Electrochemical Energy Storage

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Module - 02
Definitions and measuring methods
Lecture - 10
Measurement of Rechargeable Cell: Case Study

Welcome to my course Electrochemical Energy Storage; this is module number 2, where I am describing Definitions and measure measuring methods. And this is lecture number 10, where Measurement of Rechargeable Cell as a Case Study that I will introduce.

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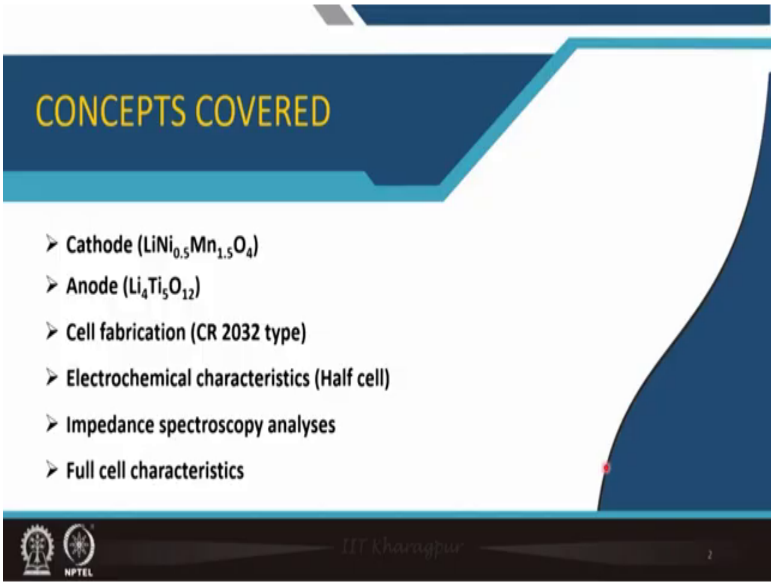

CONCEPTS COVERED

- Cathode ($LiNi_{0.5}Mn_{1.5}O_4$)
- Anode ($Li_4Ti_5O_{12}$)
- Cell fabrication (CR 2032 type)
- Electrochemical characteristics (Half cell)
- Impedance spectroscopy analyses
- Full cell characteristics

You know that so far in all these previous lectures, we are talking about various principles, the thermodynamic principles, the characteristics of the batteries; then the measurement protocol, that usually we use and several other things.

Now, it is important to show you that, if you construct a lithium ion cell in the laboratory, then what are the characteristic that actually you will be getting and how much it is relevant; whatever you have learned through my earlier lectures, the experimental results how much they are relevant to the knowledge that you have gained and I will do it time to time in order to make this lecture more meaningful.

So, you know that any battery it is having a positive electrode, which I should not defined as cathode, but it is positive electrode. Here I have selected one material which is spinel type all of you know; one specialty of this particular material that it is having a high voltage positive electrode.

So, 5 volt positive electrode, this is the positive electrode we will talk about. Anode so far we have talked about graphite; but this is also a spinel electrode, which is lithium titanium oxide, we abbreviate as LTO, so that we will introduce. Then in order to measure the electrochemical properties, we need to construct the cell in coin cell configuration and there are various types of coin cell.

So, the fabrication facilities that we are having in my laboratory; this is we can make CR 2032 type cell, where this 20 is the diameter of the cell, 20 millimeter and 3.2 millimeter is the thickness. So, that turns this name.

Then we will talk about the electrochemical characteristics in half cell configuration; then impedance spectroscopy measurement we introduced, we taught about it; then I will show that how this impedance spectroscopy characteristics are actually reflected in this type of half-cell and also the full cell characteristics we will define.

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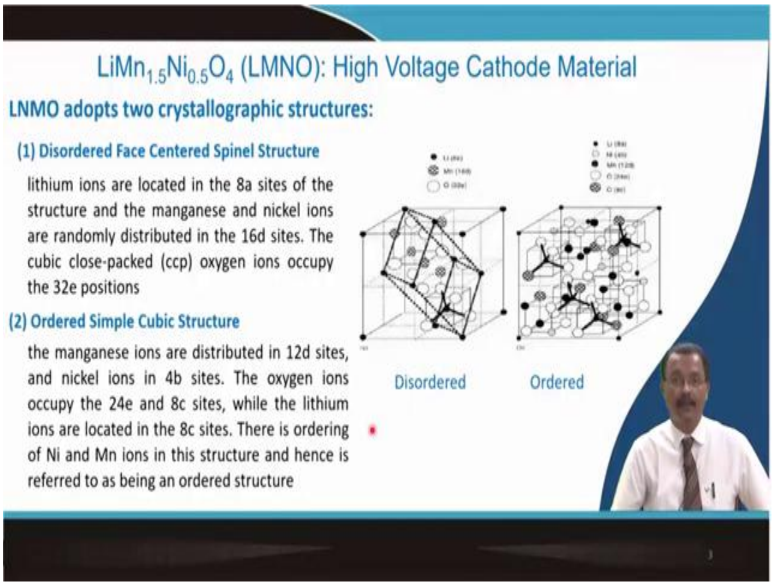

$LiMn_{1.5}Ni_{0.5}O_4$ (LMNO): High Voltage Cathode Material

LNMO adopts two crystallographic structures:

(1) Disordered Face Centered Spinel Structure

lithium ions are located in the 8a sites of the structure and the manganese and nickel ions are randomly distributed in the 16d sites. The cubic close-packed (ccp) oxygen ions occupy the 32e positions

(2) Ordered Simple Cubic Structure

the manganese ions are distributed in 12d sites, and nickel ions in 4b sites. The oxygen ions occupy the 24e and 8c sites, while the lithium ions are located in the 8c sites. There is ordering of Ni and Mn ions in this structure and hence is referred to as being an ordered structure

So, this lithium manganese nickel oxide this is from the parent, one can synthesize from the parent lithium manganese oxide LiMn2O4, which is a spinel kind of ceramic and dope part of manganese with nickel with plus 1.5 instead of 2, so 0.5 atomic fraction I have introduced replacing part of manganese.

And as I said this is high voltage cathode material. So, it will have when it crystallizes, it can crystallize either in a disordered face centered cubic structure. So, this is the disordered structure, where lithium is located in a tetrahedral 8a site and manganese and nickel ions they are randomly distributed in the octahedral sites; you know that this is the tetrahedral site and these two are there in the octahedral sites.

