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Department of Chemical and Biological Engineering

化學及生物工程學系

Project Title : Synthesis of the Recycle Lithium Ion Battery NMC Cathode Materials by Sintering

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Supervisor(s) : Prof. Ka Ming Ng

Work Plan No. : 17036

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Signature of Approval :

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The Hong Kong University of Science and Technology

Department of Chemical and Biomolecular Engineering

Research Work Plan

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Name of researcher	ZHANG Shouchi
Name of project supervisor	Professor Ka Ming, Ng
Date	May 31, 2017

1. General Information

Name of Researcher: ZHANG Shouchi

Name of Supervisor: Prof. Ka Ming NG

Project Type:	Synthesis of NMC cathode materials by sintering
Project Title:	Synthesis of the Recycle Lithium Ion Battery NMC Cathode Materials by Sintering
Research Area:	CENG-Laboratory
Location:	Room 6116, 7101, 7250, 7252, 7253
Start Date:	May 31, 2017

2. Project Description

1) Introduction

Due to $LiNi_{1-x-y}Mn_xCo_yO2$ (NMC) cathode materials-based lithium ion batteries' light weight, high energy and good performance, the usage of NMC cathode materials has rapidly increased. As an indispensible process for synthesizing NMC cathode materials, sintering or calcination conditions have direct influences on their properties (i.e. crystallinity, cation mixing, particle size, specific surface area and morphology). In the literature, some researchers synthesized NMC cathodes with different discharge capacities by changing sintering temperature, time, or cooling rate, and they found that the cathode materials' crystallinity, cation mixing, and particle size have correlation with the discharge capacity. But the properties of NMC cathode products reported by different publications are always not the same even under same sintering conditions. What's more, the sintering temperature to make cathode products is high at the range of 800 °C to 1000 °C, the sintering time often reaches 20h. Thus, determining the effects of sintering conditions on cathode materials' crystallinity, cation mixing, particle size, specific surface area and morphology, and these characteristics on electrochemical performances is of great importance.

2) Objectives

a) To develop simple sintering conditions for lithium ion batteries' cathode materials with excellent electrochemical performances.

b) To characterize the properties (i.e. crystallinity, cation mixing, particle size, specific surface area and morphology) and summarize their relations with the electrochemical performances of NMC cathode products.

3) Research Tasks

a) Determine the effects of sintering temperature on NMC cathode materials' crystallinity, cation mixing, particle size, specific surface area, morphology, and electrochemical performances.

b) Determine the effects of sintering time on NMC cathode materials' crystallinity, cation mixing, particle size, and electrochemical performances.

c) Determine the effects of cooling rate on NMC cathode materials' crystallinity, particle size, and electrochemical performances.

d) Determine the effects of two-step sintering process on NMC cathode materials' crystallinity, particle size, and electrochemical performances by comparing with one-step sintering.

3. Equipment List

- Electronic balance (correct to mg level) in Room 7250
- Pestle and mortar.
- Oil press and stainless die
- Oil bath
- Power basic stirrer
- Furnace/ Muffle furnace

4. Experimental Procedures

A. **Determine the effects of sintering temperature on NMC cathode materials' crystallinity, cation mixing, particle size, specific surface area, morphology, and electrochemical performances**.

1) NMC precursor is mixed into 1mol/L LiOH·H2O solution with the Li:M (metal) ratio of 1.05:1. Stir continuously at 60 °C till the totally evaporation of water.
2) The obtained mixtures will be performed by ball-milling (or hand grinding), and Oil press.
3) Then, the powder is heated to 450 °C with a rate of 5 °C/min and maintain for 4h, and cooled down to room temperature. Ground in an auto grinder and the powder was pressed into pellets
4) And then the powder is heated to **700 °C, 800°C, or 900 °C** with a rate of 5 °C/min and maintain for 12h, and cooled down to room temperature. Ground in an auto grinder and the powder was pressed into pellets.
5) Finally, the products will be characterized by XRD, SEM, BET and TEM for verifying the identity. And the electrochemical performances will be characterized.

B. **Determine the effects of sintering time on NMC cathode materials' crystallinity, cation mixing, particle size, specific surface area, morphology, and electrochemical performances**.

1) NMC precursor is mixed into 1mol/L LiOH·H2O solution with the Li:M (metal) ratio of 1.05:1. Stir continuously at 60 °C till the totally evaporation of water.
2) The obtained mixtures will be performed by ball-milling (or hand grinding), and Oil press.
3) Then, the powder is heated to 450 °C with a rate of 5 °C/min and maintain for 4h, and cooled down to room temperature. Ground in an auto grinder and the powder was pressed into pellets
4) And then the powder is heated to 900 °C with a rate of 5 °C/min and maintain for

8h, 12h, or 16h, and cooled down to room temperature. Ground in an auto grinder and the powder was pressed into pellets.

5) Finally, the products will be characterized by XRD, SEM, BET and TEM for verifying the identity. And the electrochemical performances will be characterized.

