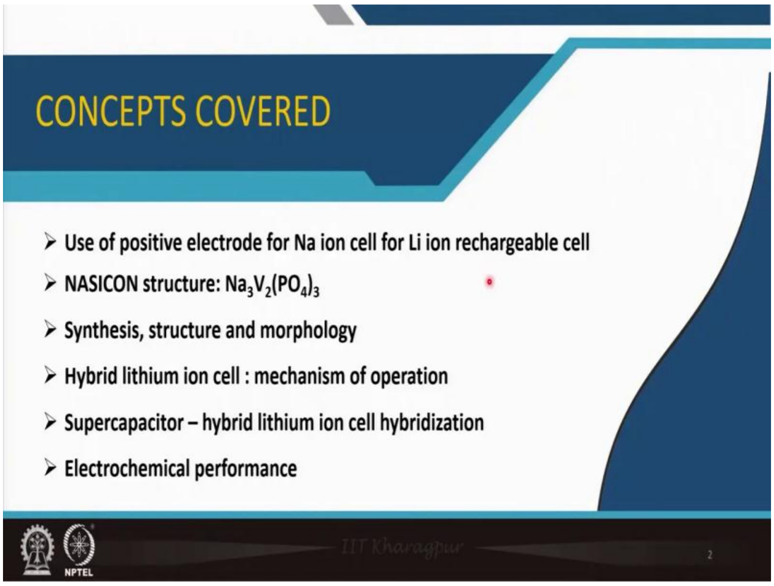

CONCEPTS COVERED

- Use of positive electrode for Na ion cell for Li ion rechargeable cell
- NASICON structure: $Na_3V_2(PO_4)_3$
- Synthesis, structure and morphology
- Hybrid lithium ion cell : mechanism of operation
- Supercapacitor – hybrid lithium ion cell hybridization
- Electrochemical performance

So, so far whatever we have described as you can understand that these are only some countable material as positive and negative electrode. Negative electrode they are in commercial perspective they are very limited. Only graphite and MCMB that is used silicon also as alloy element that is coming into the market.

And, in positive electrode either it is layer kind or spinel based or olivine type structure. And, the capacity that is not being improved that much and the power density for example, it is difficult to enhance more, but for not for consumer electronic application.

But, if you go for electric vehicles, then suddenly you know you want to have cells, which are having both energy density, large energy density, and power density simultaneously.

So, something which are novel that is needed to be done. So, I will cite the examples that how you can actually introduce novelty in the material development. We call that material engineering, we are using known type of material, but engineered them for a specific purpose.

So, one of such things is use the positive electrode, which is actually for sodium ion cell, studied mainly on sodium ion cell. And, use this for lithium ion rechargeable cells. So, this is a novel concept that was introduced some 5 to 6 years back, and then they are not pursued right, because of a variety of reasons.

So, I will show you that how you can actually make a high performance lithium ion battery. Particularly serving high power density, which is important for having a better acceleration of electric vehicles. So, this material they are having a NASICON type of structure I will define the structure is sodium ion super ionic conductor. So, that NASICON structured material is typically this Na 3 V 2 PO 4 whole 3. So, this is one of the examples.

So, we will talk about their synthesis their structure and their morphology. Then, we will introduce the concept of hybrid lithium ion cell, using a sodium ion battery material in lithium ion. So, it is some kind of duel ion characteristics. What is their mechanism of operation? And, then what can be done is this type of material they are kinetics that diffusion controlled. And, super capacitor you know that they are having adsorption of the charge layer to give the high capacity.

So, making some kind of hybrid of this dual ion positive electrode with super capacitor. So, we termed this as a hybrid lithium ion cell and then another hybridization in super capacitors and what could be their electrochemical performance. So, that is the novelty that I am planning to discuss in this particular lecture.

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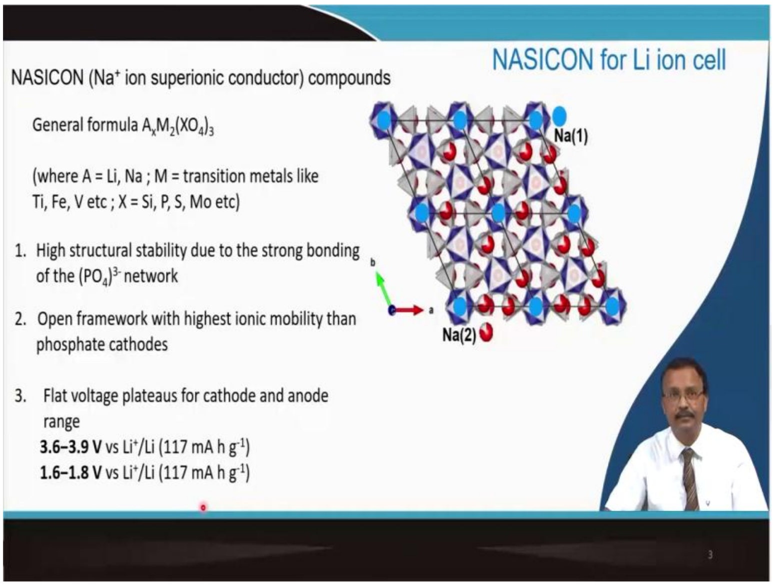

NASICON for Li ion cell

NASICON ($Na^+$ ion superionic conductor) compounds

General formula $A_xM_2(XO_4)_3$

(where A = Li, Na ; M = transition metals like
Ti, Fe, V etc ; X = Si, P, S, Mo etc)

1. High structural stability due to the strong bonding of the $(PO_4)^{3-}$ network
2. Open framework with highest ionic mobility than phosphate cathodes
3. Flat voltage plateaus for cathode and anode range
   **3.6–3.9 V** vs $Li^+/Li$ (117 mA h $g^{-1}$)
   **1.6–1.8 V** vs $Li^+/Li$ (117 mA h $g^{-1}$)

Now, this sodium ion superconduct superionic conductors. They have a general formula like A x where a could be lithium in this case whatever we have considered it is sodium and M is this one is a transition metals. Like, titanium, vanadium, iron and X here it is it constitutes this tetrahedral criteria tetrahedral kind of construction, it constitute silicon, phosphorus, sulfur, molybdenum. So, there is a general formula.

Now, this type of material they are having very high structural stability. Because, mainly the strong bonding of this phosphate PO 4 whole 3 due to this network. And, also they have relatively open structure; you know the sodium is not very structurally integrated in that way. So, it is having a relatively open framework structure. And, it yields higher ionic mobility, then the phosphate based cathode that we have considered like lithium ion phosphate, because of their structures.