And this 8a and 16d they are Wyckoff notation. So, this is the notation of this octahedral name of the octahedral and tetrahedral sites. And oxygen is in a cubic close pack arrangement, which is having 32e positions. So, this is the disordered spinel structure which we are familiar with; I have already introduced the spinel structure in my crystal structure in module 1 lectures.

Then sometimes this is ordered; ordered simple cubic structure of the same material; the manganese ions are distributed into another site, which is 12d sites and nickel ions in 4b site. So, this actual sites you can see it corresponding to this figures and oxygen ion is also different, the Wyckoff notation is 24e instead of 32e and 8c sites.

So, and lithium are also located in 8c sites. So, this causes a ordering of nickel and manganese ions in the structure and hence this is referred to an ordered structure. So, oxygen here is in the 24e site only and 8c site actually this is devoted to lithium; lithium are located in 8c sites.

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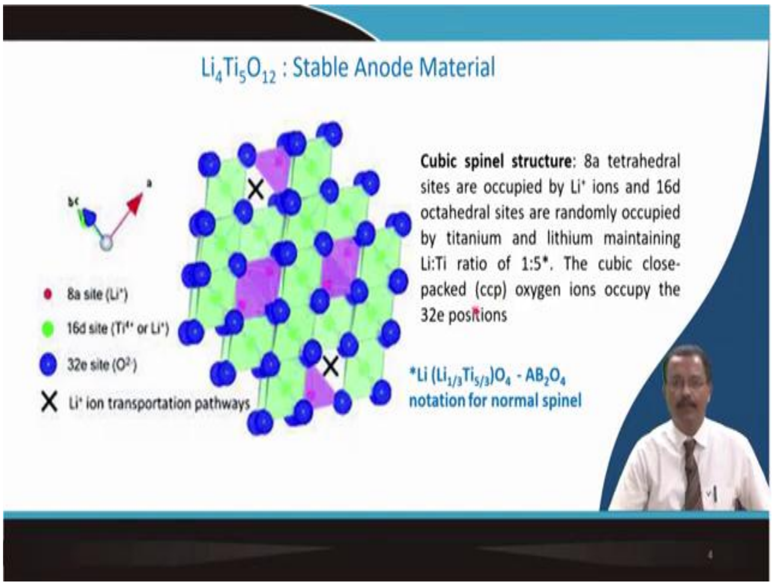

$Li_4Ti_5O_{12}$: Stable Anode Material

Cubic spinel structure: 8a tetrahedral sites are occupied by Li^+ ions and 16d octahedral sites are randomly occupied by titanium and lithium maintaining Li:Ti ratio of 1:5*. The cubic close-packed (ccp) oxygen ions occupy the 32e positions

*$Li(Li_{1/3}Ti_{5/3})O_4$ - AB_2O_4 notation for normal spinel

The second material which is anode that is also having a cubic spinel structure and it has a 8a site tetrahedral coordination, where lithium is occupied and then 16d site, where titanium as well as part of lithium also is there, they are occupied there and 32 sites is cubic close back oxygen.

And this lithium pass pathway which is a three dimensional kind of thing, so this is shown in the free space here marked as cross. So, here through here lithium can diffuse. So, the formula looks a bit weird Li 4 Ti 5 O 12, but one can always write it in AB 2 O 4 structure.

So, here you can see that these two constitutes 2 and lithium is 1 and so, that is AB 2 O 4 structure. And here you can see this lithium and titanium they are in the ratio of 1 is to 5 in a cubic close pack arrangement, which assumes the octahedral site. So, that is the structural definition.

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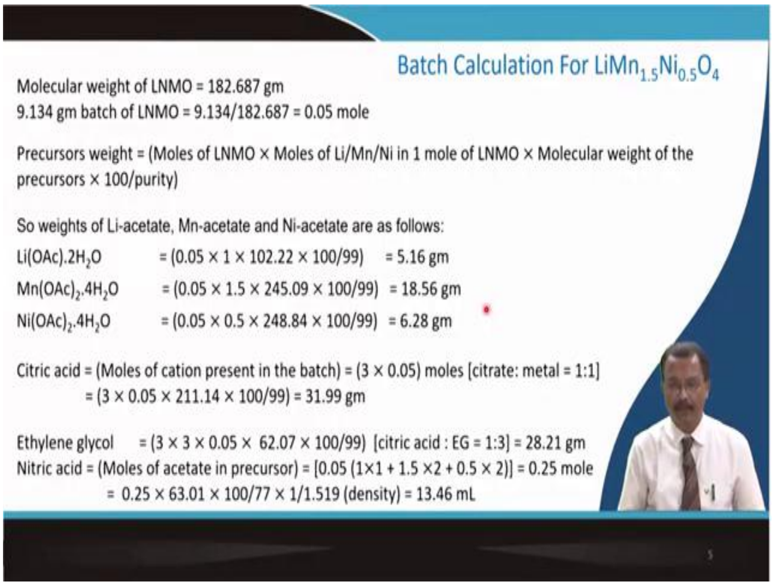

Batch Calculation For $LiMn_{1.5}Ni_{0.5}O_4$

Molecular weight of LNMO = 182.687 gm
9.134 gm batch of LNMO = 9.134/182.687 = 0.05 mole

Precursors weight = (Moles of LNMO × Moles of Li/Mn/Ni in 1 mole of LNMO × Molecular weight of the precursors × 100/purity)

So weights of Li-acetate, Mn-acetate and Ni-acetate are as follows:
$Li(OAc).2H_2O$ = (0.05 × 1 × 102.22 × 100/99) = 5.16 gm
$Mn(OAc)_2.4H_2O$ = (0.05 × 1.5 × 245.09 × 100/99) = 18.56 gm
$Ni(OAc)_2.4H_2O$ = (0.05 × 0.5 × 248.84 × 100/99) = 6.28 gm

Citric acid = (Moles of cation present in the batch) = (3 × 0.05) moles [citrate: metal = 1:1]
= (3 × 0.05 × 211.14 × 100/99) = 31.99 gm

Ethylene glycol = (3 × 3 × 0.05 × 62.07 × 100/99) [citric acid : EG = 1:3] = 28.21 gm
Nitric acid = (Moles of acetate in precursor) = [0.05 (1×1 + 1.5 ×2 + 0.5 × 2)] = 0.25 mole
= 0.25 × 63.01 × 100/77 × 1/1.519 (density) = 13.46 mL

Now, what you will have to do; you will have to synthesize this material. So, to synthesize this material, you will have to do a batch calculation; if you need say about 10 grams of batch, then what are the things, what are the precursor material that you will take, so that finally, this lithium manganese nickel oxide in calcine form you get those spinel structure.

