Various Methods to Prepare and Synthesis Cathode Active Material (NMC) of Lithium Ion Batteries

Osama Ahmed and Dhia'A Mohammed

June 15, 2021

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***Abstract*— Due to NMC cathode active material of lithium ion batteries have promising advantage, like hiegh capacity, thermal stability, safety, and low cost, the researcher exert much effort to discover and find excellent method to prepare and produce better product of NMC.As we find in the literature there are many method synthesis such as, solid-state method, sol-gel method, and co-appreciation method, etc. .and any method have economic, electrochemical, structural, safety, and energy density features, so we collect a number of method of preparation and synthesis to provide, researchers, and developer by many thinking to inspire a suitable method which combine many features of the different method and we also give to commercial company many method to make them build their manufacturing system of production of NMC cathode active material.**

Keyword :Lithium-ion batteries, NMC Cathode active material, synthesis, preparation.

I. INTRODUCTION

Lithium ion batteries is considered the main source of energy since the few past decade and these source of energy has a hiegh trend in the future because it is the best choice of energy source for electric vehicles and hybrid electric vehicles ,in general Lithium ion batteries contain of three basic component , cathode ,anode and electrolyte ,the important from those three components is the cathode active materials because it is considered the source of current and energy in the batteries .Currently there are many commercial cathode active material for lithium ion batteries like LiCoO2, LiFePO4, LiMn2O4,and Li(k)Co(x)No(y)Mn(z)O2 ,and these later is very promising for lithium ion batteries because its heigh specific capacity, excellent safety feature, and heigh discharge voltage, so, for this attractive feature it is consider the best type of cathode active material of lithium ion batteries. The main motivation to do these reviewing is to coolects many routs of preparation of cathode active material in one journal. When we want to produce these cathode active material we adopt many sequence process and many devices to convert its raw material to these component, as we mention in abstract there are many method to preparation and synthesis of this component like copredication method, sol-gel method, solid state method and firring processing ,etc. and any method above is economic and suitable under many constrains like limitation of raw material ,and devices availability ,volume of production, and experience existence ,etc. Many researchers focused their effort of how they find economic and suitable way to prepare and synthesis NMC component of cathode active material of lithium ion batteries to face the excessive demand of lithium ion batteries, the researchers and commercial companies also, want to adopt and study more method to improve the presence component of cathode active material NMC of lithium ion batteries, and providing many solution for multiple interest of energy in the future.

II. MATERIALS & METHODS

As mention above, There are many methods to prepare and synthesis NMC cathode active materials, and each method different with the other by raw materials and processing ,time of preparation ,devices and teqnic and the performance of the final product of preparation.so we display many examples of preparation to give the developer and commercial production companies various method to inspire their best selective of their demand.

A. Example-1

solid state preparation and synthesis of Production NMC cathode active material by using three metal sulfate, metal precursors including (NiSO4,CoSO4,MnSO4,NaOH) This metal supplied solution is added in continuously stirrer tank at 60 C° by concentration of (2/3)mol/L ,then added reductive agent (NaOH) to the solution by stoichiometric amount, after that added 0.24 mol/L ammonia (NH4OH) to reduce time of reactant by increase reaction rate, reaction above need energy to stirring and heating the reactor and energy for drying and the energy of the reactor is 60 C° for 12 hours ,as mention above the material need three process to produce (Ni(x)Co(y)Mn(z)(OH)2)) this mix by stochiometric amount of LiOH these two component is grind and Pelletize to precursors amount and then precalcinated in the muffle at from room temperature to 450 C° for Ten hours after that reground and repalletize ,finally Heating the product from room temperature to 800 C° for eight hours to gain black powder of Li(Ni(x)Co(y)Mn(z))O2 as a one of cathode active material of lithium ion batteries.