So, there are two position of this sodium; one position we will call position number 1 and another is position number 2. So, there are 3 sodium in our structure whatever structure we will be talking about Na 3 V 2 PO 4 whole 3. So, there are per unit cell there are 3 sodium ion. So, out of these 3 whatever is there in position 1, 2 sodium ions are there you can take them out quite easily, but another position where sodium stays that are very stubborn they cannot be taken out.

So, this material being a polyanion kind of structure, you have seen you remember this spinodal decomposition type of features on this free energy composition whatever I discussed earlier. So, it is having a flat plateau. So, here the flat plateau is in this voltage range, which is quite good around 4 volt range. Additionally in the lower voltage ranges also there are plateaus. So, the same material you can use one as anode and the same material as cathode. And, operated two different voltage range and use a symmetric electrode battery, unlike your graphite lithium cobalt oxide, which is asymmetric. Here you can have a symmetric kind of batteries.

Now, this has been studied for sodium ion battery, it is not a new material, but it has been studied there, but what we plan to do or plan to show that this particular material now we want to use for lithium ion intercalation. So, sodium is there you think of it that we need to get rid of the sodium first and somehow put lithium inside the structure and then you cycle it. So, sodium is being not that effluent, they cannot enter into the structure, but lithium will go in and come out. So, that is the whole idea.

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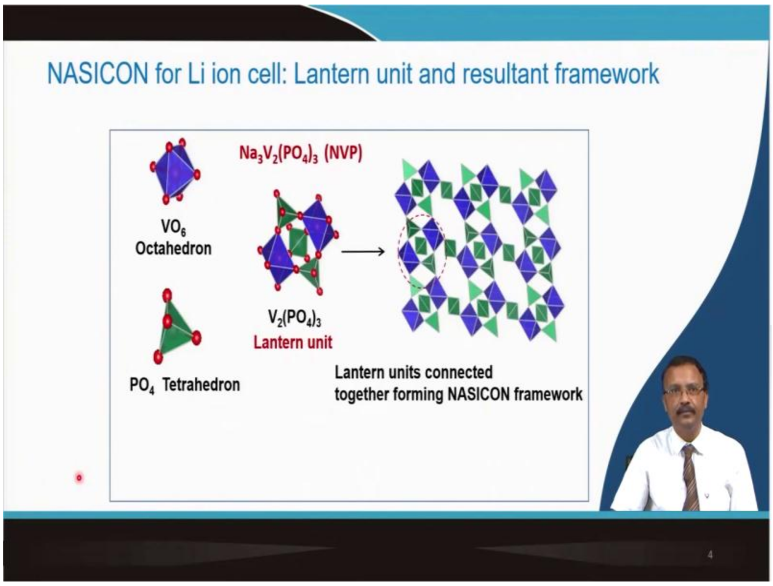

NASICON for Li ion cell: Lantern unit and resultant framework

$VO_6$ Octahedron

$PO_4$ Tetrahedron

$Na_3V_2(PO_4)_3$ (NVP)

$V_2(PO_4)_3$ Lantern unit

Lantern units connected together forming NASICON framework

Now, look at this structure of this NASICON type of material we are using it for lithium ion cell. You can see this VO 6 kind of octahedron.

So, this Na 3 V 2 PO 4 this vanadium they stay in an octahedral configuration this VO 6 type of octahedral configuration. And, PO 4 phosphorus stay here this small green button. So, that is in a tetrahedral configuration.

So, they consistent constitutes together a so, called lantern structure and there you have 3 such PO 4 and 2 such V 2. So, this is the lantern structure. So, it constitutes V 2 PO 4 whole 3.

And, in between somewhere these two sites that is occupied by 3 sodium. So, total there are 3 sodiums, but crystallographic Wyckoff position of them are not 3, 1 for 2 and another for the remaining one. So, it forms this kind of lanterns unit first and they are connected together to form this type of NASICON structure.

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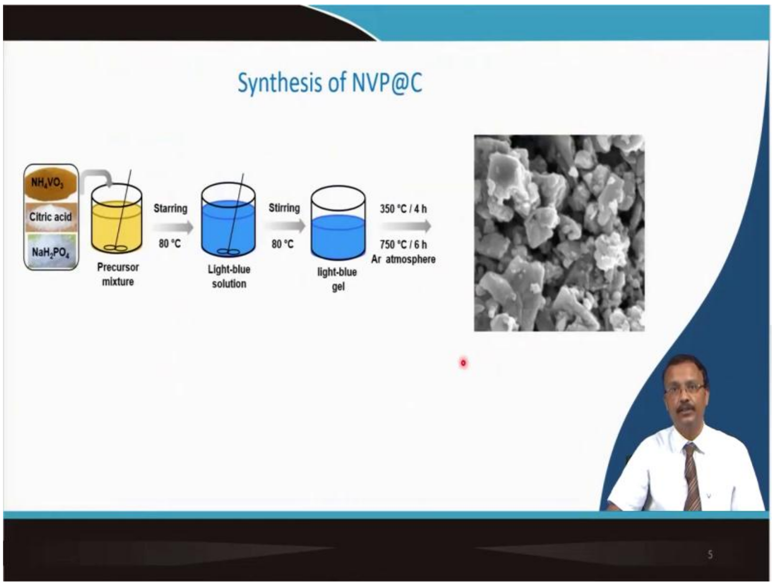

Synthesis of NVP@C

Now it is relatively easy to make this kind of structure. So, usually this ammonium V PO VO 3, citric acid and sodium dihydrogen phosphate, they are mixed together here they are start at 80 degrees Celsius.

And the light blue colour solution results, then again stirring continues and finally, we got a gel and you anneal this gel in organ ambient because your phosphorus is there it should not get oxidized. And, finally, you get this type of Na 3 V PO 4 kind of structure. So, this is simple solution process one can adopt only complicacy is that this will have to be annealed in organ or inert ambient.