So, usually that is done by this process and we call it is a batch calculation. So, you need to know the molecular weight of LNMO; so all these atomic weights are needed, so you can have the molecular weight. And the amount that you need you divide by molecular weight, so you need this you, you will get that how much moles you need.

Molecular weight of LNMO = 182.687 gm

9.134 gm batch of LNMO = 9.134/182.687 = 0.05 mole

So, the precursor weight this is according to the mole fraction. So, if I talk about this, then this is the mole fraction; if I take 0.05, so 0.05 lithium is required, then 1.5 into 0.05 manganese is required and so on and so forth and oxygen will be adjusted accordingly.

Precursors weight = (Moles of LNMO × Moles of Li/Mn/Ni in 1 mole of LNMO × Molecular weight of the precursors × 100/purity)

So, exactly that has been done lithium 1, this is its molecular weight and you need to need you need to know the yield of the chemical that you are using. So, it is 99 percent pure high pure lithium acetate we had taken. So, the amount of lithium acetate that is this much; similarly we calculated the manganese and we calculated the nickel. So, I have all these amounts right.

$Li(OAc).2H_2O$ = (0.05 × 1 × 102.22 × 100/99) = 5.16 gm

$Mn(OAc)_2.4H_2O$ = (0.05 × 1.5 × 245.09 × 100/99) = 18.56 gm

$Ni(OAc)_2.4H_2O$ = (0.05 × 0.5 × 248.84 × 100/99) = 6.28 gm

Now, there are various process that you can adopt for this particular process, we went for a auto combustion synthesis. Now, auto combustion synthesis is something like you have a oxidizing and reducing agent and upon reaction, it catches fire and at room temperature. So, there are lot of nucleation densities are there in the solution and there is minimal grain growth.

So, this is not the scope to teach you about the nucleation and growth theory. In one of my earlier courses on nonmetallic material, I had a detailed description on auto combustion synthesis. So, if you have access of that course, you can know more about it. So, here what we do, there is a chelating agent, we call citric acid; citric acid and this total metal usually we keep 1 is to 1.

So, accordingly you know the molar fraction of this metal and accordingly you select how much citric acid you need. We also use ethylene glycol and a strong oxidizing agent that is nitric acid. So, this specific composition of citric acid and ethylene glycol that is based on our experimental criteria and also we have a tentative calculation that guide us that, what are this precursor we will take to make a phase pure material and what are the science behind it.

Citric acid = (Moles of cation present in the batch) = (3×0.05) moles [citrate: metal = 1:1]

$$= (3 \times 0.05 \times 211.14 \times 100/99) = 31.99 \text{ gm}$$

Ethylene glycol = $(3 \times 3 \times 0.05 \times 62.07 \times 100/99)$ [citric acid : EG = 1:3] = 28.21 gm

Nitric acid = (Moles of acetate in precursor) = $[0.05\,(1\times1 + 1.5 \times2 + 0.5 \times 2)]$ = 0.25 mole

$$= 0.25 \times 63.01 \times 100/77 \times 1/1.519 \text{ (density)} = 13.46 \text{ mL}$$

So, that is why you need to go through this auto combustion synthesis lecture, if you have access to my earlier courses. So, ethylene glycol and nitric acid as a oxidizer that is also added into the solution.

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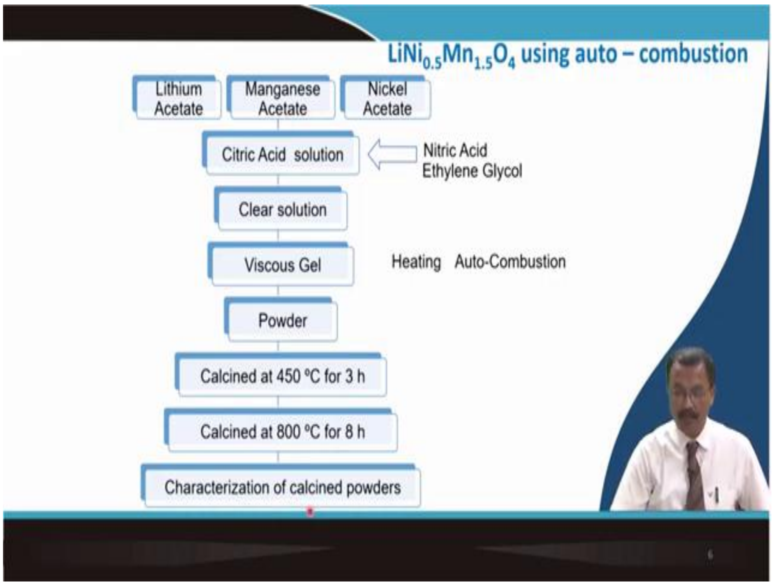

$LiNi_{0.5}Mn_{1.5}O_4$ using auto – combustion

Lithium Acetate | Manganese Acetate | Nickel Acetate

Citric Acid solution ⇐ Nitric Acid, Ethylene Glycol

Clear solution

Viscous Gel — Heating Auto-Combustion

Powder

Calcined at 450 °C for 3 h

Calcined at 800 °C for 8 h

Characterization of calcined powders

And this is the process that you take this salt, then citric acid solution, you put nitric acid and ethylene glycol stoichiometrically.

Then there is a clear solution, then keep on heating, you will form a viscous gel and then it will start to auto combust, this viscous gel. And as I said the nucleation density is very high and grain growth is limited, so you get the powders. Now, the powder is not completely phase pure; so you need to calcine it typically at 450 degree Celsius for 3 hours in air.

Then you will have to calcine it further and this first calcination is to get rid of all these organic components and the second calcination is for the improvement of crystal structure; although the as combusted powder is also crystalline, but it may not be free from organic moieties. And then we do the characterized characterization of this calcine powder.