C. Determine the effects of cooling rate on NMC cathode materials' crystallinity, particle size, and electrochemical performances.

1) NMC precursor is mixed into 1mol/L LiOH·H2O solution with the Li:M (metal) ratio of 1.05:1. Stir continuously at 60 °C till the totally volatilization of water.
2) The obtained mixtures will be performed by ball-milling (or hand grinding), and Oil press.
3) Then, the powder is heated to 450 °C with a rate of 5 °C/min and maintain for 4h, and cooled down to room temperature. Ground in an auto grinder and the powder was pressed into pellets
4) And then the powder is heated to 900 °C with a rate of 5 °C/min and maintain for 12h, and cooled down to room temperature normally or with a rate 2 °C/min or 15 °C/min. Ground in an auto grinder and the powder was pressed into pellets.
5) Finally, the products will be characterized by XRD, SEM, BET and TEM for verifying the identity. And the electrochemical performances will be characterized.

5. Procedure Template

Experimental Procedure No.	Experimental Procedure Description	Scale (Mass/Volume)	Location (Fumehood,benctop,etc)	Method New or Existing
A1	Mix NMC precursor into LiOH solution and dry	1mol/L LiOH, Li:M (metal) ratio of 1.05:1, stir at 60 °C	6116 benctop	Existing
A2-A4	Sinter the composite and cool down	Sinter at 450 °C for 4h, then 700 °C, 800°C, or 900 °C for 12h, and cool down at 15 °C/min	6116 furnace and fumehood	Existing
B1	Mix NMC precursor into LiOH solution and dry	1mol/L Li2CO3, Li:M (metal) ratio of 1.05:1, stir at 60 °C	6116 benctop	Existing
B2-B4	Sinter the composite and cool down	Sinter at 450 °C for 4h, then 900 °C for 8h, 12h, 16h, and cool down at 15 °C/min	6116 furnace and fumehood	Existing
C1	Mix NMC precursor into LiOH solution and dry	1mol/L Li2CO3, Li:M (metal) ratio of 1.05:1, stir at 60 °C	6116 benctop	Existing
C2-C4	Sinter the composite and cool down	Sinter at 450 °C for 4h, then 900 °C for 12h, and cool down to room temperature normally or with a rate 2 °C/min or 15 °C/min	6116 furnace and fumehood	Existing

6. Hazard and Operability Analysis (HAZOP)

NO	HAZARD	HAZARD EFFECT	SEVERITY	PROBABILITY	RISK	MINIMISE RISK BY	RESIDUAL RISK
A.1	Corrosive materials	Skin corrosion, eyes irritation	M	L	M	Wearing protecting gloves and goggles to avoid contact	L
A.2	High temperature furnace	Finger burned	M	L	M	Wearing heat resistant	L
B	High temperature furnace	Finger burned	M	L	M	gloves to avoid contact	L
C	High temperature furnace	Finger burned	M	L	M	Wearing heat resistant gloves to avoid contact	L
FINAL ASSESSMENT:						OVERALL RISK:	L

Remark: Severity - L=Low (Minor injuries, first aid); M=Medium (Hospitalization, medical leave); H=High (Serious injuries, fatality)

Probability - L=Low (Unlikely); M=Medium (Possible); H=High (Very Likely)

Note: Severity x Probability = Risk [eg. LxL=L; LxM=M;LxH=H; HxM=H; the product follows the higher severity or probability]

Higher Risk requires extensive risk minimization procedures

7. Operating Conditions

The sintering procedures are operated at high temperature, normal pressure and air atmosphere.

8. Service List

1) Electricity, single phase
2) Distilled and tap water

9. Chemicals List

Raw Material	*Product*
$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, LiCl, $LiNO_3$, Li_2SO_4, $Mn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2$, NaOH, LiOH, NH_3H_2O, $Na_2C_2O_4$, Na_2CO_3, HCl, HNO_3, $H_2C_2O_4$, H_2SO_4, H_2O_2, $NaHCO_3$	Li_2CO_3, Co_3O_4, MnO_2, NiO, $LiNi_xCo_yMn_{1-x-y}O_2$

10.Biological Agents List

No biological agents would be used in Experimental Procedures

11.Summary of Relevant Hazards and Incompatibilities

Raw Material / Product	*Hazards*	*Incompatibilities*
Standard Mixture Salt $CoCl_2 \cdot 6H_2O$	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion. Hazardous in case of skin contact (corrosive, sensitizer, permeator), of eye contact (corrosive), of inhalation (lung sensitizer).	Reactive with oxidizing agents, organic materials, metals, alkalis.
$NiCl_2 \cdot 6H_2O$	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Severe over-exposure can result in death.	Reactive with acids.
$MnCl_2 \cdot 4H_2O$	Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation.	Not available.