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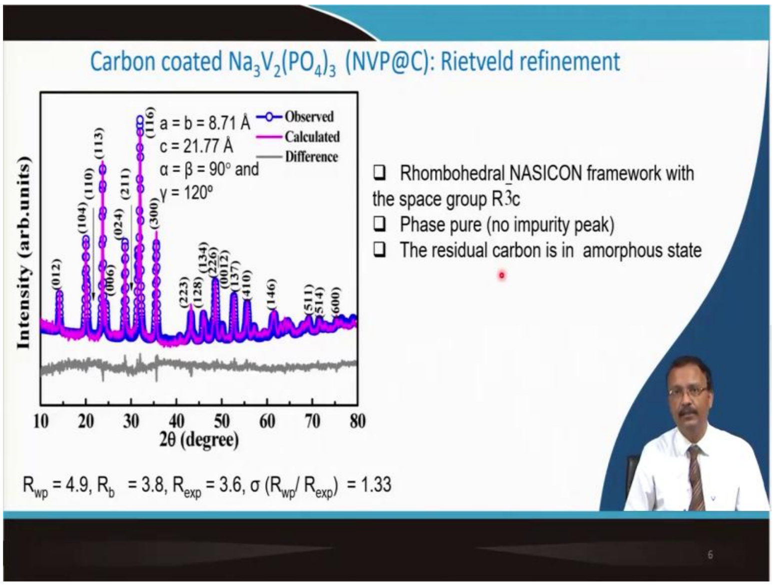

Carbon coated $Na_3V_2(PO_4)_3$ (NVP@C): Rietveld refinement

- ❑ Rhombohedral NASICON framework with the space group R$\bar{3}$c
- ❑ Phase pure (no impurity peak)
- ❑ The residual carbon is in amorphous state

$R_{wp}$ = 4.9, $R_b$ = 3.8, $R_{exp}$ = 3.6, σ ($R_{wp}$/ $R_{exp}$) = 1.33

Now, again you will have to do rietveld refinement to see that, whether there is any impurity phase. So, this is the space group is R 3 bar c. So, you may not be familiar with this space group. But, you need to provide this space group so, that theoretically the structural x r d can be generated in a program.

And, then we match it with the experimental curve and then finally, we get whether this is phase pure, what are the lattice parameters? So, you can see it is the rhombohedral type of structure is we are familiar with rhombohedral structure is equal to b, c parameter is a bit larger and alpha and beta that is 90 degree and gamma is 120.

So, that is a phase pure thing and not only that, you can also identify that, the position of this sodium, where exactly they are sitting, whether it is 1 or 2 Wyckoff position. So, that is also identified. And, this was coated with amorphous carbon layer, because the conduct electronic conductivity of this material is not that good.

So, it was coated with conducting carbon. And, from this X ray diffraction we can also identify that the coated layer is amorphous. We know that many instances the active material they are coated with oxide or phosphide either to impart electronic conductivity, or to reduce the reactivity of the electrolyte and several other purposes.

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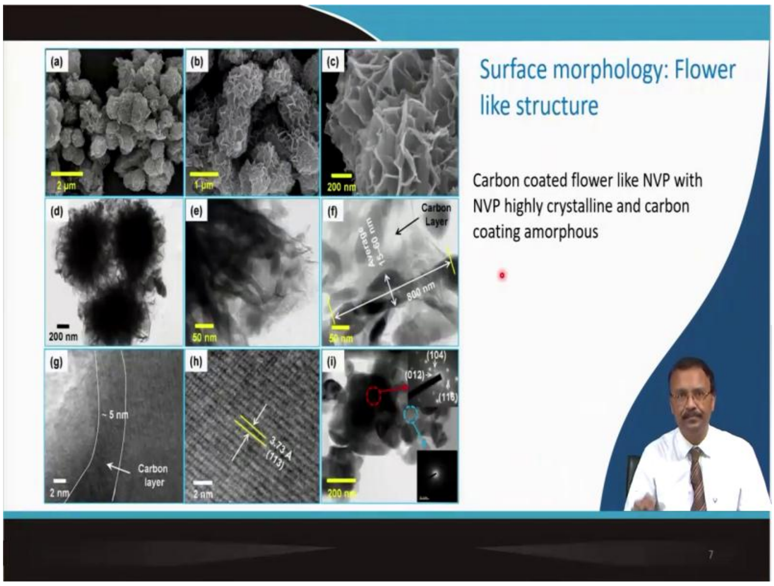

Surface morphology: Flower like structure

Carbon coated flower like NVP with NVP highly crystalline and carbon coating amorphous

Now, the structure is very interesting you see that once you do and prepare this. So, this carbon coated particles they are having a flower like structure. So, this flower have petals and they are coated with carbon. So, by doing a lot of microscopy you can identify this carbon layer, they are amorphous by TM analysis. But, the crystalline part is almost like single crystal very very highly crystalline.

So, how they are coated, how the carbons are coated, how the structure looks like and how the lattice fringe is there these are atom atomic planes you can see. So, you can know what is there d spacing that indeed this NVP has found.

So, a lot of characterization is required to understand this structure in a better way.

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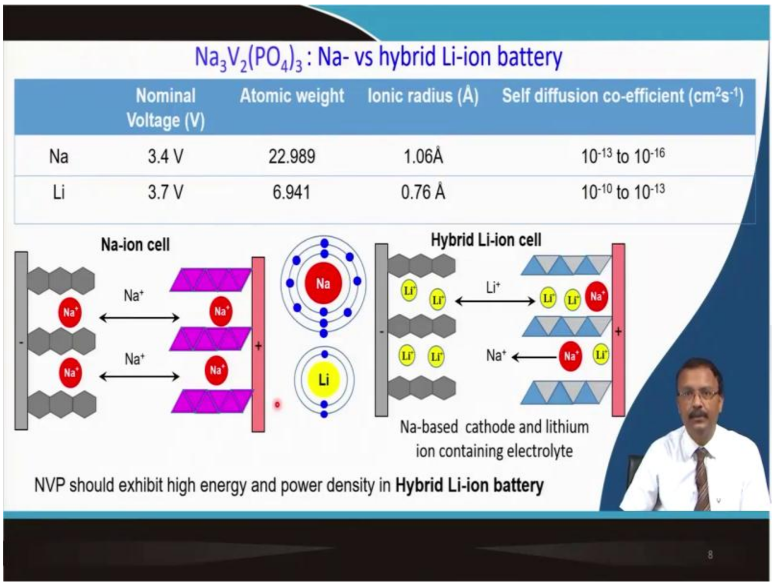

$Na_3V_2(PO_4)_3$ : Na- vs hybrid Li-ion battery

| | Nominal Voltage (V) | Atomic weight | Ionic radius (Å) | Self diffusion co-efficient ($cm^2s^{-1}$) |
|---|---|---|---|---|
| Na | 3.4 V | 22.989 | 1.06Å | $10^{-13}$ to $10^{-16}$ |
| Li | 3.7 V | 6.941 | 0.76 Å | $10^{-10}$ to $10^{-13}$ |

Na-based cathode and lithium ion containing electrolyte

NVP should exhibit high energy and power density in **Hybrid Li-ion battery**

Now, the mechanism of using this sodium ion battery is something like this. In sodium ion cell, it is exactly like lithium ion cells I have a separate module to talk about sodium ion battery. So, they are also you will find that instead of lithium here sodium is intercalating. So, you may have a layer structure here, you may have a layer structure here, but the difference is there between sodium and lithium, because this molecular weight is quite high as compared to this one.