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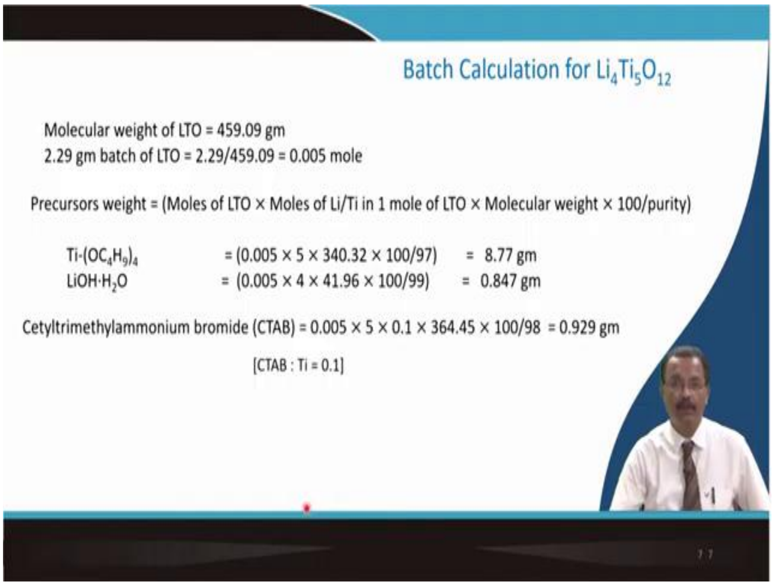

Batch Calculation for $Li_4Ti_5O_{12}$

Molecular weight of LTO = 459.09 gm
2.29 gm batch of LTO = 2.29/459.09 = 0.005 mole

Precursors weight = (Moles of LTO × Moles of Li/Ti in 1 mole of LTO × Molecular weight × 100/purity)

$Ti\text{-}(OC_4H_9)_4$ = (0.005 × 5 × 340.32 × 100/97) = 8.77 gm
$LiOH{\cdot}H_2O$ = (0.005 × 4 × 41.96 × 100/99) = 0.847 gm

Cetyltrimethylammonium bromide (CTAB) = 0.005 × 5 × 0.1 × 364.45 × 100/98 = 0.929 gm

[CTAB : Ti = 0.1]

Similarly, we can do the batch calculation for lithium titanate formation in the same way. So, I will not repeat this, you can go through this and you can have that this much grams of batch, how much precursor you will have to take. Only one difference is there, earlier one all salts precursor we had taken; but here it is a alkoxide precursor we have taken.

Molecular weight of LTO = 459.09 gm

2.29 gm batch of LTO = 2.29/459.09 = 0.005 mole

Precursors weight = (Moles of LTO × Moles of Li/Ti in 1 mole of LTO × Molecular weight × 100/purity)

$Ti\text{-}(OC_4H_9)_4$ = (0.005 × 5 × 340.32 × 100/97) = 8.77 gm

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Cetyltrimethylammonium bromide (CTAB) = 0.005 × 5 × 0.1 × 364.45 × 100/98 = 0.929 gm

[CTAB : Ti = 0.1]

So, in that way this is a sol gel kind of synthesis and the earlier one is a weight chemical synthesis and of course, this does not undergo the auto combustion like the other one. So, it is a pure sol gel synthesis.

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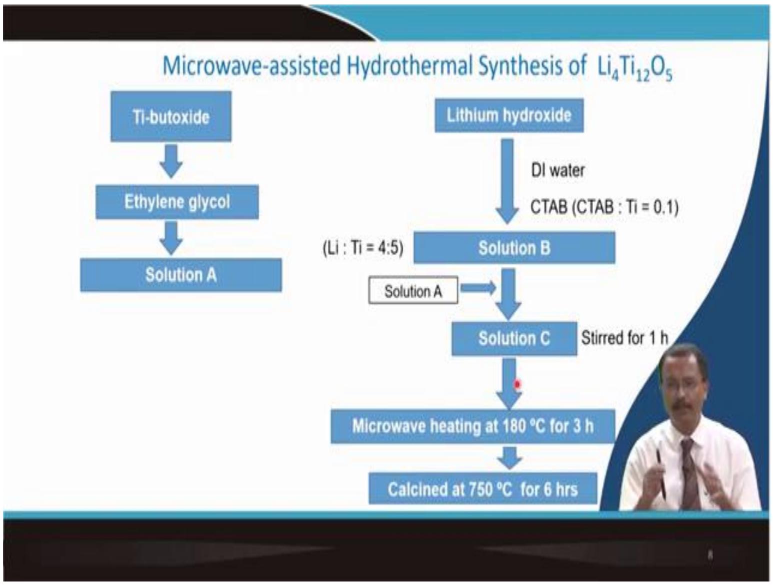

Microwave-assisted Hydrothermal Synthesis of $Li_4Ti_{12}O_5$

Ti-butoxide

Ethylene glycol

Solution A

Lithium hydroxide

DI water

CTAB (CTAB : Ti = 0.1)

(Li : Ti = 4:5)

Solution B

Solution A

Solution C

Stirred for 1 h

Microwave heating at 180 °C for 3 h

Calcined at 750 °C for 6 hrs

So, this is the way we prepare the titanium butoxide and lithium hydroxide was the salt and we did use some kind of surfactant for the process need and then finally, this solution we did a microwave heating.

So, it has certain implication to control the phase purity as well as the morphology of the powder and calcined at 750 degree Celsius for 6 hours. So, in that way it is sol gel and microwave assisted hydrothermal synthesis. So, the process sometimes it looks like quite complicated; sometimes it is not as simple as solid state synthesis, where you mix different constituent and then shake it and bake it and get the material.

We work lot of chemistry aspects to exactly pinpoint the synthesis that will be beneficial for making this kind of complicated electrode materials.

