Electrochemical Energy Storage

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Module - 06
Sodium ion rechargeable cell
Lecture - 29
Performance of Na ion Rechargeable Cell

Welcome to my course on Electrochemical Energy Storage and this is module number 6, where we are talking about the Sodium ion rechargeable cell. In the last couple of lectures, we have talked about the positive electrode material, negative electrode materials, and electrolyte material in sodium ion battery.

So, now it is important that if you club together everything, then how a sodium ion cell, rechargeable cell actually performs. So, this is part of our own laboratory research work and in fact, a PhD work of a student and let us see that, how we can understand whatever concept I have taught in earlier classes, how experimental data whether it is in line to that or not.

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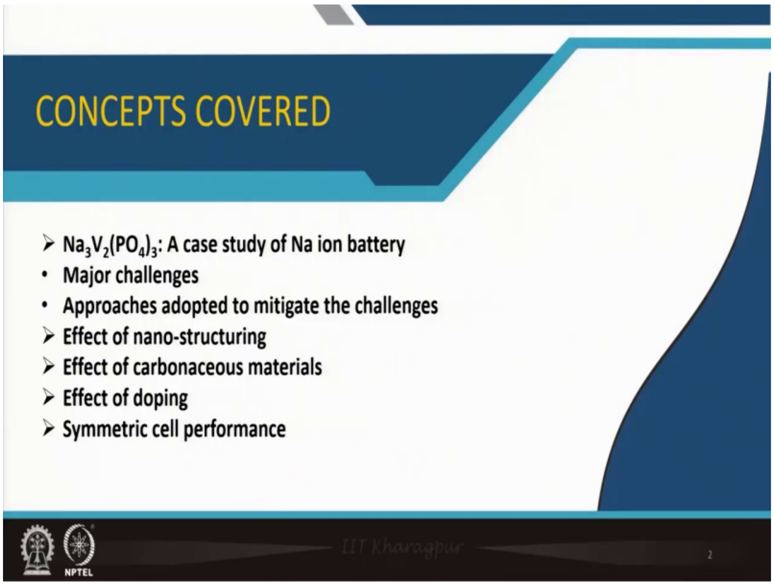

CONCEPTS COVERED

- ➢ $Na_3V_2(PO_4)_3$: A case study of Na ion battery
  - Major challenges
  - Approaches adopted to mitigate the challenges
- ➢ Effect of nano-structuring
- ➢ Effect of carbonaceous materials
- ➢ Effect of doping
- ➢ Symmetric cell performance

So, in this particular lecture, we will talk about one particular sodium ion positive electrode and I told you it is a NASICON type material that is quite interesting to the community. So, this N a 3 V 2 P O 4 whole 3 that is a as a case study, so that I will describe. What are the major challenges of this materials, this NASICON base material; what are the approaches that one can make to mitigate the challenges that is faced by this material for commercial adaptation.

Then whether really nano structuring is helpful, what is the role of any coating; because we are talking about this things to mitigate the problems, we will have to go for nano structured material, you will have to go for carbonaceous coating, that is the surface modification of the electrode material or the bulk modification in terms of the doping.

So, we will be also talking about this doping effect as well. And this is followed by the symmetrical cell performance; it is interesting as I told that, there is no need to use dissimilar material in case of N V P, which is abbreviated form for N a 3 V 2 P O 4 whole 3.

Because it can accept one more sodium into the structure three is already there; so fourth one also can be accepted at it a little bit lower voltage. So, you can use that part as our negative electrode and the other part as positive electrode. So, we can build a symmetric full cell. So, whether it is expand experimentally feasible or not that we will check.

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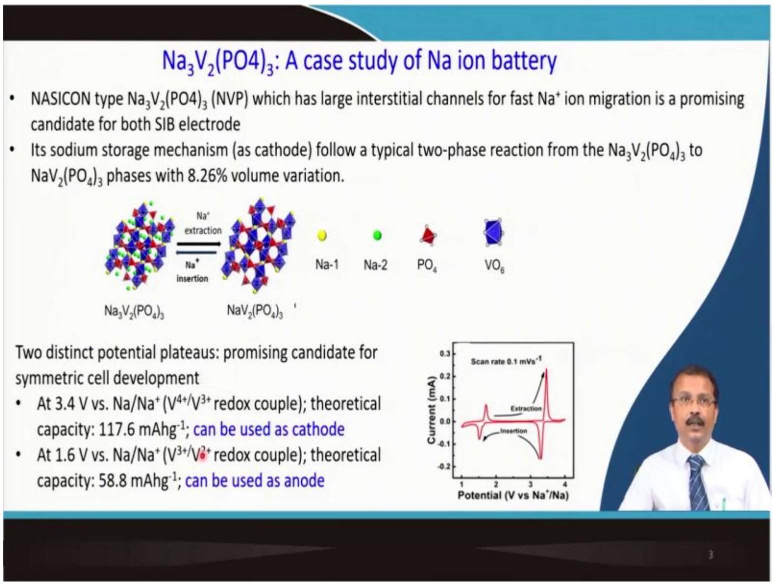

$Na_3V_2(PO4)_3$: A case study of Na ion battery

- NASICON type $Na_3V_2(PO4)_3$ (NVP) which has large interstitial channels for fast Na^+ ion migration is a promising candidate for both SIB electrode
- Its sodium storage mechanism (as cathode) follow a typical two-phase reaction from the $Na_3V_2(PO_4)_3$ to $NaV_2(PO_4)_3$ phases with 8.26% volume variation.

