Green Manufacturing and Direct Recycling of Lithium-Ion Batteries

Yingqi Lu

Dissertation Submitted to the Faculty of the Virginia Polytechnic Institute and State University in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in Mechanical Engineering

Zheng Li, Chair
Rui Qiao
Michael W. Ellis
Weinan Leng

August 5th, 2020
Blacksburg, VA

Keywords: Green manufacturing, Energy storage, Battery recycling, Materials processing, Machine learning
Green Manufacturing and Direct Recycling of Lithium-Ion Batteries

Yingqi Lu

ABSTRACT (academic)

According to the International Energy Agency, the global Electric Vehicle (EV) sales are experiencing approximately 24% annual growth and the total market could reach 4 million in 2020 and 21.5 million by 2030 . However, the mass production of lithium-ion batteries (LIBs) to power EV creates concerns over environmental impacts and the long-term sustainability of critical elements for producing the major battery components. Although much investment has been made, it is still imperative to develop an effective LIB production and recycling process.

This dissertation demonstrates a green and sustainable paradigm for LIBs where the batteries are manufactured and direct recycled to form a closed loop. The water-based cathode electrode delivers comparable cycle life and rate performance to the ones from the conventional organic solvent-based process. The direct recycling process has the advantages to regenerate the cathode material from electrode instead of decomposing into elements. Utilization of a water-soluble binder enables separating the cathode compound from spent electrodes using water, which is then successfully regenerated to deliver comparable electrochemical performance to the pristine one.

When scaled up, the degraded cathode material can be directly regenerated by an optimized relithiation thermal synthesis (RTS) method to resynthesize the homogeneous cathode powder of high quality. The key factors and sintering procedures are studied to ensure the
performance of the product. The pilot scale test successfully scales up to Kg-level with recycled output materials delivering good electrochemical performance.

To automate the direct recycling process and improve the efficiency, machine learning and sensors are utilized in a novel battery disassembly platform. It can classify different batteries based on their types and sizes. The processing temperature is instantly monitored using thermal imager, and the prediction model is trained to give the prediction for measures taken by a closed loop control system. Furthermore, the image recognition is employed for quality control after the cutting process and the defect can be mitigated to ensure effective dismantling of End-of-life (EOL) batteries. The integration of machine learning techniques makes the elaborate dismantling process safer and more efficient.
Green Manufacturing and Direct Recycling of Lithium-Ion Batteries

Yingqi Lu

GENERAL AUDIENCE ABSTRACT

According to the International Energy Agency, the global Electric Vehicle (EV) sales are experiencing approximately 24% annual growth and the total market could reach 4 million in 2020 and 21.5 million by 2030. However, the mass production of lithium-ion batteries (LIBs) to power EV creates concerns over environmental impacts and the long-term sustainability of critical elements for producing the major battery components. In this work, a green and sustainable manufacturing and recycling paradigm for LIBs is ushered and scaled up to pilot-scale test. Compared with the electrodes produced by conventional organic solvent-based process, the water-based electrodes can deliver comparable battery performance, meanwhile reduce the cost as well as the pollution to the environment. The spent batteries are successfully regenerated to form the closed loop system with minimal external toxic solvent used. At pilot-scale, Kg-level battery material can be directly regenerated to deliver high-quality cathode powder. It provides the guidance of design parameters for large-scale battery recycling in industry. To automate the direct recycling process and improve the efficiency, machine learning and sensors are utilized in a novel battery disassembly platform. The integration of machine learning techniques makes the elaborate dismantling process safer and more efficient.
Acknowledgments

Looking back at my Ph.D. journey, I feel fortunate to know so many genuine people and to continuously follow my heart to tap my potential in LIB recycling. Blacksburg really treats me well through these four years, and I’m proud to say it gradually becomes a second home to me. All my laughers, struggles, tears, and my endless effort at Virginia Tech will become a lifetime memory.