	Slightly hazardous in case of skin contact (permeator).	
$Al(NO3)3 \cdot 9H2O$	Causes skin irritation. Causes serious eye irritation.	Not available.
LiCl	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation	Reactive with acids. Slightly reactive to reactive with moisture.
LiNO3	Slightly hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.	Reactive with oxidizing agents. Non-reactive with moisture.
$Mn(NO3)2 \cdot 4H2O$	Hazardous in case of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (irritant). Non-corrosive for skin. Non-sensitizer for skin. Non-permeator by skin. Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.	Not available.
$Co(NO3)2 \cdot 6H2O$	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.	Not available.
$Ni(NO3)2$	Very hazardous in case of ingestion, of inhalation. Hazardous in case of skin contact (irritant), of eye contact (irritant). Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.	Highly reactive with combustible materials.
Li_2SO_4	Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Not available.	Reactive with oxidizing agents

	DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to kidneys, the nervous system, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.	
Acid HCl	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.	Not available.
HNO3	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Prolonged exposure may	Not available.

	result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering	
H2SO4	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion, of inhalation. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.	Not available.
H2C2O4	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator), of eye contact (corrosive). Slightly hazardous in case of skin contact (corrosive). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust	Not available

	will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.	
Base NaOH	Hazardous in case of skin contact (corrosive, irritant), of eye contact (irritant), of ingestion. Slightly hazardous in case of inhalation. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract.	Extremely reactive or incompatible with acids.
LiOH	Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of eye contact (corrosive). Corrosive to eyes and skin. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is	Not available

	characterized by itching, scaling, reddening, or, occasionally, blistering	
NH3H2O	Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant), of ingestion, . Non-corrosive to the eyes. Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.	Highly reactive with metals. Reactive with acids. Slightly reactive to reactive with oxidizing agents.
Other reagents Na2CO3	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation (lung irritant).	Reactive with acids. Slightly reactive to reactive with moisture.
H2O2	Hazardous in case of eye contact (irritant). Slightly hazardous in case of skin contact (irritant, permeator), of ingestion, of inhalation (lung sensitizer). Non-corrosive for skin. Non-corrosive to the eyes. Non-corrosive for lungs. Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory	Not available.

	irritation.	
Na2C2O4	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (corrosive), of eye contact (corrosive).	Reactive with oxidizing agents, acids.
Product Li2CO3	Hazardous in case of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (irritant).	Not available.
Co3O4	Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation.	Not available.
MnO2	Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.	Reactive with reducing agents, combustible materials, organic materials, acids.
NiO	Very hazardous in case of inhalation. Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of eye contact (irritant).	Not available.

12. Waste List

The waste generated in this project is mainly the washed water containing inorganic salts, such as LiOH, $NaNO_3$ and $LiNO_3$. After dilution, the waste water can be disposed into sinks. LiOH can be put in the alkaline waste container.

13. Assessment of Significant Risk

There is no significant risk associated with the use of the muffle furnace. However, heat resistant gloves should be worn at all times when taking samples out from muffle furnace, and samples should be taken only when the furnace is at room temperature. The researchers should wear proper personal protective equipments when taking chemicals and performing the stirring experiments.

14. Safety Precautions

1) Personal Protective Equipment

Personal protective equipment including laboratory coats, safety glasses, nitrile gloves and heat resistant kevlar gloves should be worn at all times when performing an experiment.

2) Warning Signs

All sample bottles should have a clear label stating their identity and quantity. The furnace should also have a clear label stating high temperature when running.

3) Safety Training

Safety training courses organized by the Health, Safety & Environment Office (HSEO) at HKUST should be completed before the experiments are carried out. These courses include Chemical Safety I and II for Laboratory Users.

4) Fire Hazards

The raw materials used are not flammable. However, no smoking is allowed in the laboratory in general.

5) Emergency Shut Down Procedures

When using the furnace, if emergency happens, the furnace should be switched off immediately.

15.Actions in Case of Abnormal or Emergency Situations

1) Action in case of service failure

- Switch off the furnace.

2) Action in case of fire

- Activate the fire alarm by pressing the breakglass fire alarm button.
- Report to Security Control Centre by dialling 8999.

- Alert other people.
- If SAFE to do so, try to put out the fire using fire fighting equipment.
- DO NOT take any personal risk. If the fire gets beyond your control, evacuate immediately by following the evacuation procedures.
- Close the door of the room on fire.

3) Other possible abnormal situations

- If chemicals come in contact with eyes, immediately flush the eyes with tap water for at least 15 minutes.
- Consult laboratory officer for further detailed instructions.
- Hazardous Chemical Spill in a Research Laboratory

  Alert co-workers.

  If safe to do so, perform the following. Ask for assistance if necessary.

  i) Confine the spill with appropriate materials.

  ii) Turn off remotely all heat/ignition sources if flammable vapour is involved.

  Press the Emergency Ventilation button (do not activate this button in case of fire).

  Inform the Security Control Centre by dialing 8999 from a safe location.

  Evacuate everyone in the affected area. Leave contaminated clothing and close the door.

  Activate local warning system to prevent others from entering the room.

  If possible, maintain a safe distance from the scene, keep the entrance or access routes in sight and help to prevent entry to the affected room.

4) If conditions allow, remain to assist the emergency response team.