Two distinct potential plateaus: promising candidate for symmetric cell development

- At 3.4 V vs. Na/Na^+ (V^{4+}/V^{3+} redox couple); theoretical capacity: 117.6 mAhg^{-1}; can be used as cathode
- At 1.6 V vs. Na/Na^+ (V^{3+}/V^{2+} redox couple); theoretical capacity: 58.8 mAhg^{-1}; can be used as anode

So, this structure I will not go into much details, because already we talked about it. So, it has a large interstitial channel for fast sodium ion transport. But out of this three sodium, you cannot take all three; because you know that your capacity is dependent on this sodium ion extraction, number of electron that is involving in this reaction. So, that part is difficult. So, two of them you can take it out, accordingly I will ask you to calculate the theoretical capacity of this material.

You need to know that two electron is involved and molecular weight you need to know and you can calculate the theoretical capacity and check whether you are getting the experimental discharge capacity or charge capacity which is in line to the theoretical capacity. So, sodium storage mechanism follow a typical two phase reaction with this N a 3 V 2 P O 4 whole P O 4 whole 3 to N a V 2 P O 4 whole 3; because two sodium you are taking out.

And 8.26 percent volume variation will be there; you can test it, you just charge it and then stop the charging, take the electrode out, go for the extra diffraction, see what phase it has formed and through rietveld refinement you know that, what is the lattice parameter you are getting, you know the crystal structure, you can estimate the volume expansion or contraction and accordingly you can satisfy that what whatever I am saying whether it is true.

So, this is the structure of N a 3 V 2 P O 4 whole 3 and this is in the charge stage. And there are two different types of sodium ion you can see, one is marked with this yellow and another one is green. And this P O 4 tetrahedra is marked as red, it forms a lantern structure and V O 6 octahedra is marked blue.

So, two distinct potential plateau, that is very promising candidate for symmetric cell development. If you do a cyclic voltammetry. So, this is a typical cyclic veltam voltammetry of the N V P that we prepared in our laboratory; you can see that this is the high voltage redox and this is due to the insertion of sodium at relatively low voltage.

So, at 3.4 Volt sodium plus that influence this redox couple and theoretical capacity will be getting for 117.6 milli ampere hour per gram. This can be used as cathode and at 1.6 Volt around we are getting; this is due to the redox of V 3 to V 2. So, this is vanadium, it is having multiple valence states; so that is one advantage that, it can change it valence state like manganese, so it has multiple valence states.

So, this redox couple is useful; here theoretical capacity is about 58.8 milli Ampere hour per gram and that can be used as anode. Now, you remember when we talked about the capacity balance, so one theoretical capacity is 58.8 milli Ampere hour per gram and another one is 117.6. And apart from that, this ACI formation, the reversible capacity, reversible capacity will also be there.

So, I think that this is a complicated problem to you, to do the actual mass balance and see construct a symmetric full cell, which we have done later on. And probably I will ask some time how exactly we will calculate this depending on the half cell data, of course half cell data is required what you will be able to see to construct your full cell. And what is the theoretical prediction of the capacity and voltage that you are expecting from your full cell?

One is operating at 3.4 Volt and another one is operating at 1.6 Volt; so you can understand how much voltage window you are having.

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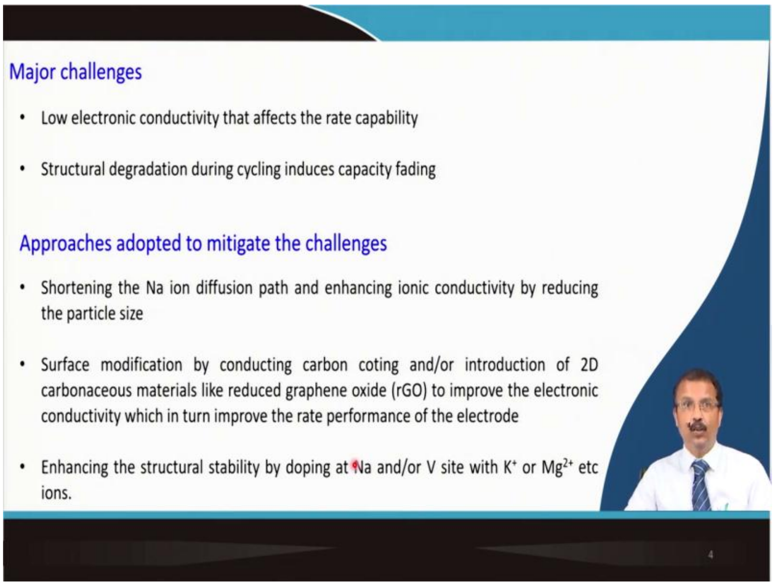

Major challenges

- Low electronic conductivity that affects the rate capability
- Structural degradation during cycling induces capacity fading

Approaches adopted to mitigate the challenges

- Shortening the Na ion diffusion path and enhancing ionic conductivity by reducing the particle size
- Surface modification by conducting carbon coting and/or introduction of 2D carbonaceous materials like reduced graphene oxide (rGO) to improve the electronic conductivity which in turn improve the rate performance of the electrode
- Enhancing the structural stability by doping at Na and/or V site with K^+ or Mg^{2+} etc ions.

Major challenge for this material is low electronic conductivity that basically affects the rate performance and structural degradation during cycling induced capacity fading. So, these are the two major challenges we need to solve. So, what we did, if you reduce shorten the sodium diffusion path, enhancing the ionic conductivity by reducing the particle size.