I can still remember receiving my offer to be admitted to the Ph.D. program at Virginia Tech four years ago. It feels like yesterday. I would like to take this opportunity to thank everybody who has helped me during this incredible journey. I would like to thank my supervisor, Dr. Zheng Li for taking me in as his graduate mentee. During these four years, Dr. Li has helped me not only in my academic career but also in my personal life. His guidance has walked me through all the struggles and happiness to what I’ve become today. Also I would like to thank all my committee members, including Dr. Michael Ellis, Dr. Rui Qiao, and Dr. Weinan Leng. They have also offered me constructive suggestions and comments to my research projects and development directions.

I’m fortunate to have full family support to set aside four years and dive into a research field. My parents not only provide me additional financial support to my current Ph.D. assistantship so that I can have a decent and comfortable life, but also love me throughout my whole life unconditionally. My parents always cheered me up through video calls whenever I felt that I wanted some emotional support. They offered lots of useful pieces of advice from their life experience and asked me to look at the bright side of a problem. As they always tell me, “practice accomplishes everything and details determine success or failure,” I deeply bear in mind to explore the dawn of my research project.

All these four years, I felt loved by all my friends at Virginia Tech. As an old Chinese proverb said, “you can count on your parents when you are at home, but you have to rely on your friends when traveling around the world,” I would first like to thank my group members, Tairan Yang, Liurui Li for putting up with me through the past four years. I cannot ask for a better friendship to go through graduate school than them. In addition, I
want to thank my roommates for their support in my personal life. Also, I would like to thank every friend in Blacksburg. It is their accompaniment that helps me go through this unforgettable period.

I would also very much like to thank all the staff members in our department, especially Gail Coe for her meticulous taking care of our packages, which are the basis of our research. Also I would like to thank Johnny Underwood, who helped a lot in repairing infrastructures in our lab.

I would thank the opportunities of internship given by National Renewable Energy Laboratory (NREL) and Li Industries, Inc. For this dissertation, the chapter 3.1.2 is completed in NREL and the whole chapter 4 is done in Li Industries, Inc. For other chapters, they are completed in Virginia Tech.

All my accomplishment today should be attributed to the love and strong support from my advisor, my family members, my dear friends, and the Virginia Tech community. I hope I make all of you proud during and after these four years.

Thank you, Virginia Tech! Once a Hokie, always a Hokie.
# Contents

## Chapter 1 - Introduction

1.1 Introduction of LIB and the LIB manufacturing  
1.1.1 The development of LIB  
1.1.2 The manufacturing process of LIB  

1.2 Overview of LIB supply chain  
1.2.1 The critical material flow of LIB supply chain  
1.2.2 Challenges in material supply chain for LIB  
1.2.3 The application of Internet of Things (IoT)  

1.3 LIB recycling: state of the art  
1.3.1 Pyrometallurgical process  
1.3.2 Hydrometallurgical process  
1.3.3 Direct recycling process  

1.4 The progress and challenges of LIB direct recycling  
1.4.1 The progress of direct recycling process  
1.4.2 The challenges of direct recycling process  

1.5 Organization of the Dissertation

## Chapter 2 - EOL battery disassembly for the direct recycling

2.1 System architecture  
2.2 Vision-based battery classification  
2.3 The temperature spike control  
2.3.1 Investigation of factors that influence the processing temperature  
2.3.2 Prediction of temperature spike position  
2.3.3 Closed loop control system
2.4 Vision based quality control of cutting cross-section 52
2.5 Conclusion 55

Chapter 3 - Green manufacturing and direct recycling of LIBs 56

3.1 Water-based electrode manufacturing and direct recycling process 56
  3.1.1 Water-based electrode manufacturing 57
  3.1.2 Degradation analysis of the LIB cathode material 58
  3.1.3 The direct recycling of water-based electrode 60

3.2 Experiment results of the water-based electrode and the recycled material 61
  3.2.1 Electrochemical performance of pristine materials 61
  3.2.2 Structure of NCM523 64
  3.2.3 Morphology of NCM523 66
  3.2.4 Electrochemical behavior 67