So, the gravimetric energy density of this material is quite low. And, these are bulky because of their size. So, the diffusion is also slower. So, as a battery it is good for storage, storage battery, but for mobility is not that good. So, it is not that lighter you will have to carry this weight in your scooter or in your cycle or in a bus. So, huge battery you will have to carry, but if it is a storage for the renewable energy is the stationary battery like your redox flow battery. So, that is ok.

So, now, what we can do that during charging you can first extract this sodium through a lithium ion salt. So, this sodium using a lithium ion base electrolyte, they cannot be going here, it cannot be completely stopped, but there is a limited possibility for it to intercalate inside, this anode material during charging.

But, there are plenty of lithium, plenty of lithium is there. So, although sodium cannot go here, but lithium from the electrolyte that can pass and go to the anode site. So, you are taking out all the sodium and leaving them in the electrolyte right. Not all the sodium two out of three in the unit cell. And, you are living it here and then during charge your lithium from the electrolyte that is going to the anode. And, during discharge this lithium go and then they occupy the position of sodium. So, advantage is that lithium is having a smaller size as compared to sodium.

So, this diffusion is quite faster. So, in the subsequent cycle whenever they will start to diffuse that will be quite fast. So, that is the advantage of making this kind of structure. So, here is an comparison, voltage wise you will increase the voltage as compared to sodium. Atomic weight this is quite low as compared to this. Ionic radius it is quite low at compared to this it will be faster. And, diffusion coefficient you can see that, this is also quite faster as compared to sodium.

So, we call this kind of technology is hybrid lithium ion battery.

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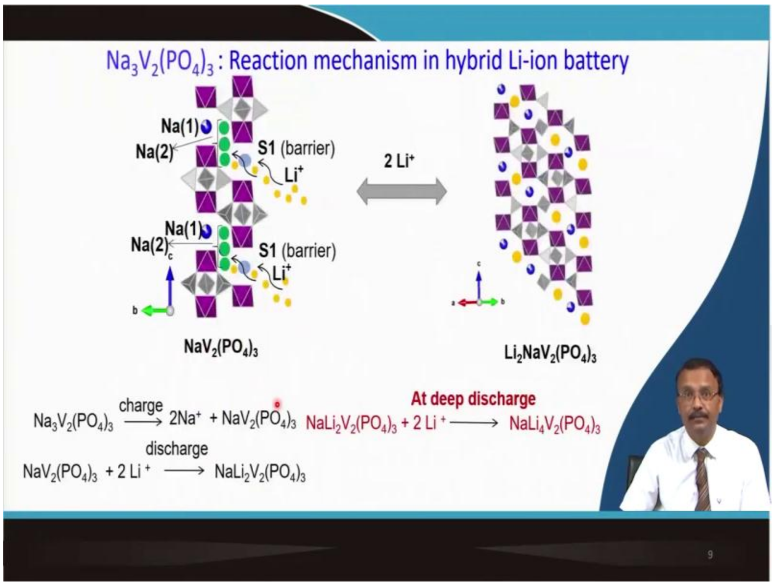

$Na_3V_2(PO_4)_3$ : Reaction mechanism in hybrid Li-ion battery

$Na_3V_2(PO_4)_3 \xrightarrow{charge} 2Na^+ + NaV_2(PO_4)_3$

$NaV_2(PO_4)_3 + 2\,Li^+ \xrightarrow{discharge} NaLi_2V_2(PO_4)_3$

At deep discharge

$NaLi_2V_2(PO_4)_3 + 2\,Li^+ \longrightarrow NaLi_4V_2(PO_4)_3$

So, what is happening here that is pictographically shown here? So, you can now see that within the lantern structures there are two different types of position of sodium 1 and sodium 2. So, there are 2 and 1 this 3 total your material and you are extracting two of them one still remained there and you are pushing lithium into it.

So, during charge sodium is coming out during discharge you are replace it by lithium, you can do deep discharge the same thing that we did for spinel type of positive material. So, you can do deep discharge and you can insert extra sodium into sorry extra lithium into it at lower voltage. And, that is why I told that you can use this material as a both anode and cathode. So, one will operate at lower voltage will we use at anode and higher voltage as a cathode to make a symmetric kind of battery.

One can actually make this kind of compound artificially, but it will not have this kind of structure. So, there is a structural limitation of having it.

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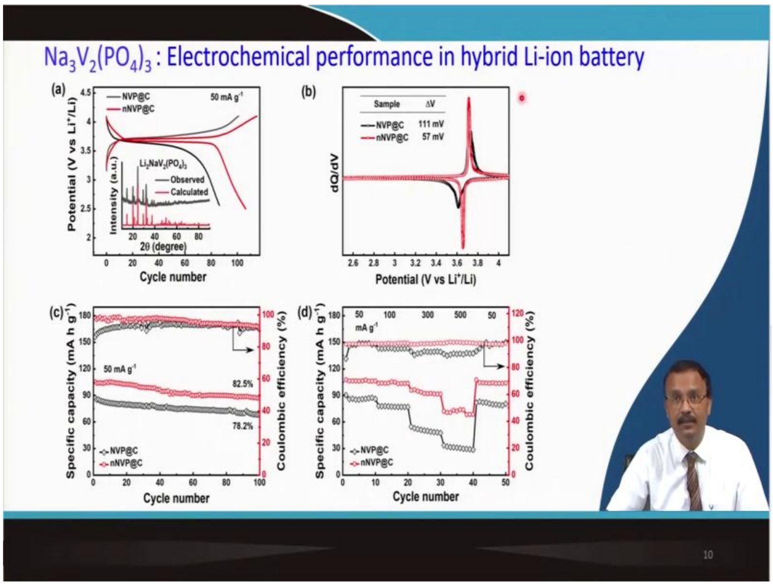

$Na_3V_2(PO_4)_3$ : Electrochemical performance in hybrid Li-ion battery

So, if you see the electrochemical performance of the half cell configuration. Again we will do the four types of characteristics one is cyclic voltammetry. Although, I have not shown cyclic voltammetry here, this is the differential capacity analysis.