So, diffusion distance is less. So, if you have a diffusion coefficient which is not that fast but you know x is equal to root over d diffusion coefficient into time, so this diffusion distance you are reducing. Then surface modification is another way by conducting carbon coating or introduction of a 2 D carbonaceous material like reduced graphene oxide, that you can improve the electronic conductivity externally and that in turns will improve the rate performance of the electrode.

And then enhancing the structural stability by doping that is one thing which is quite interesting that the second one is the surface modification, external modification and this one is a bulk modification of the structure. And doping is possible both in the sodium site and also in the vanadium site and we choose this alkali ions, potassium and magnesium to actually modify the properties.

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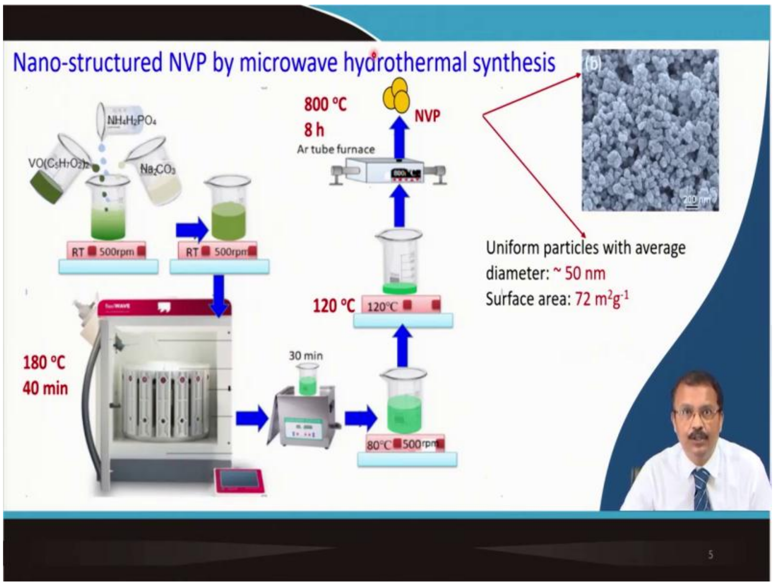

Nano-structured NVP by microwave hydrothermal synthesis

Uniform particles with average diameter: ~ 50 nm

Surface area: 72 m^2g^{-1}

So, this is the way usually we prepare the nano structured NVP and microwave hydrothermal synthesis was performed.

So, all the precursor material they are mixed together at room temperature followed by mixing and then we do a hydrothermal treatment for the phase formation. And then some part of calcination is required, followed by this is this treatment is required to form the powder. And then finally, in argon tube furnace, we heat treat it; because of phosphate radical you cannot do it in oxygen ambient and temperature was about 800 degree Celsius.

And then we got this kind of particle, you can see the average diameter for this particle is about 50 nanometer; it is in nano size and the surface area we measured by BET is also reasonably good 72 meter square per gram.

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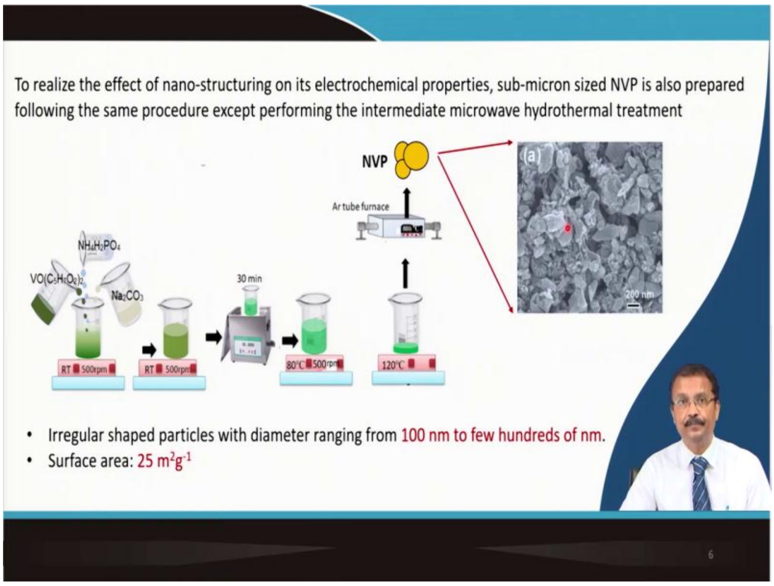

To realize the effect of nano-structuring on its electrochemical properties, sub-micron sized NVP is also prepared following the same procedure except performing the intermediate microwave hydrothermal treatment

- Irregular shaped particles with diameter ranging from 100 nm to few hundreds of nm.
- Surface area: 25 m^2g^{-1}

To realize the effect of this nano structuring to the electrochemical properties, you need to compare it with the micron size particle. So, submicron size NVP also we could prepare following the same procedure, except the intermediate microwave assisted hydrothermal treatment was omitted.

So, then also we got this kind of microstructure; if you compare the earlier one with this one, suddenly the average particle size you can see it is quite large about 100 nanometer, a few hundred nanometers I should say and surface area therefore, it drops down to 25 meter square per gram.