3.3 Method optimization 68
3.4 Preliminary study of the anode graphite recycling 74
3.5 Conclusions 77

Chapter 4 - Scaling up the direct recycling of cathode material 78

4.1 Lab scale experiment of LiCoO$_2$ direct recycling 78
  4.1.1 Battery deactivation and separation 78
  4.1.2 The mechanical separation of cathode powder from aluminum substrate 79
  4.1.3 The novel relithiation thermal synthesis process 84
  4.1.4 Material characterization and method analysis 85

4.2 Optimization of the direct recycling process for scaling up 86
  4.2.1 Mechanism of Relithiation Thermal Synthesis of the LCO 86
  4.2.2 Factors on Relithiation Thermal Synthesis of the LiCoO$_2$ 87
  4.2.3 Product characterization for lab scale 90
  4.2.4 Liquid leaching for impurity removal 93

4.3 Pilot scale experiments and assessment 98
4.3.1 Product characterization for pilot scale 98
4.3.2 The improved relithiation thermal synthesis process of the LCO in pilot scale 100

4.4 Conclusion 103

Chapter 5 - Summary and Perspective 104
Reference 108
List of Figures

Figure 1. The flow chart of the lab scale pouch cell battery manufacturing. ...................... 4

Figure 2. The flow chart of the manufacturing process and material flow of the 24kWh Li ion battery pack used in commercial EV .............................................................. 7

Figure 3. The energy intensity of cathode active material production and contributions of different components (a). LCO (b). LFP (c). NCA (d). NCM523......................................................... 9

Figure 4. The life cycle energy consumption of components in LIBs for different cathode materials. ............................................................................................................. 10

Figure 5. The end use of lithium and cobalt element as a percentage of consumption. ... 11

Figure 6. Material flow of the LIB manufacturing, consuming and recycling............. 22

Figure 7. The flow chart of pyrometallurgical recycling process for LIBs............. 23

Figure 8. The flow chart of hydrometallurgical recycling process for LIBs............. 24

Figure 9. The flow chart of the direct recycling process of LIBs. ................. 26

Figure 10. The energy consumption comparison between hyrdo, pyro and direct recycling process for LIBs................................................................. 31

Figure 11. The green and sustainable closed loop model for battery manufacturing and direct recycling process................................................................. 35

Figure 12. The process flow chart for the cyber-enabled and machine. ................. 38

Figure 13. (a) The cell cutting station prototype equipped with thermal camera. (b) A cell phone battery with hard aluminum case (c) Thermal camera view of the cell and the cutting blade during the cutting process......................................................... 39

Figure 14. (a) CNN architecture for battery type classification and its confusion matrix (b) Battery type classification confusion matrix (c) Some test images together with their predicted classes and the probabilities of those classes. .............................................. 42
Figure 15. Measuring the size of the battery by computer vision based on the standard reference object.

Figure 16. Examples of the temperature patterns during the cutting process.

Figure 17. (a) The block diagram of LSTM cell. (b) LSTM model structure for temperature spike position prediction.

Figure 18. (a). The comparison of LSTM prediction results with experiment results. (b). The comparison of the spike temperature with and without closed loop control.

Figure 19. (a) The structure of the closed loop model predictive control system (b) The model predictive control feedback system.

Figure 20. (a) The input image of defect cutting (b) CNN architecture adapted for cut quality classification (c) Cutting quality classification confusion matrix.

Figure 21 (a) The cycling data of the discharge capacity for cells at different temperatures. (b) The impedance measured at 3.8V for cells cycled at different temperatures. (c) The voltage profile of the relithiation process for the EOL NCM electrode at C/10 rate.

Figure 22. The process flow chart of the direct recycling process for the water-based cathode electrode.

Figure 23. Electrochemical performance comparison. (a) Rate capability of the baseline NMP/PVDF cells; (b) rate capability of the cells with water-processed electrodes; and (c) comparison of cycle life between NMP/PVDF baseline cells and cells with water-process.