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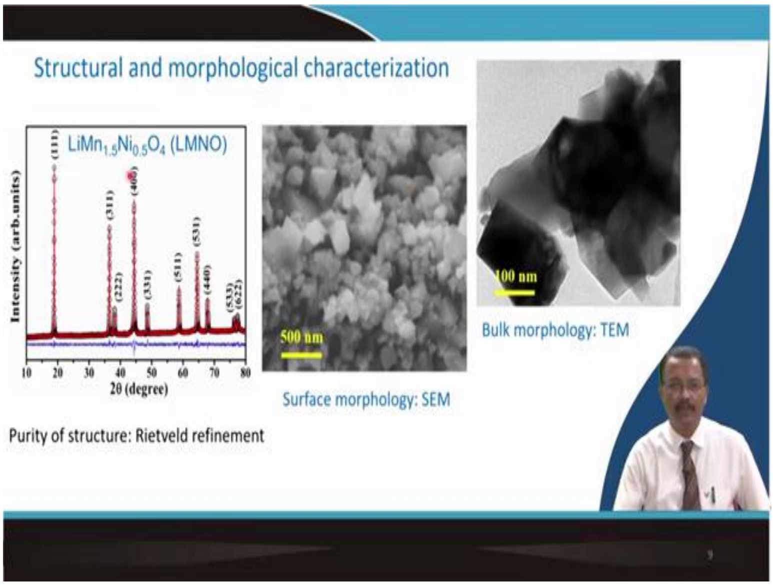

Structural and morphological characterization

Purity of structure: Rietveld refinement

Surface morphology: SEM

Bulk morphology: TEM

So, first you will have to see the structure and usually we do Rietveld refinement to know exactly what is the precise lattice parameter; whether there is any impurity phase, what is the theoretical density, what are the positions of atom.

I already talked about it that, there are certain position this atom sits in spinel structure, ordered spinel structure or disordered spinel structures; so Rietveld refinement will exactly tell you that whether this kind of atom they have assumed this position.

Now, actually what it does you construct your crystal lattice, you know the lattice, you know the space group now by knowing the points group and then following the X-ray diffraction theory, you can basically calculate what it would be the exact X-ray diffraction pattern, and match that X-ray diffraction pattern with your experimentally observed X-ray diffraction pattern.

Now, if you subtract the X-ray diffraction experimentally obtain an X-ray diffraction obtained by this kind of simulation; then if it exactly matches, then this will certainly be a straight line, which is the case here. So, lot of good things you can do from Rietveld refinement and we do it quite regularly.

Then the surface morphology, how the powder looks like both the surface part as well as it is bulk part by scanning electron and transmission electron microscopy.

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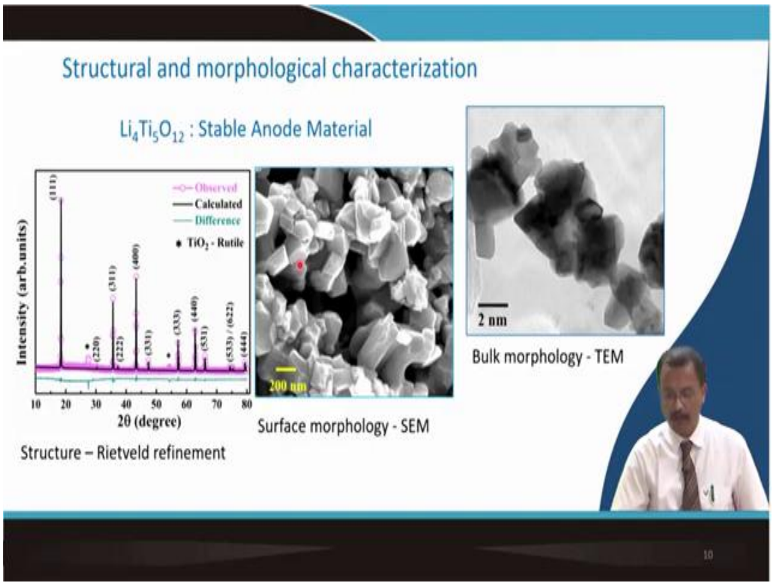

Structural and morphological characterization

$Li_4Ti_5O_{12}$: Stable Anode Material

Structure – Rietveld refinement

Surface morphology - SEM

Bulk morphology - TEM

Similarly, for lithium titanate exactly the same things we could do and this is the surface morphology and each particle you can see there are different faceted structures, not necessary everything will be circular.

But from this scale, you can measure the particle size and this is a agglomerated kind of thing and then this particle size distribution also can be measured if required. And the major importance is that this is having a faceted kind of structure that purposefully we did by adding the surfactant, so that the growth of a particular plane is inhibited, where the lithium ion diffusion is marginalized.

So, we only allowed the growth of the planes, where lithium ion can diffuse very fast for our own purpose.

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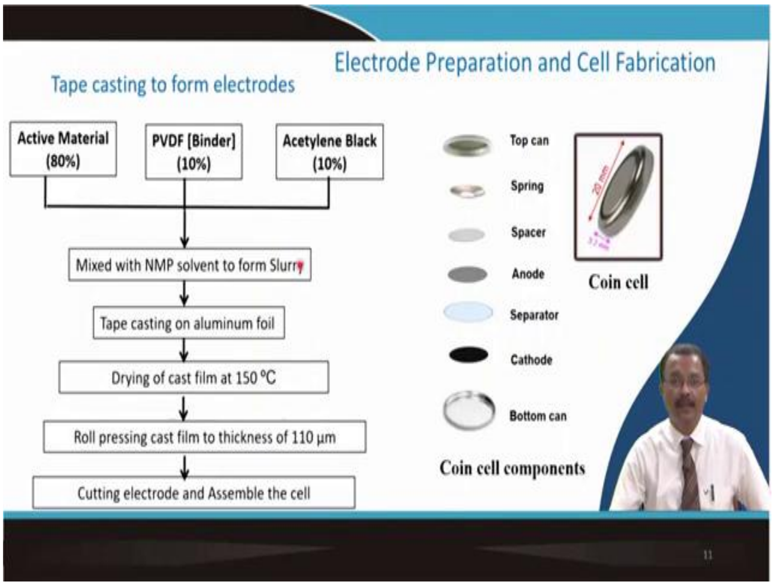

Electrode Preparation and Cell Fabrication

Tape casting to form electrodes

Active Material (80%)

PVDF [Binder] (10%)

Acetylene Black (10%)

Mixed with NMP solvent to form Slurry

Tape casting on aluminum foil

Drying of cast film at 150 °C

Roll pressing cast film to thickness of 110 μm

Cutting electrode and Assemble the cell

Coin cell components

Coin cell

Now, you will have to make an ink using this process. So, actually the active electrode material 80 percent mixed with the binder and conducting agent; in one of my lectures you have seen it that it is not simply active material, because they are ionically conducting, but electronically insulating. So, you will have to mix it with a this conducting acetylene black, which is about 10 percent and you will have to bind it with the current collector.