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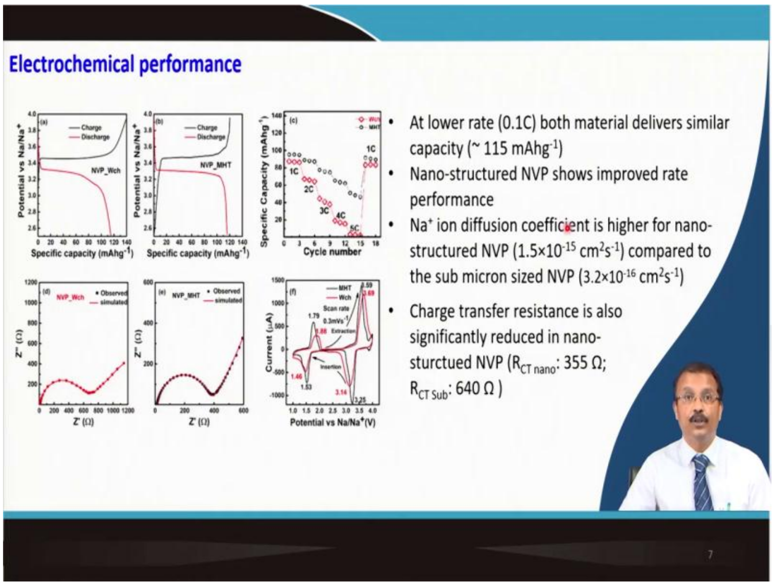

Electrochemical performance

- At lower rate (0.1C) both material delivers similar capacity (~ 115 $mAhg^{-1}$)
- Nano-structured NVP shows improved rate performance
- Na^+ ion diffusion coefficient is higher for nano-structured NVP (1.5×10^{-15} cm^2s^{-1}) compared to the sub micron sized NVP (3.2×10^{-16} cm^2s^{-1})
- Charge transfer resistance is also significantly reduced in nano-sturctued NVP ($R_{CT\ nano}$: 355 Ω; $R_{CT\ Sub}$: 640 Ω)

Now, the electrochemical performance if you see that at lower rate, both material delivers similar capacity. So, you compare with this one is wet chemical part, the soluble one the last slide and this one is by microwave assisted hydrothermal synthesis.

So, here you see the capacity, you do not see much difference, right. So, except this plateau is quite uniform flat as compared to this one, it is slight slope is there. So, some structural change or in terms of the phase might be there, so that is reflecting here. But this. so called nano size NVP that shows improved rate performance. So, if you compare this red one with the black one; so red one is your wet chemical part and black one is your microwave assisted (Refer Time: 12:44) thermal part.

You see this is giving much more better rate performance as compared to this one. Sodium ion diffusion coefficient is higher for nanostructure. So, that was our speculation. So, this is your wet chemical part and from the slope itself you can identify; I already told that from the Nyquist plot slope, you can basically estimate and I think I showed you also one example that, how to estimate the diffusion coefficient from this workbook tell and the slope is much steeper here.

So, that is basically in accordance to our theoretical prediction, it is indeed 10 raise to minus 15 here; although it is quite so small, but one order of magnitude you can say it is better. And charge transfer resistance also significantly reduce. So, if you just do a proper simulation of this which is the red line here and this is also the red line and this these are the small, these are the symbols the experimental plot and then we fitted with one of the randles circuit of our interest and we found that the charge transfer resistance significantly reduced in nano structured NVP.

So, here it is 355 Ohms and in case of your wet chemical part, this is about 640. So, if you reduce the particle size, in this case it is improving the electrochemical properties.

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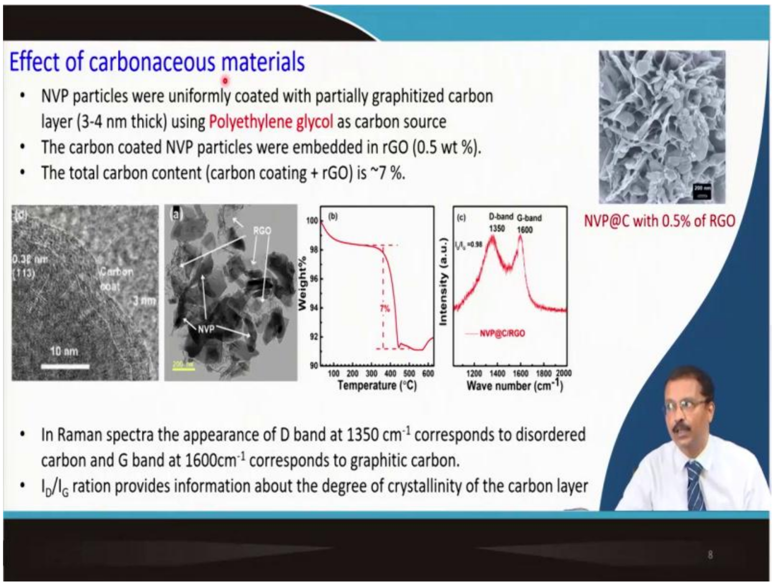

Effect of carbonaceous materials

- NVP particles were uniformly coated with partially graphitized carbon layer (3-4 nm thick) using Polyethylene glycol as carbon source
- The carbon coated NVP particles were embedded in rGO (0.5 wt %).
- The total carbon content (carbon coating + rGO) is ~7 %.

NVP@C with 0.5% of RGO

- In Raman spectra the appearance of D band at 1350 cm^{-1} corresponds to disordered carbon and G band at 1600cm^{-1} corresponds to graphitic carbon.
- I_D/I_G ration provides information about the degree of crystallinity of the carbon layer

Then we did this carbonaceous material coatings, on top of that we coated with carbonaceous material; partially graphitized carbon we quote, we used a polyethylene glycol as a carbon source this carbon coated NVP particles were further embedded in a reduced graphene oxide.

Because you see that we planned this experiment based on our understanding that what could go wrong in this material and how to actually improve it. So, we had a bare material and then we adopted all this nano structuring or the carbonyl carbon carbonaceous coating or embedded in the a conducting wrap of graphene oxide, reduce graphene oxide. And then by Raman spectra indeed we got these two characteristics band and we thought that this is indeed the disordered carbon which has been coated.