B. Example-2

Metal precursors, including: CH3COOLi.2H2O, Ni(CH3COO)2.4H2O, Co(CH3COO)2.4H2O, Mn(CH3COO)2·4H2O, and oxidation state in these cathode component of (Co,Ni,Mn) is (+2) and oxidation state of Li is(+1) , all above raw material stoichiometrically mixed and then dissolve in aqueous solution(deionized water) and then the complexing agent C6H8O7·H2O was dropped slowly into the aquas solution under stirring 100C° oil ,The mixtures were kept under vigorous stirring until convert to gel form and this gel is wet by the solution effects, after that the gel is dried at 100C° to rid of wet gel and get of an amaranth dry gel like powder, finally the powder was put in muffle at 400 C° for three hours and then calcined for eight hours at 800 C°. Preparation of $Li(Ni1/3Co1/3Mn1/3)O2$ Samples by using rout in example 2 give excellent result from this preparation .XRD analysis of these example display the , Lattice parameters a/ Å equal 2.8532 , c/Å equal 14.1653 c/a equal 4.9647 and I003/I104 equal 1.482.

C. Example-3

Firring processing to preparation and synthesis of Production NMC cathode active material by using three metal sulfate, metal precursors including (NiSO4,CoSO4,MnSO4,NaOH) This metal supplied solution is added in continuously stirrer tank at 60 C° by concentration of (2/3)mol/L ,then added reductive agent (NaOH) to the solution by stoichiometric amount, after that added 0.24 mol/L ammonia (NH4OH) to reduce time of reactant by increase reaction rate, reaction above need energy to stirring and heating the reactor and energy for drying and the energy of the reactor is 60 C° for 12 hours ,as mention above the material need three process to produce (Ni(x)Co(y)Mn(z)(OH)2)) this metal hydroxide precursors mix with stoichiometric amount of lithium carbonate (Li2CO3) in an oxygen-rich environment by firring method at 900 C° to gain black powder of Li(Ni(x)Co(y)Mn(z))O2 as a cathode active material of lithium ion batteries.

D. Example-4

coprecipitation method to prepare and synthesis of NMC cathode active materials and first we mix (NiNO3,CoNO3,MnNO3) solution in stoichiometric amount with NaOH solution the precipitates were collected and dried at 120 C° after that the precipitates mixed by Stoichiometric amounts of Li2CO3 and then ground. Finally, the powder heated by oven at 750 C° for 36 hours and these heating reactants occur in air.

E. Example-5

synthesis of 0.2 mole of Li [Li(1-2y)/3, Ni(y), Mn(2-y)/3] O2, where y=0.416 the row material of these component is 24.446 g of Ni (NO3).6H2O and 26.614 g of Mn (NO).4H2O this material was dissolving in in 50 mls of deionize water until complete transition metal solution.in the same time of doing this and by other beaker, 19.15 g of LiOH.H2O was dissolved in 300 mls of distilled water. Then the transition metal solution of (Ni (NO3).6H2O, Mn (NO).4H2O) was added to the lithium hydroxide Solution by using buret over period of 3 or 4 hours approximately, above step is caused of co-precipitation of a Ni-Mn hydroxide therefore the formation of dissolved LiNO3.after that we use vacuum filtration method to recover the precipitate by filtrated and washed it repeatedly. Then the result was putting in muffle at 180 C° for drying purpose, after that we mix these results by 8.89 g LiOH.H2O by an auto- grinder and pressed result into a number of pellets, each pallet weighting 3 gram. Then we put these pellet in the muffle oven at 450 C° in air for 3 hours approximately. after that we quench the product to room temperature, after that we collect the pellets and reground it to form powder, these powders pressed again to form new pellets, finally heated these pellet for 3 hours to around 900 C°. This method is very good because it is yielded the cathode material by grinding/re-grinding, quenching/re-quenching to room temperature and heating/re-heating of the pellet to around 450 C° and 900C°.