So, PVDF binder was used. So, PVDF dissolves in N methyl pyrrolidone solvent. Then we do tape casting on aluminum foil, because this is the positive electrode; then we dry it and then roll press it to improve the tap density further and then cut the electrode in the circular fashion and these are the components of the coin cell.

So, you have the cathode, then electrolyte you dip it in the liquid electrolyte LiPF 6 in ECDNC; we will talk separately about separator material, electrolyte material, why ECDNC or ECDEC we are using later. Then you will have to put anode. So, in half cell the anode is lithium foil itself; then certain spacer and spring is required and then finally, you have a gasket with a top can and you crimp everything together to get this kind of coin cell.

So, as you can see the diameter is 20 and this is 3.2 millimeter. So, that is why the name came 2032 CR 0 point cell.

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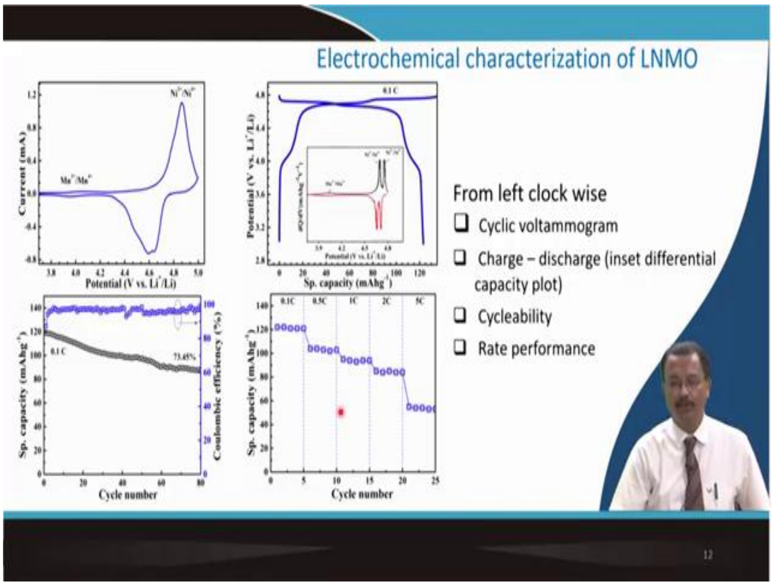

Electrochemical characterization of LNMO

From left clock wise

- ❑ Cyclic voltammogram
- ❑ Charge – discharge (inset differential capacity plot)
- ❑ Cycleability
- ❑ Rate performance

Then suddenly you will have to do the cyclic voltammetry, where the oxidation and reduction peaks are clearly visible. So, oxidation peak what will happen that, if the manganese is not in plus 3 valence state, only in plus 4 valence state.

Then once lithium you are taking out during charging, which is the anodic process, oxidation process; then there will be no valence state change. So, the fact that manganese 3 plus is there; so that means little bit this is a disordered structure. And nickel will also get oxidized, so this is the from nickel 2 to nickel 4, it will get oxidized.

And similar things you will get during reduction when lithium is going back. So, the process is reversible that, you can easily see here. Then you do the charge discharge measurement and the genesis of this voltage profile what, why this the plateau is there; this is by this time you know that we talked about the composition versus lithium content curve and then the tangent we put the chemical potential, we know the chemical potential is related to open circuit voltage.

So, eventually from free energy diagram, you can constitute this kind of curve. In a separate lecture, I will talk about it the genesis of these types of curve. And then you differentiate this curve and you will get something similar to this. So, if you differentiate this curve, exact peak position you will be getting. So, nickel as you can see it goes from 2 to 3 and 3 to 4 that will be very clearly identifiable.

And this kind of thing we call a differential capacity plot. Then cycleability we do; so repeatedly you cycle at a different current rate to see that how the discharge capacity falls, it is not a very great electrode, because you can see within 80 cycles there is a tremendous fall.

So, this is some of our initial work by a PhD student. So, we improved it quite further and coulombic efficiency that define the difference between the charge capacity and the discharge capacity over cycles. So, that should be very near to 100, so that is important.

So, coulombic efficiency has been plotted in the right part of the ordinate. And then we do this charge discharge at different rate; you know that at lower rate when you drain C by 10 current then the capacity is quite high. But as you progressively go to higher current about 5 C, the capacity drops down; because of the several reasons, which while the course goes I will talk about it.

So, this is cyclic voltammetry this is charge discharge measurement, along with that you do the differential capacity measurement; then cycleability, coulombic efficiency and these are the rate performance. These are the things that you must do in a half cell configuration to see that whether the electrode whatever you have prepared that is of good quality.

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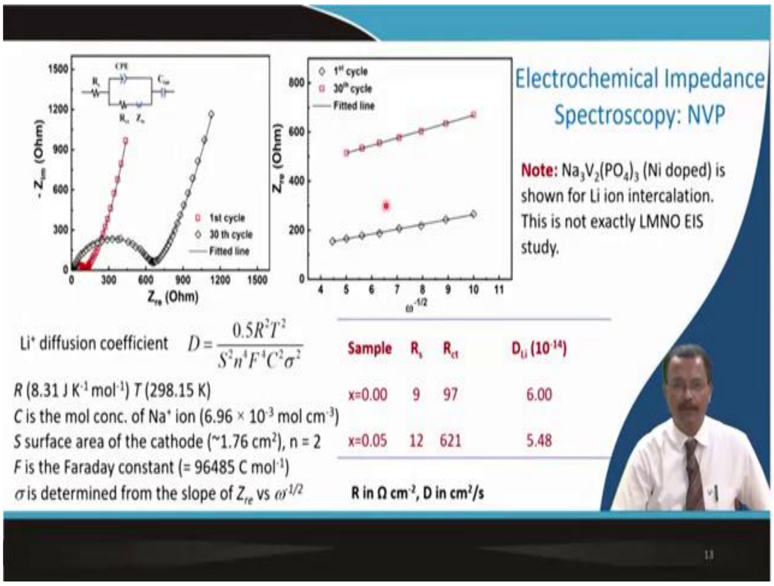

Electrochemical Impedance Spectroscopy: NVP

Note: $Na_3V_2(PO_4)_3$ (Ni doped) is shown for Li ion intercalation. This is not exactly LMNO EIS study.