And this is actually, this defect band intensity and this actual graphite intensity that provides the information of the crystallinity the ratio; the number that provides the this thing that carbon layer crystallinity, whether it is non crystalline or crystalline. And this

TGA analysis what was done that, to tell you that how much carbon is basically coated; you can see that about 7 percent carbon is coated on the NVP.

And we just define this thing as NVP at the rate means it is coated with carbon and about 0.5 percent of reduced graphene oxide. So, that is our final structure that we are having.

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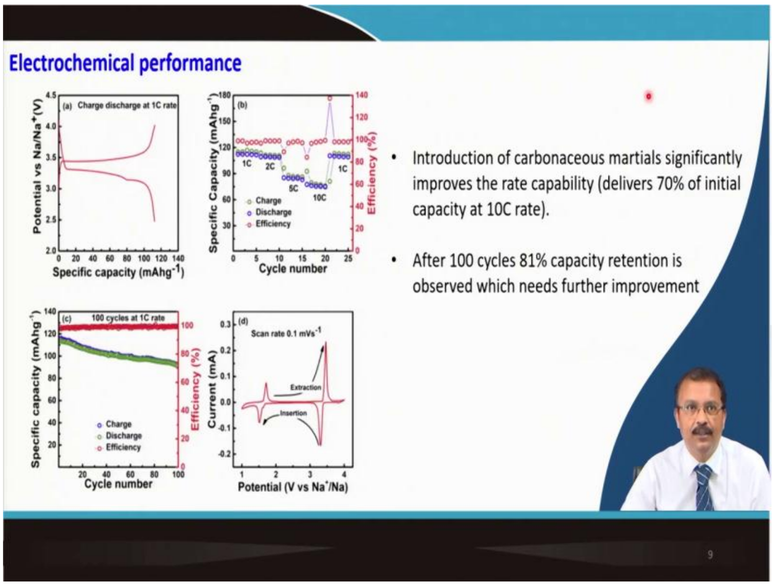

Electrochemical performance

- Introduction of carbonaceous martials significantly improves the rate capability (delivers 70% of initial capacity at 10C rate).
- After 100 cycles 81% capacity retention is observed which needs further improvement

Again we do electrochemical performance and as you can see; this introduction of carbonaceous material that significantly improves the rate performance. So, rate performance charge, discharge and efficiency if you compare that is significantly improves. And the cyclability here the 100 cycles at 1 C rate this is the efficiency part.

And this part is the cyclability and it has the same kind of behavior, which I predicted that it is in 3 point more than 3 Volt and this is around 1.5 Volt you have this electrochemical activities. So, carbonaceous materials significantly improve the rate performance and as I told 70 percent of its initial capacity you can hold, even if you have a 10 C kind of charge discharge. So, 10 C is a quite high rate.

And after 100 cycles about 81 percent of the capacity is retained, that you can see from this view graph. So, that is also a good indication, but in half cell configuration.

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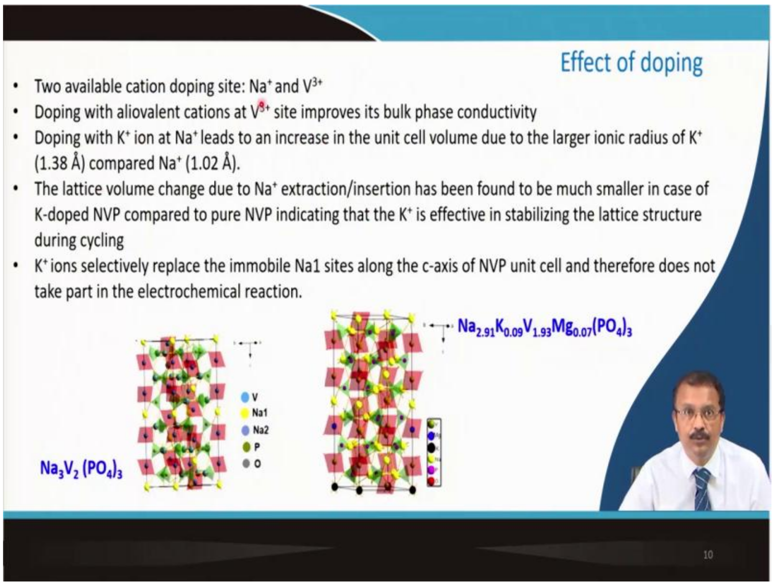

Effect of doping

- Two available cation doping site: Na^+ and V^{3+}
- Doping with aliovalent cations at V^{3+} site improves its bulk phase conductivity
- Doping with K^+ ion at Na^+ leads to an increase in the unit cell volume due to the larger ionic radius of K^+ (1.38 Å) compared Na^+ (1.02 Å).
- The lattice volume change due to Na^+ extraction/insertion has been found to be much smaller in case of K-doped NVP compared to pure NVP indicating that the K^+ is effective in stabilizing the lattice structure during cycling
- K^+ ions selectively replace the immobile Na1 sites along the c-axis of NVP unit cell and therefore does not take part in the electrochemical reaction.

Then we start to do the bulk modification. So, as I told the available site was sodium and vanadium. So, we doped it this vanadium site to improve the bulk phase conductivity; because here the defects are involved, if you just dope it with the a cation with a reduced balance, then oxygen vacancy or some other types of vacancy can be incorporated within the band gap.

An electron or hole can be trapped and that constitutes the increase of the electronic conductivity. Additionally this dopant which you replace sodium that, also increase the unit cell volume; because of the larger ionic radius of sodium and there is considerably large as compared to sodium.