And, you can get this kind of plateau and after a charge if you take out, after first discharge the electrode and do X ray diffraction you will see difference between the pristine positive electrode and the discharged positive electrode. And, indeed you will see that this lithium based compound is artificially been prepared.

So, that can be tested to support our postulation. The cyclability is quite good, rate performance is excellent, because of the fact that you can very fast way lithium can be transported. So, a lot of advantage of this, so, called hybrid lithium ion batteries.

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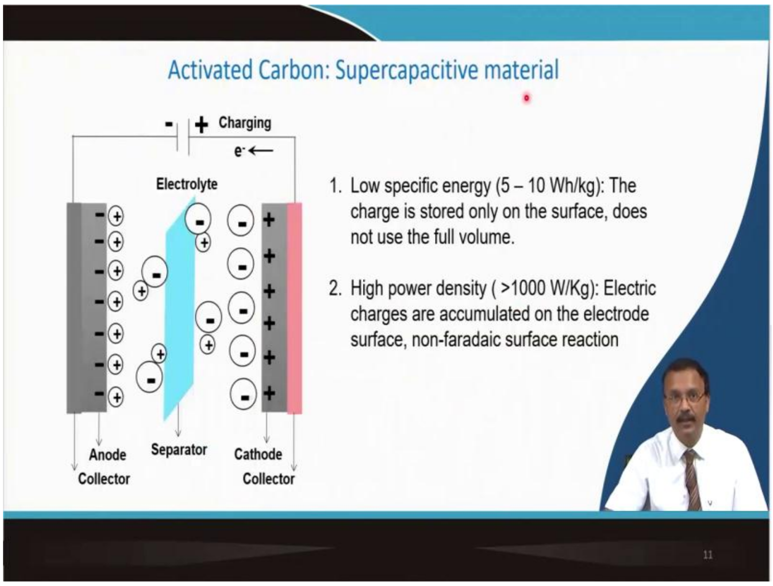

Activated Carbon: Supercapacitive material

1. Low specific energy (5 – 10 Wh/kg): The charge is stored only on the surface, does not use the full volume.
2. High power density ( >1000 W/Kg): Electric charges are accumulated on the electrode surface, non-faradaic surface reaction

Now, what do you what can be done is to make a composite with activated carbon, which is supercapacitative material. We already talked about it is having low specific energy about 5 to 10 watt hour per kg. So, charge is stored only at the surface, but it is having very good power density more than 1 kilowatt per kg.

So, electric charger just accumulated on the electrode surface and it is a non-faradaic kind of surface reaction.

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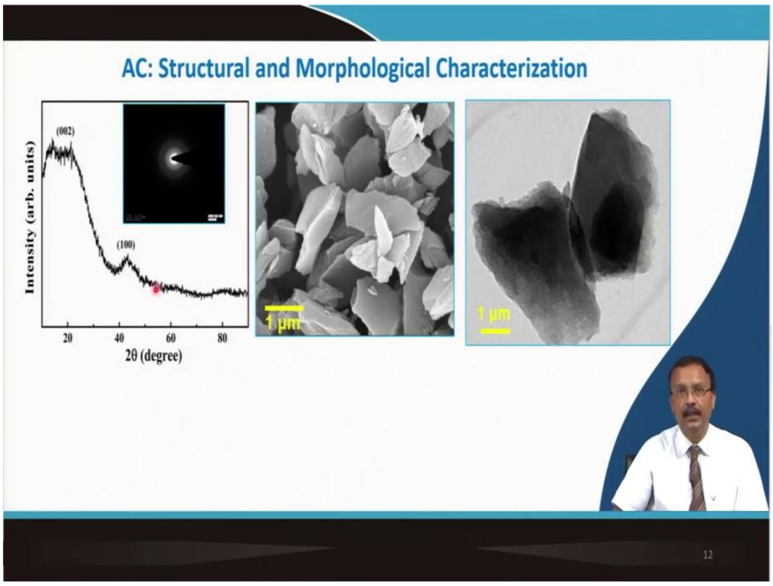

AC: Structural and Morphological Characterization

The material that is useful for this is activated carbon. And, you can see the their morphological characteristics of a commercial activated carbon, there are a lot of fine pores available. So, that the electrolyte can be pushed through insight and a lot of charge can be stored. It is almost activated carbon is amorphous kind of material. So, that is used in a super capacitor.

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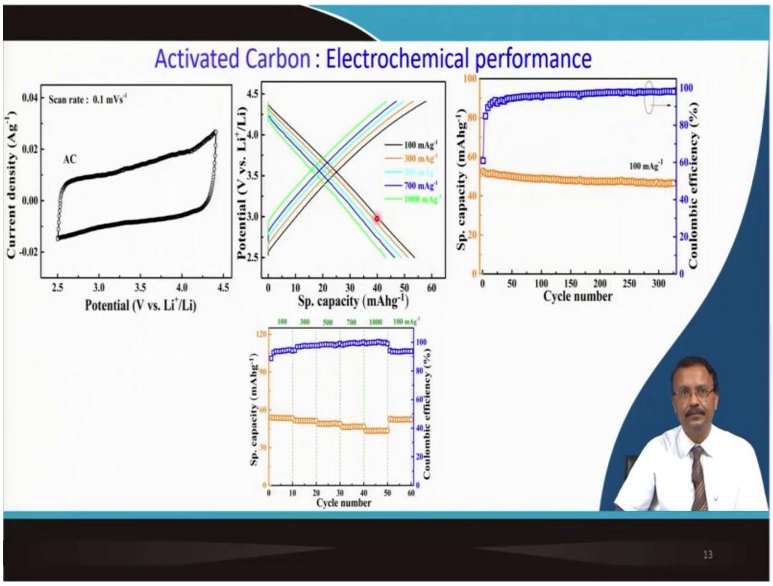

Activated Carbon : Electrochemical performance

So, all the characteristics of the super capacitor that is there. So, there is no oxidation reduction reaction, the charge and discharge they are very fast and almost straight line there is no plateau, no S type of voltage profile that you will find because of the mechanism is completely different. And, almost no change in the discharge capacity with cycling excellent cyclability, but the specific capacity is low not like faradaic type of material coulombic efficiency is also reasonably good.

And, also you can see that it has excellent rate performance, because current there is no diffusion involved. So, rate performance is quite impressive.