Li^+ diffusion coefficient $D = \frac{0.5R^2T^2}{S^2n^4F^4C^2\sigma^2}$

R (8.31 J K^{-1} mol^{-1}) T (298.15 K)
C is the mol conc. of Na^+ ion (6.96 × 10^{-3} mol cm^{-3})
S surface area of the cathode (~1.76 cm^2), n = 2
F is the Faraday constant (= 96485 C mol^{-1})
σ is determined from the slope of Z_{re} vs $\omega^{-1/2}$

Sample	R_s	R_{ct}	D_{Li} (10^{-14})
x=0.00	9	97	6.00
x=0.05	12	621	5.48

R in Ω cm^{-2}, D in cm^2/s

Then the diffusion coefficient you can easily measured by the impedance spectroscopy measurement, which I talked about and you can see that this is the randle circuit that we talked about. Initially this charge transfer resistance you can see it is very low. So, charge transfer resistance was 97 from this randle circuit, it quite good fit.

Li^+ diffusion coefficient $D = \frac{0.5(RT)^2}{S^2n^4F^4C^2\sigma^2}$

So, that means this kind of circuit is operative here. And this after cycling, after cycling you can see that this has progressively increased. So, the charge transfer resistance is somehow increased, so that your capacity falls with the number of cycles; that is why the cycleability was not that good for this electrode which I mentioned in the other thing.

So, this is a representative, representative curve which occurs for many material; unfortunately for LMNO this is not the data, this is another material, but that does not matter. But this the fall of the cycleability it is somewhere related to the charge transfer resistance increment with the number of cycles.

From the tail here, you can also measure the diffusion coefficient by using this equation and all the terminologies are defined, which is the gas constant and temperature, then concentration of this material is for sodium ion battery. So, sodium ion concentration that you can calculate, if you know the unit cell and how many sodiums are there per unit volume, you can calculate the concentration.

Then surface area of the electrode is important; how much electron is transferred, because out of these 3 sodium only 2 you can extract in and out. So, this is 2 and F is the faraday constant and the sigma is determined from the slope of this real part of Z which you get from the impedance spectroscopy analysis versus omega 2 pi sorry omega that is 2 pi F 1 by omega to the power minus half.

So, from there you can get this slope. So, you can easily calculate the diffusion coefficient. So, as you can see that for this particular sample, diffusion coefficient is not really that much affected; but cycleability still remains poor. So, that is one usefulness of doing the impedance spectroscopy analysis.

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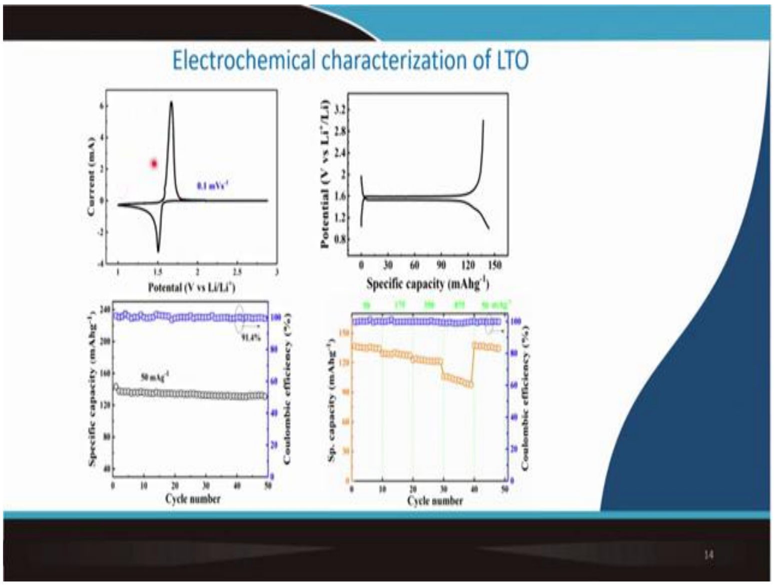.

Electrochemical characterization of LTO

Similarly, we did exactly the same thing for LTO. So, as you can see only titanium is there, which undergoes this redox reactions and this is the flat part. So, the voltage profile is very different. If you see the earlier curves for lithium manganese, I will go back the earlier thing it is very different; sorry earlier thing is very different; here you see it is flat, but suddenly it drops down.

But in case of LTO, it is totally flat and then drops down. So, these are all related to the type of the material, whether it is a solid solution type or whether it is a two phase type that is contributing to this. So, cycleability for this material is quite good as you can see up to 50 cycles almost there is marginal fall in capacity.

So, anode is behaving in one way, cathode is behaving in other way, coulombic efficiency is also very close to 100 and your rate performance is also quite good. So, as you can see different current rate we applied to this electrode and there is fall only at very high drainage current. So, this is quite good anode as compared to the cathode that the student prepared.

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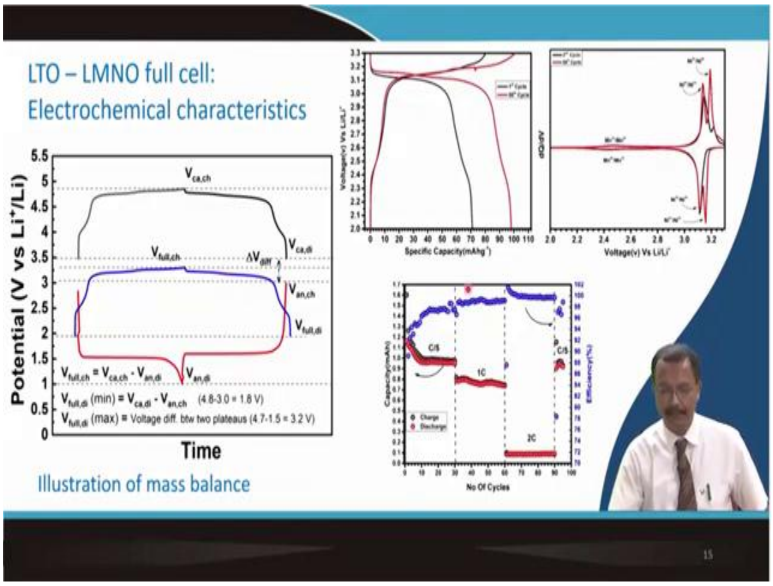

LTO – LMNO full cell:
Electrochemical characteristics

Illustration of mass balance

Now, you will have to construct a full cell and these two half-cell they have different capacity. So, you will have to make the capacity balance. So, capacity balance also I will introduce as a part of my other lectures.