And this lattice volume change that make this sodium extraction and insertion that is really relatively easier; because you know you have this much of space, sodium is a big ion, so it is trying to go and come coming out.

So, if you can increase it little bit, then it will be easier, so that was a concept. So, this ion selectively replace the immobile sodium 1 site; because you know that there are out of three, one was sodium 1. So, that does not really take part in any electrochemical reaction, only structural modification that it does.

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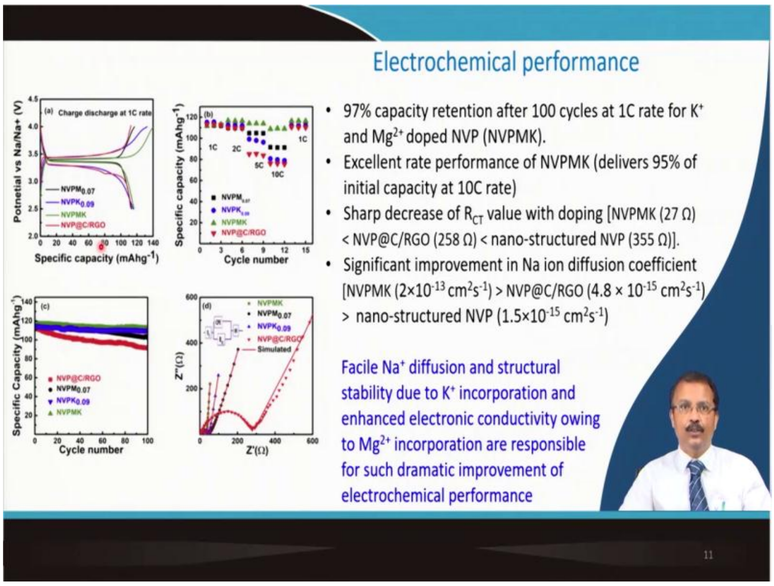

Electrochemical performance

- 97% capacity retention after 100 cycles at 1C rate for K^+ and Mg^{2+} doped NVP (NVPMK).
- Excellent rate performance of NVPMK (delivers 95% of initial capacity at 10C rate)
- Sharp decrease of R_{CT} value with doping [NVPMK (27 Ω) < NVP@C/RGO (258 Ω) < nano-structured NVP (355 Ω)].
- Significant improvement in Na ion diffusion coefficient [NVPMK (2×10^{-13} cm^2s^{-1}) > NVP@C/RGO (4.8×10^{-15} cm^2s^{-1}) > nano-structured NVP (1.5×10^{-15} cm^2s^{-1})

Facile Na^+ diffusion and structural stability due to K^+ incorporation and enhanced electronic conductivity owing to Mg^{2+} incorporation are responsible for such dramatic improvement of electrochemical performance

So, electrochemical performance is suddenly improved. So, as you can see from this figure and compare with the others.

So, the highlights are 97 percent capacity retention, earlier it was 80 at 1 C rate for potassium and also magnesium, this co doped material. Excellent rate performance, as you can see even at 10 C, it operates it delivers 95 percent of the initial capacity. Sharp decrease of this charge transfer resistance with the doping’s; that is another good indication, because easily the charge transfer can take place in the nano structured one.

So, for this it is 258 and remember for this nano structured NVP, it was 355. So, it got reduced that, we can get out of this Nyquist plot using this kind of randles circuit, which is more or less similar to what we described earlier in case of lithium ion battery. So, you have one RS for electrolyte and then a CP is there; constant phase element we use, because of the depressed semicircle and then we use a charge transfer resistance and we have the workbook tell, which you can see here.

So, more or less reasonably good fit. And then we estimated the diffusion coefficient and there was a significant improvement of sodium ion diffusion coefficient for this material NVPMK, the double dope doped one. With respect to the one with carbon coated and embedded in NGO, RGO and that is also much higher as compared to sodium structured NVP, which I initially presented. So, this is the facile sodium and diffusion and structural stability due to potassium ion incorporation and enhanced electronic conductivity owing to magnesium ion they are responsible for such dramatic improvement of the electrochemical performance.

It is not my intention to explain that why this is happening; because this story we built to write the paper and to explain it and convince others that you see that this is the actual mechanism.

What is more important that, you think of something some kind of model and experimentally you verify, it that it is forming exactly like this. Whether this potassium is indeed replacing the sodium which is immobile, we do not have any direct proof; it may be something else, but we understood that the potassium can increase the volume of the unit cell. So, that the sodium ion movement is little bit easier.

So, that is true and that is getting reflected through the electrochemical performance. So, that was the purpose that the science of it through your experimentation, you will be able to proof and get a good material for sodium ion batteries.