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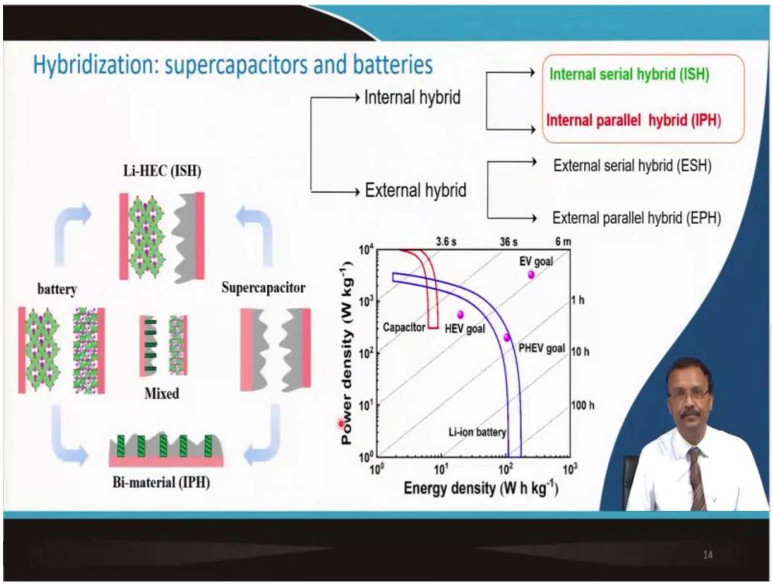

Hybridization: supercapacitors and batteries

- Internal hybrid
  - Internal serial hybrid (ISH)
  - Internal parallel hybrid (IPH)
- External hybrid
  - External serial hybrid (ESH)
  - External parallel hybrid (EPH)

Now, you can do hybridization of this super capacitor with that hybrid battery. In various way we can do one is internal hybrid and another one is external hybrid.

So, external hybrid is just to connect a super capacitor with a battery. So, this is not very lucrative, but internal hybrid that can be internal serial hybrid; that means, one part that will be battery and other part that will be super capacitor. And, this is a hybrid kind of battery a lot of names are there bat cap some people tell.

So, that is internal serial hybrid. Internal parallel hybrid is that inside each of this electrode, you are mixing both battery type material and super capacitor type of material. So, once you do that then we call that this is internal parallel hybrid material. So, this is quite interesting.

So, if you know about the ragone plot where the power density and energy density is plotted together. Then, if you want to use the material in electric vehicles, then it is power density and is a sorry it is energy density. And, power density they should be simultaneously high.

If pure lithium ion battery if you see that if you want to increase the power energy density, it is power density will be lowered, if you want to increase the power density, it is energy density will be lowered. Capacitor is always having good power density, but it has very poor energy density.

So, we will have to have the combined characteristics. And, in combined characteristics you have no other option, rather than to mix the super capacitor with the battery, there are a lot of issues involved. But, as you can see electric vehicles, then plug in electric vehicles; plug in hybrid electric vehicles, or hybrid electric vehicles, which I will define in my next lecture. Here you have the problem, because with the existing material you cannot achieve this.

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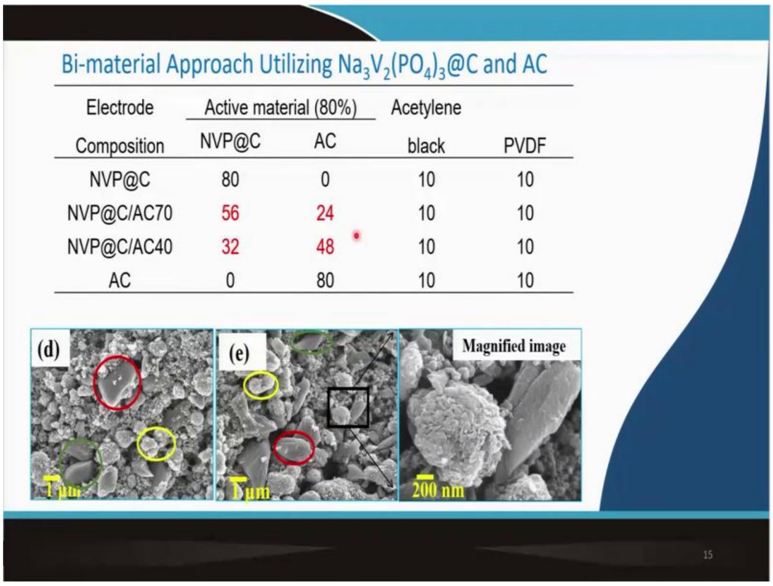

Bi-material Approach Utilizing $Na_3V_2(PO_4)_3$@C and AC

| Electrode Composition | Active material (80%) NVP@C | AC | Acetylene black | PVDF |
|---|---|---|---|---|
| NVP@C | 80 | 0 | 10 | 10 |
| NVP@C/AC70 | 56 | 24 | 10 | 10 |
| NVP@C/AC40 | 32 | 48 | 10 | 10 |
| AC | 0 | 80 | 10 | 10 |

So, here what can be done this NVP, which is coated with carbon, there we can have the fraction change of the capacitor. So, here for example, the active material is 80, this is 0 carbon black and PVDF. This is a normal hybrid capacitor, like sodium instead of sorry lithium is used instead of sodium, then you can add 70 percent of active carbon. You can add 40 percent of active carbon and this is the characteristics of pure activated carbon.

So, here the active material is 80 percent and then this active material is changed here, you see 56, 24, 32, 48. So, this type of material can be made artificially and this is the kind of microstructure, that you will get. So, we can clearly identify your flower like structure and you can clearly identify your super capacitative material, that is forming a hybrid electrode.

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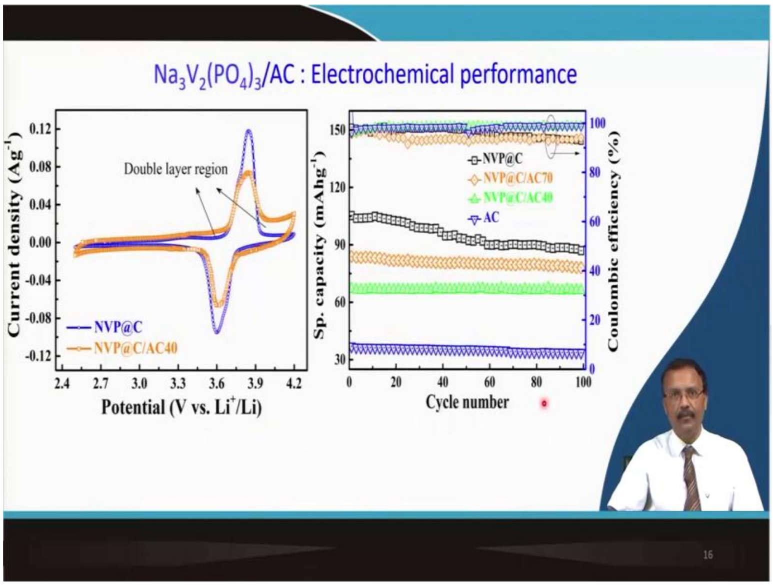

$Na_3V_2(PO_4)_3$/AC : Electrochemical performance

So, the electrochemical performance of this kind of hybrid, it shows clearly it can show the double layer region here and the battery type region and there are ways to delineate it.