So, usually the thumb rule is that, if your anode capacity is more with respect to your cathode capacity which is the case in this; then you will have to take less number, sorry less amount of anode and do the charge balance. So, the charge in both the anode and cathode they should be similar.

In other words, you know the source of lithium is always the cathode. So, lithium is coming from the cathode and you have a large quantity of anode material; then most part of the anode will remain unaffected, because you do not have sufficient lithium to it. So, this is actually done from the half cell characteristics getting the voltage profile and then match these two voltage profile.

So, this is a simple calculation you can follow; then it exactly tell you that if you have the your cathode, which is at higher potential the charge and discharge profile something like this. And in case of anode as I have shown that, this charge and discharge profile, so initially it will get discharged.

So, when it is charged, then this one is discharged; when it is discharged, this one is getting charged. Then if you construct it with proper mass balance, then certainly this capacity will be something similar to, this one, this one. So, this is a proper mass balance one. And the voltage you can estimate from the simple difference, which I told you in the very first slide that it depends on the chemical potential; chemical potential is related to partial molar free energy, and partial molar free energy versus composition is related to voltage.

So, it is basically the difference in chemical potential. So, you get after this calculation, you can exactly know that what will be the your voltage of the full cell. When you construct the full cell, it is no more lithium; but LTO as anode and your LMNO as cathode.

So, exactly that has been done. And this is the actual full cell value and here you can see that whatever was predicted around 3 volt this has been mentioned; only difference is that you know that your LMNO was not that good, because it has cycleability problem, although L 2 LTO was good material.

So, after this 1 to 10 cycles, there is a reasonable drop in the capacity. And you can calculate the value of the capacity of anode and cathode, because these are basically capacitor like. So, they are connected in series. So, if you know the capacity of anode and cathode, then you can estimate that indeed you should get at least at first cycle this much of capacity.

You can do the differential capacity plot to identify the types of reaction that is going on. And this is the typical data for the coulombic efficiency the blue part and the rate performance for this full cell.

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REFERENCES

- **Kirtan Sahoo, S.B. Majumder et. al** " Investigations on the electrochemical characteristics of rechargeable MCMB – Li Ni0.5Mn1.5O4 pouch cells" Journal of the Electrochemical Society 166 A342 – A352 (2019) (Reference paper to read and understand the case study) (Study material)
- **A. J. Bard.** "Electrochemical Methods: Fundamentals and Applications" 2nd Ed. Wiley New York, 2001. **(Reference book)**
- **R. A. Huggins.** "Advanced Batteries: Materials Science Aspects" Springer New York, 2009.

So, the reference for this particular work is published, although it is in a better form, it is published by this student of mine.

So, that will give you a good idea, although the material is a bit different; instead of LTO, we used MCMB, micro carbon meso bead that kind of carbonaceous material and this high voltage cathode material in a pouch cells configuration. So, the paper also talks about how to make the pouch cell, not the coin cell for practical purpose.

So, this needs to be read to understand whatever I talked about and for general electrochemistry, this is the bible A. J. Bards book and this is also a wonderful book that I have came across.

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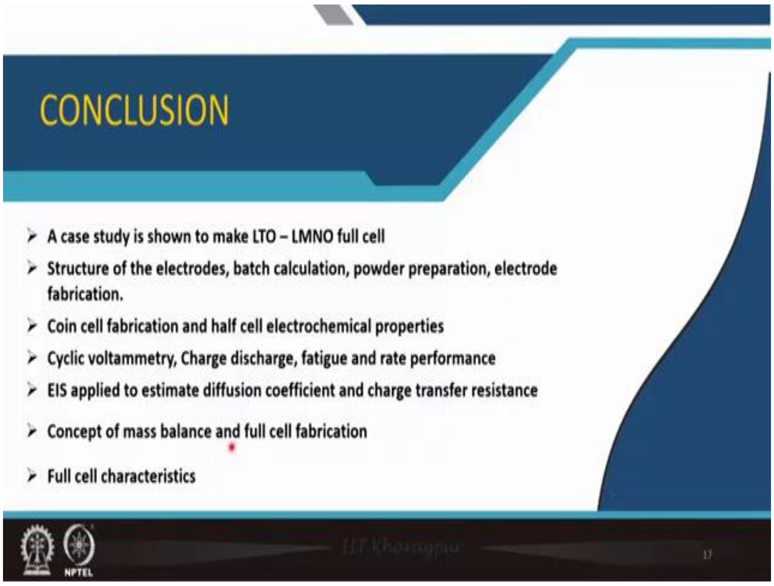

CONCLUSION

- A case study is shown to make LTO – LMNO full cell
- Structure of the electrodes, batch calculation, powder preparation, electrode fabrication.
- Coin cell fabrication and half cell electrochemical properties
- Cyclic voltammetry, Charge discharge, fatigue and rate performance
- EIS applied to estimate diffusion coefficient and charge transfer resistance
- Concept of mass balance and full cell fabrication
- Full cell characteristics

So, a case study has been shown for LTO, LMNO full cell, structure of the electrode, batch calculation, powder preparation, electrode fabrication has been described. Coin cell fabrication and half-cell electrochemical properties are described.

Cyclic voltammetry, charge discharge, fatigue and rate performance they are important characteristics that one need to do in order to qualify the synthesized material for any practical application.

And electrochemical impedance spectroscopy is applied to estimate the diffusion coefficient and charge transfer resistance; what is going on inside the battery and concept of mass balance and full cell fabrication that I have introduced and full cell characteristics has been demonstrated.

We will keep on doing lot of case study. So, whatever you are learning, you will see that experimental and theoretical there are very very close correlation.

Thank you for your attention.