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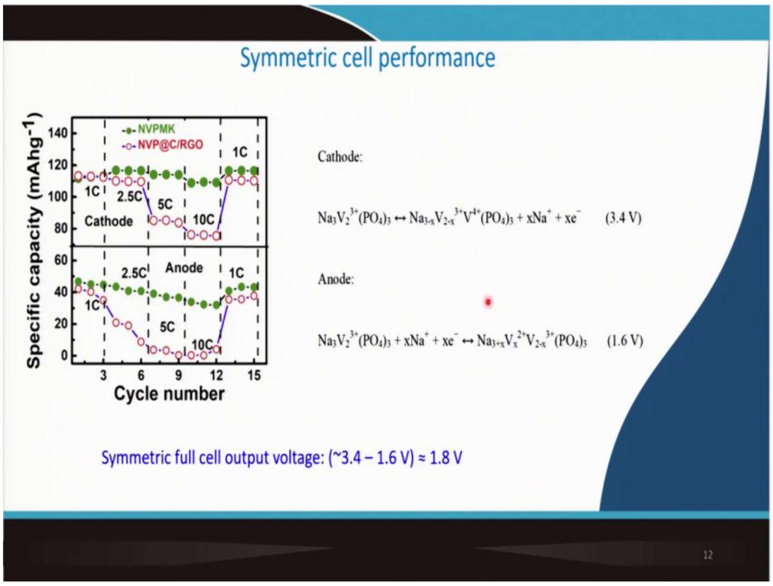

Symmetric cell performance

Cathode:

$$Na_3V_2^{3+}(PO_4)_3 \leftrightarrow Na_{3-x}V_{2-x}^{3+}V^{4+}(PO_4)_3 + xNa^+ + xe^- \quad (3.4\ V)$$

Anode:

$$Na_3V_2^{3+}(PO_4)_3 + xNa^+ + xe^- \leftrightarrow Na_{3+x}V_x^{2+}V_{2-x}^{3+}(PO_4)_3 \quad (1.6\ V)$$

Symmetric full cell output voltage: (~3.4 – 1.6 V) ≈ 1.8 V

Cathode:

$$Na_3{V_2}^{3+}(PO_4)_3 \leftrightarrow\ Na_{3-x}{V_{2-x}}^{3+}{V_x}^{4+}(PO_4)_3 + x\,Na^+ + x\,e^-$$

Anode:

$$Na_3{V_2}^{3+}(PO_4)_3 + x\,Na^+ + x\,e^- \leftrightarrow Na_{3+x}{V_{2-x}}^{3+}{V_x}^{2+}(PO_4)_3$$

So, symmetric cell performance is interesting and this is the kind of reaction that takes place in cathode during charge and discharge as I told during anode extra sodium is going in. So, you can see here N a 3 plus x, that is why it put.

So, this vanadium 2 plus 2 3 plus that is the redox and here 3 plus 2 4 plus is the redox. So, I leave it on you, if you know the kind of voltage that you are getting and the half cell voltage of the NVP that you are getting in terms of the positive electrode; then you should get that what kind of voltage range it will operate. So, 3.4 Volt minus 1.6 Volt, so it will operate at 1. 8 volt; I am not very satisfied with 1.8 volt battery. This will not serve my purpose as a practical battery.

But you can construct with the same material both as anode and cathode and demonstrate the performance, maybe its energy density will be low, its power density is quite high; because you can see that it is operating at 10 C rate. So, the power density is quite high, energy density could be a bit low; because of this voltage and you cannot do anything, because this is the redox of the vanadium that is playing a major role in it. But it operates at that voltage range, both for anode and cathode we can have the capacity.

And also you know the reaction is quite different, so it is possible that this gives a good rate performance at a high rate in the cathode side; but in another side, may maybe possible that is cyclability and the rate performance is not that good. In order to understand it, you will have to run this cell at that voltage range; say 1.6 volt range where only sodium is going in, extra sodium is going in and coming out. And then we will have to understand that if their electro chemical performance is at par with the electrochemical performance of the other cell.

So, that is also important.

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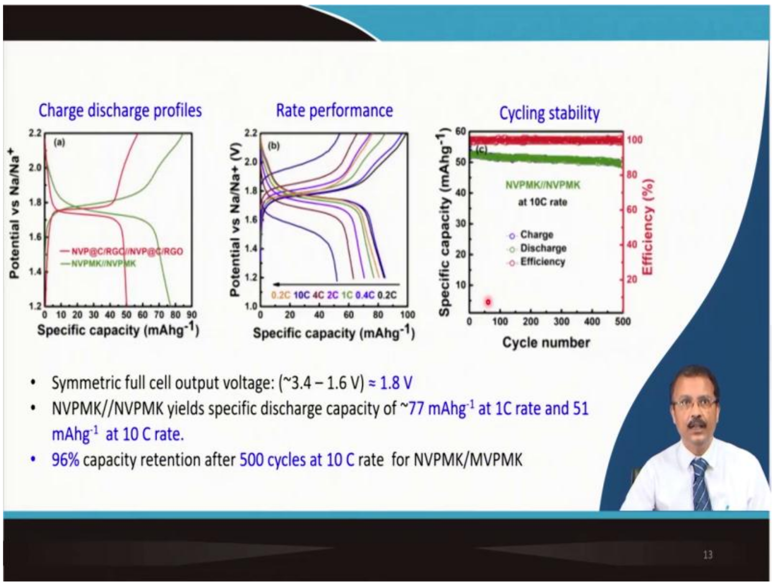

- Symmetric full cell output voltage: (~3.4 – 1.6 V) ≈ 1.8 V
- NVPMK//NVPMK yields specific discharge capacity of ~77 mAhg^{-1} at 1C rate and 51 mAhg^{-1} at 10 C rate.
- 96% capacity retention after 500 cycles at 10 C rate for NVPMK/MVPMK

So, this is the charge discharge characteristics profile. So, symmetric full cell output voltage is indeed 1.8 Volt and this NVPMK; that means magnesium and potassium doped material and here also NVPMK that is in the cathode side and this is the anode side that yields a specific discharge capacity of 77 milli Ampere hour per gram. This also you can calculate, one half cell capacity as I told is about 115 milli Ampere hour per gram.