So, I will try to explain it in one of my lectures, that how you can delineate the capacitative part yielding the capacity and the battery part from this kind of cyclic voltammetry plot. So, I am not going into the details, but you must appreciate that instead of this pure diffusion kind of battery activity, you have there is some change because of the inclusion of super capacitative battery.

So, this is the comparison of the cyclability for all this material, that exactly has been prepared. Carbon coated NVP then two different activated carbon composite with this carbon coated NVP and the activated carbon. So, activated carbon is very low specific capacity and then this is progressively higher. And, you see that in case of NVP C it is still higher, because compared to this your activated carbon has smaller capacity.

So, that is taking a little bit capacity from this composite, but there is no capacity fading at least in half cell.

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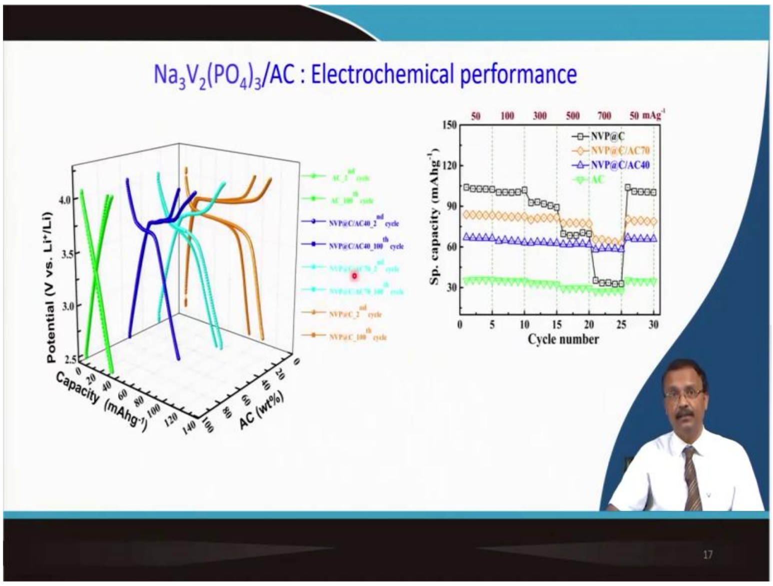

$Na_3V_2(PO_4)_3$/AC : Electrochemical performance

So, this is the electrochemical performance comparison. In case of pure battery type of material you see that the plateau is quite well developed and the straight line kind of thing in super capacitor is also quite well developed. But, once you have a composite it is in between these two.

So, therefore, this type of chair like structures of the potential versus capacity with different activated carbon concentration, that is as far as our expectation. Rate performance of this is quite good as compared to your NVP type of material, as you can see here progressively it is good because our activated carbon is taking care of the rate performance.

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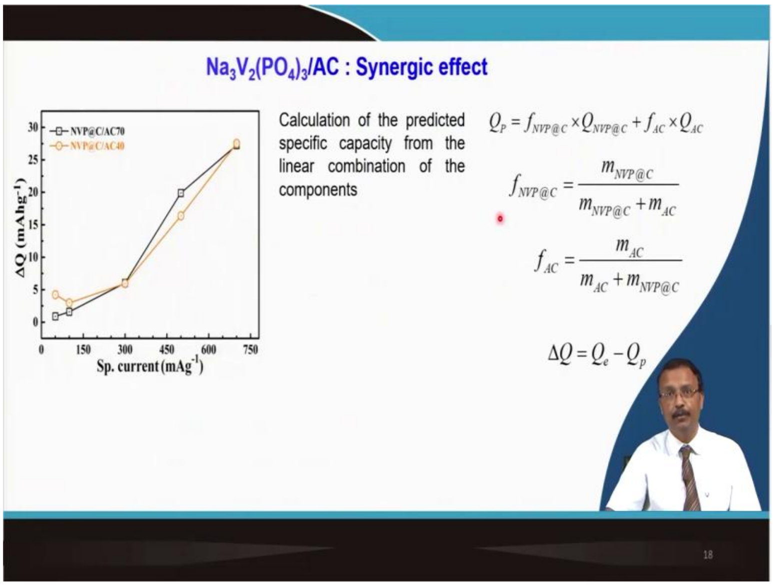

## $Na_3V_2(PO_4)_3$/AC : Synergic effect

Calculation of the predicted specific capacity from the linear combination of the components

$$Q_P = f_{NVP@C} \times Q_{NVP@C} + f_{AC} \times Q_{AC}$$

$$f_{NVP@C} = \frac{m_{NVP@C}}{m_{NVP@C} + m_{AC}}$$

$$f_{AC} = \frac{m_{AC}}{m_{AC} + m_{NVP@C}}$$

$$\Delta Q = Q_e - Q_p$$

Now, there is a synergic effect; that means, once you are actually mixing these two thing together. Following the mixing rule you can actually calculate what should be the capacity. So, the difference in capacity which is experimentally observed and which is actually practically observed so, ideally it should be 0, but it is not the case, it is not 0.

So, one can do this del Q measurement, which is the capacity difference between experimental and the practical measurement. Always you will find that this is a bit higher than expected.