F. Example-6

In these methods the raw materials are (NiOH, CoOH, MnOH) is mixed by stochastic amount and heating for 2 day at 1000 C° in air to produce (Co(x)Ni(y)Mn(z)) O4 and this precursor mixed by stochiometric amount of Li2CO3 for 5 days at 750 C° in air to produce black powder of Li(y) (Co(x)Ni(y)Mn(z)) O2 as a one of cathode active materials of lithium-ion batteries.

G. Example-7

*i*n these methods we mixing powder of metal oxide of all element in thise components (CoO, NiO, MnO, Li2O) this metal oxide is grinding by ball milling to produce homogenous precursors then heating the precursors oxide in an oxygen containing atmosphere at (500-100) C° wherein the reaction is carried out for at least 12 hours.

H. Example-8

sol-gel method using to prepare and synthesis cathode active materials of NMC component, we mix stoichiometric amounts of this raw materials (Ni (NO3)2.6H2O. (AR), Co (NO3)2.6H2O (AR), C4H6MnO4.4H2O (AR), CH3COOLi.2H2O (AR),) these was dissolving in distilled water. And then added chelating agent like citric acid and after that added ammonia as a precipitation agent, the reaction temperature was kept in 80 C°, then the solution is added in stirring temperature of 130 C° for 10 hours to forming sol-solution and these sols solution is vaporizing at 130 C° till the dry gel formed, after that the heat treatment was applied on this gel at 500 C° for 6 hours in the presence of air with heating rate of 5 C°/min to avoiding the organic residues. Finally, the powder ground and reheated at 800 C° for 20 hours and this process called calcination.

I. Example-9

preparation and synthesized of cathode active material NMC of lithium ion batteries using a facile solvothermal method, the procedure of these preparation as follow, we mix stochiometric amount of (CoCl2• 6H2O and MnCl2• 4H2O) and dissolved it in suitable amount of ethylene glycol (EG) in a Teflon-lined stainless steel autoclave with a suitable volume to form a homogeneous solution, then suitable amount of NH4HCO3 is added to the solution under vigorous continues stirrer for 0.5 hours .after that the autoclave was sealed in an muffle oven at 200 C° for 20 hours ,then slowly cooled to room temperature .the optical properties of above result is light purple precipitate. This precipitate was collected by centrifuge method and then washed several times by deionized water and ethanol. After that it dried by vacuumed oven at 60 C° to obtain Co(y) Mn (3-y) (CO3)3 precursors. then this result calcinate in muffle oven at 600 C° with a ramp rate 4 C°/min for 5 hours we obtain by these calcination Co(y)Mn(3-y)O4 porous microspheres, after that soloistic amount of (Ni(NO3)2• 6H2O, LiOH• H2O) precursors were dispersed amount of ethanol solution ,then a suitable amount of Co(y)Mn(3-y)O4 powder was added into solution ,after that the ethanol evaporated due to magnetic stirrer .then the precipitate result collected and grouped manually for 6 min ,finally the result heated in a pipe furnace for 10 hours at 900 C° with a ramping rate of 1.0 °C/ min, followed by cooling into room temperature .

J. Example-10:

Preparation and synthesis of cathode active material NMC of lithium ion batteries by solid-state methode .the precursors and grade chemical of this method is (CoC4H6O4• 4H2O, NiC4H6O4• 4H2O, MnC4H6O4• H2O,) and three different lithium source use in thise methode in the same time (LiOH• H2O, Li2CO3, CH3COOLi• 2H2O) the impurity in above grade chemical don’ t exceed 6%. Stoichiometric amount of above material were mixed for 1 hour through balled milled (200 rpm).Then amount of ethanol were added and to the mixture and balled milled (200 rpm) for 3 hours. After that to gain a uniform mixture precursors dried the precursors in an oven for 12 hours at 80 C°.then ball milled again the dried precursors for 0.5 hour .finally sintered the precursor in muffle oven at 900 C° for 10 hours with a ramp rate 5 C°/min in the air atmosphere to obtain the final product of cathode active material.