And another one is given if I remember correctly is about 78 milli Ampere hour per gram. So, you can estimate now that what should be the full cell capacity. But of course, if you increase the rate, at lower rate it will follow the theoretical trend; but at higher rate as I told that anode and cathode they can behave a little bit differently. So, it may not be properly correct. So, you can see at 10 C rate, only you are getting 51 milli Ampere hour per gram.

So, this is the kind of voltage that you are getting 1. 8 Volt the capacity is quite low. So, its ragone plot, which is a plot of power density and energy density that may not be that great; but the idea was to show you that, one of the cathode material if I take it, then we can build a symmetric cell and see how this electrochemical performance, how it is performing. It is performing quite good, because you see that the cyclability up to 500 cycles is quite good. So, very marginal fall is there, about 85 percent you are getting. So, in fact, it is 96 percent sorry.

This is yeah from here to here. So, about 96 percent capacity retention after 500 cycles and that too at 10 C rate. So, this symmetric cell has a good power density material sodium ion cell; this is reasonably good and in consult configuration of course we did that.

So, much work needs to be done and if you understand the basics of the electrochemistry and the way I taught in our earlier class; I get that will give you a vivid picture that how to design the material, what are the parameters that you should think of in improving the material quality.

And then you try different types of material; what types of material is available you should target, that is also vividly you can take from my lectures, be that electrolyte or positive electrode or negative electrode for different types of chemistry and you will get a vivid idea how to do research and that is the purpose of this elective course.

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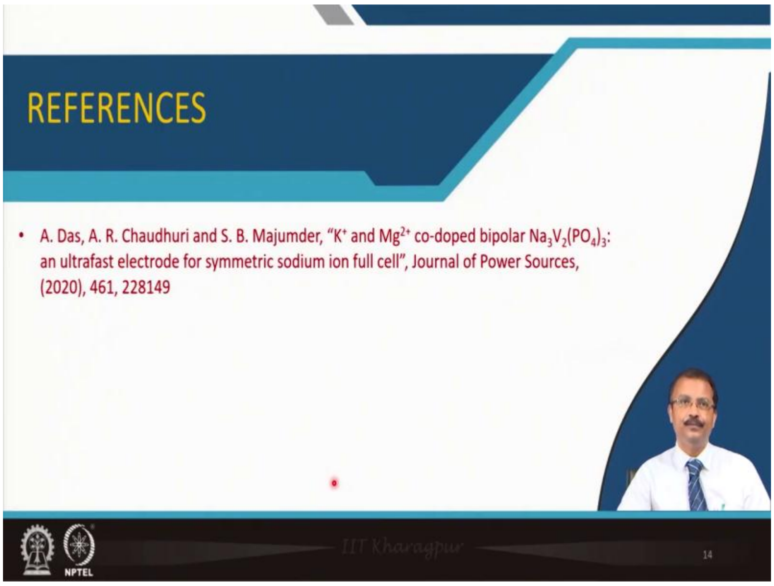

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So, this is only one reference; because you see that I am talking about one specific material and as a case study.

So, this is published by one of my PhD students and this paper you can read and this is reasonably good details we have described this.

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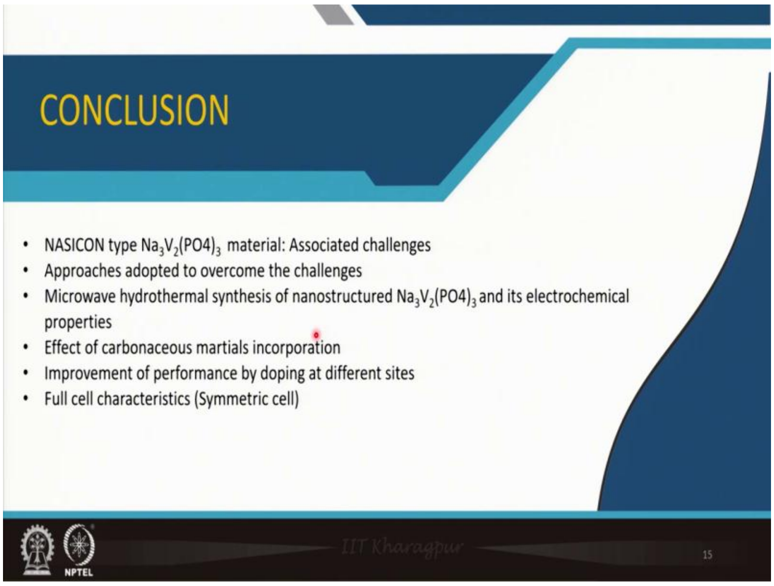

CONCLUSION

- NASICON type $Na_3V_2(PO4)_3$ material: Associated challenges
- Approaches adopted to overcome the challenges
- Microwave hydrothermal synthesis of nanostructured $Na_3V_2(PO4)_3$ and its electrochemical properties
- Effect of carbonaceous martials incorporation
- Improvement of performance by doping at different sites
- Full cell characteristics (Symmetric cell)

So, I have taken a NASICON type NVP as a case material and you remember that the same material I have used as a case study for lithium ion battery intercalation for dual ion battery and this is exclusively for sodium ion battery. So, this is the idea and what was the associated challenge and approaches to adopt the overcome the challenges; then both microwave assisted synthesis to make this nano structured material and also by wet chemical synthesis we could prepare micron such particle.

Then what is the effect of the carbonaceous material incorporation, what is the effect of their bulk doping improving the properties. And finally, the asymmetric, symmetric full cell. And some part I uttered the word as symmetry; it is not asymmetric you understand, is a slip of the tongue, it is symmetric cell full cell characteristics we have defined.

Thank you for your attention.