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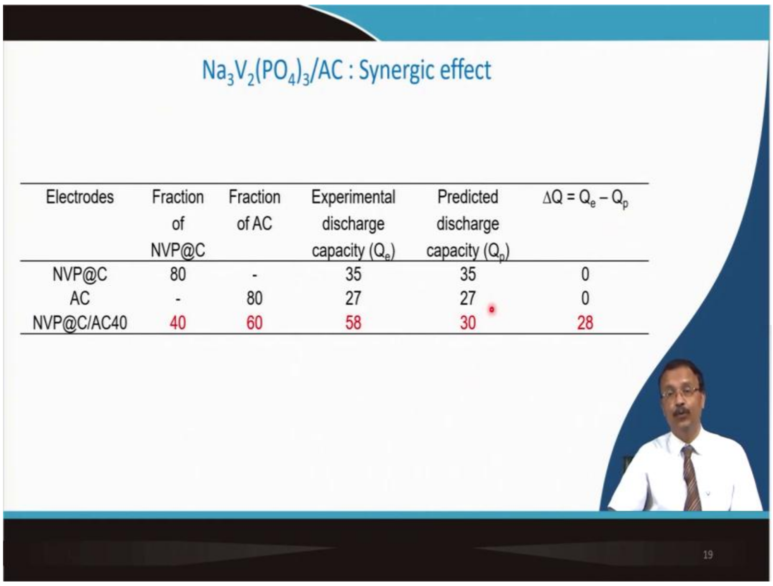

## $Na_3V_2(PO_4)_3$/AC : Synergic effect

| Electrodes | Fraction of NVP@C | Fraction of AC | Experimental discharge capacity ($Q_e$) | Predicted discharge capacity ($Q_p$) | $\Delta Q = Q_e - Q_p$ |
|---|---|---|---|---|---|
| NVP@C | 80 | - | 35 | 35 | 0 |
| AC | - | 80 | 27 | 27 | 0 |
| NVP@C/AC40 | 40 | 60 | 58 | 30 | 28 |

For example, if you take this normal carbon coated NVP, it is fraction is 80 the discharge capacity you can calculate only 35 percent sorry 35 is the discharge capacity, but predicted discharge capacity is also 35. So, the change is 0 here.

Pure activated carbon if you take, then also whatever is expected practically you get it. So, the del Q value is 0, but if you take for example, this composite then your experimental discharge capacity is 58 and actual predicted capacity is 30. So, there is a gain of 28. So, there is some kind of synergic effect due to the presence of both this component somehow the capacity can be enhanced.

So, this is a good set of material and research should be initiated in this direction. And, therefore, I consider this is one of the novel material for next generation battery, particularly where high power density is required.

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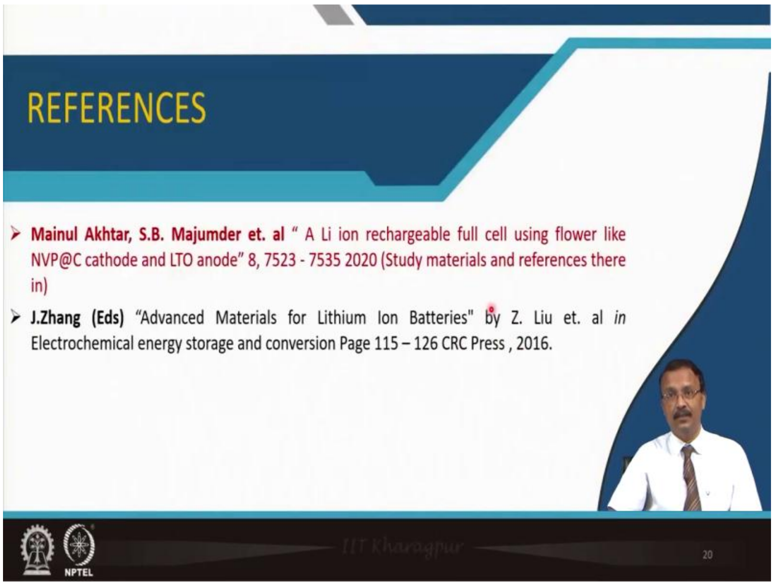

REFERENCES

- **Mainul Akhtar, S.B. Majumder et. al** " A Li ion rechargeable full cell using flower like NVP@C cathode and LTO anode" 8, 7523 - 7535 2020 (Study materials and references there in)
- **J.Zhang (Eds)** "Advanced Materials for Lithium Ion Batteries" by Z. Liu et. al *in* Electrochemical energy storage and conversion Page 115 – 126 CRC Press , 2016.

So, most of the work that has been taken from my ongoing PhD students work, and this is a reasonably good paper nicely explained all this come concepts so, this is your study material. And, out of this advanced material for lithium ion battery, you will find something similar people are thinking about.

So, we all in the community whoever works in lithium ion battery, were trying different types of thing. So, that we can actually catered the need of the requirement of electric vehicles battery, which will be coming in a big way in next two decades.

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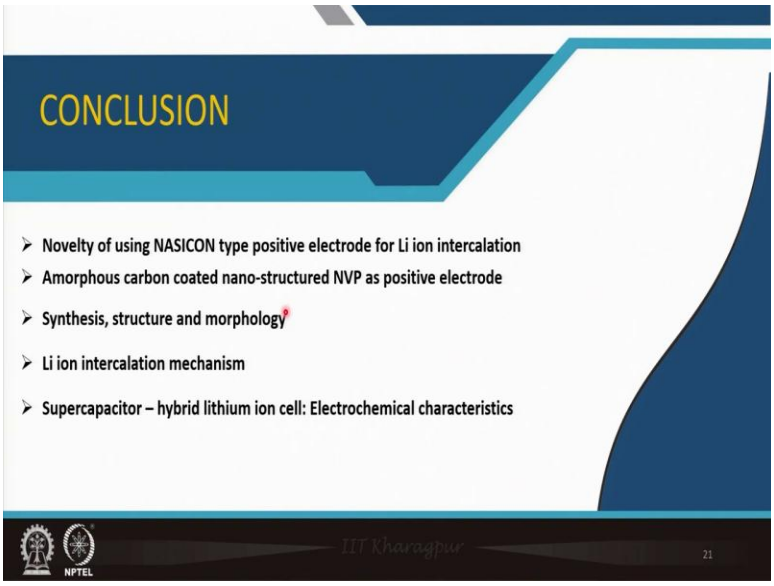

CONCLUSION

- Novelty of using NASICON type positive electrode for Li ion intercalation
- Amorphous carbon coated nano-structured NVP as positive electrode
- Synthesis, structure and morphology
- Li ion intercalation mechanism
- Supercapacitor – hybrid lithium ion cell: Electrochemical characteristics

So, here is the conclusion that novelty of using NASICON type of positive electrode for lithium ion intercalation. And, remember the source of lithium here is entirely the electrolyte, because there is no lithium in the positive part and no lithium in the negative part as well. Although we have tested so far using sodium sorry lithium foil, but actual source in full cell will be entirely from the electrolyte.

Amorphous carbon coated nano structured NVP that was used as a positive material, how they are synthesize what is their structure and morphology etcetera that has been covered. Then, in one slide we have explained that, what is the exact lithium ion intercalation mechanism in this material? And, finally, super capacitor and this hybrid lithium ion cell their electrochemical characteristics in half cell configuration, I have shown to you.

Thank you for your attention.