K. Example-11

Synthesis and preparation of cathode active materials NMC by using sol-gel rout and used ethylene glycol to enhance the overall performance of the product of cathode active material and additionally alternate the viscosity of the products and make the reaction rate in the sol-gel stage very easier. The preparation of this rout is very fixable and variety raw material acceptance these suggest any component of raw material have medium or hiegh solubility can use in this rout ,Li-Mn-Co-Ni hydroxide, chloride, nitrate or sulphate we can use in this rout, the manner of these rout as follow :we use soluble raw material for example nitrate ,we put stoic metric amount of raw materials (LiNO3,MnNO3,CoNO3, NiNO3) with excessive distilled water in vigorous magnetic stirrer ,then we added stochiometric amount of citric acid slowly to the solution ,and then added stoic metric quantity of ethylene glycol to the solution ,after that let the solution in 90 C° with vigorous magnetic stirrer for around 2 hours till convert this solution to gel form ,after that we dry this gel at one hundred C° for 6 hours to ride of wetting from the gel ,then we put these end result from drying in the muffle oven at 700 C° for around eight hours to convert the product into black powder these powder is cathode energetic cloth of lithium ion batteries. When the developer test final product from this rout of preparation the have determined that from X-Ray Diffraction analysis that the lattice parameters of the NCM-EG. a(Å) 2.86539, c(Å) 14.2683, c/a 4.9795 V(Å3) 101.45 and I (003)/I (104) 1.4245 and found from SEM analysis that the particle floor of NCM-EG is smooth, the particle structure is regular, the edges and corners are distinct, and there is no agglomeration phenomenon and these machines. All these indicate that NCM-EG has a larger specific surface area and is easy to fully contact with the electrolyte in the process of electrochemical reaction, which probably makes the electrochemical reaction faster, so that the material has better rate performance. we find all Electro-chemical structural and physical information by using X-RD and SEM analysis for the products. Also, after 200 cycles, the capacities of NCM-EG 133 mAhg-1 and capacity retention 63.9%.

III. RESULTS AND DISCUSSION:

We conclude that the performance, electrochemical, thermal, structural feature of final NMC cathode active materials dependent on the type of rout preparation, and type of raw material used in the preparation. For instance when we compare with conventional sol-gel method and sol-gel method assist by ethylene glycol we find NMC-EG have higher c/a value ,smaller particle size ,more regular shape and display better orderly structure ,The c/a values of NMC-assist by ethylene glycol (EG) and NMC are 4.9795, and 4.9765 respectively, by use above c/a comparing value we conclude that NMC-EG has better diffusion ability of Li+ ions than other, also by revering to the same reference we find that NMC-EG has smoother particle surface ,more regular particles shape, and better edge and corner distinct, therefore all above feature indicate that NMC-EG has larger specific surface area which allow fully contact between cathode active material and electrolyte surface ,thus improve electrochemical process by faster it's reaction therefore improve their performance. So we conclude from all above example that the difference between entropy and gibes energies of reactants and resultants manipulate and controls of the preparations and Spontaneity of reactions.

IV. CONCLUSION .

In summary, we have collected many methods used for synthesis and preparation of NMC cathode active materials and these method give researchers many knowledge of NMC component preparation, raw materials, equipment and device used for preparation, and time of synthesis, we conclude from all method above that we need muffle oven to ride of some suffixion of raw material by evaporation and need chelating agent to chemical combine the elements of the NMC component. Finally the purpose of these article group and collect many rout and methods of synthesis of NMC component rather than its result of preparation. Also the results of preparation cannot mention her because the result of preparation dependent on the type and amount of elements in the NMC component.

ACKNOWLEDGMENT

This work was supported by my supervisor Rockstar Ali teacher of material science in Taizé university ,faculty of engineering ,Yemen .and the author thank Niyaz Al-Areqi and Elyas Alaghbari .we want to offer those above doctors my gratitude of him scientific helping and guidance for me to reach to this level of knowledge..

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