Figure 24. Comparison of XRD patterns for pristine NCM523, Li$_x$Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ in EOL pouch cells, and recycled NCM523.

Figure 25. SEM images of (a,b) EOL NCM523 powder after DI water washing, (c,d) recycled NCM523 powder, and (e,f) pristine NCM523 powder.

Figure 26. Cycling performance of (a) Li/commercial LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ coin cell and (b) Li/recycled LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ coin cell at C/5. The voltage profiles of first two
cycles. (c) Li/commercial LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 coin cell and (d) Li/recycled LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 coin cell at C/5.

Figure 27. The electrochemical result of recycled NCM523 with improve washing process.

Figure 28. (a), (b) and (c) SEM images of the EOL NCM523 powder after 400C heating in air for 1 hour. (d) EDS mapping of element distribution.

Figure 29. (a), (b) and (c) SEM images of the EOL NCM523 powder after water&ethanol wash and vacuum dry. (d) EDS mapping of element distribution.

Figure 30. The ThermalGravimetric Analysis of the aqueous EOL NCM523 through 400C heating and water wash under oxygen or nitrogen atmosphere.

Figure 31. SEM images of the anode material powder from spent LIBs.

Figure 32. (a) The solution turned brown after the oxidation process. (b) The solvent turned black during the reduction process.

Figure 33. The XRD pattern of the spent graphite (SG), graphite oxide (GO) and the reduced graphene oxide (rGO).

Figure 34. The TEM images of the synthesized graphene material (rGO).

Figure 35. (a) The viable speed mixer to separate the cathode powder from aluminum sheet using NMP solvent. (b) The EOL cathode sheet being shredded into 1cm square flakes.

Figure 36. The cathode electrode flakes after NMP washing under different conditions. The separation efficiency increases from the left to right.

Figure 37. Process flow chart for the close-loop recycling process by RTS method.

Figure 38. The charge/discharge voltage profiles of sintered recycled cathode materials with 0%, 2% and 5% Li excess and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 0%, 2% and 5% Li excess and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.
Figure 39. The charge/discharge voltage profiles of sintered recycled cathode materials with 750C, 850C and 900C sintering and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 750C, 850C and 900C sintering and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.

Figure 40. The XRD patterns of EOL cathode material, commercial LCO from Sigma and the recycled LCO (a) with different Li addition and sintering temperatures in the lab scale, (b) and (c) the enlarged view of Figure (a) for lab scale experiment. (d) The 0% excess Li addition sintered LCO in pilot experiment batch, (e) and (f) the enlarged view of Figure (c).

Figure 41. The SEM images of (a) EOL electrode materials and sintered recycled cathode materials with (b) 900C 0% Li excess sintered, (c) 900C 2% Li excess sintered, (d) 900C 5% Li excess sintered, (e) 750C 2% Li excess sintered, (f) 850C 2% Li excess sintered LCO and (g) Commercial sigma LCO.

Figure 42. The XRD patterns of EOL cathode materials, sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma.

Figure 43. The charge/discharge voltage profiles of sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.

Figure 44. The SEM images of (a) EOL cathode materials, (b) 500g large batch sintered LCO under 850C with 0% of excessive lithium, (c) 500g large batch, 500°C heated & mixed and 850°C sintered LCO with 0% Li excess. (d) commercial sigma LCO.

Figure 45. The charge/discharge voltage profiles of the 850°C 2% lithium excess sintered recycled cathode materials in small batch (black line) and pilot large batch (red line) sintering and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V.
Figure 46. The charge/discharge voltage profiles of sintered recycled cathode materials with 0% Li excess addition, 0% Li excess with double mixing and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials above at 1C rate between (c) 3-4.2V and (d) 3-4.45V.

Figure 47. The green and circular model of the future city.
List of Table

Table 1. Summary of 60 kWh NCM523/Graphite battery materials .......................... 13

Table 2. Comparison of the Hydro, Pyro and direct recycling technologies of LIBs ...... 26

Table 3. The key temperature points of the electrolyte components. ........................... 45

Table 4. The factors for the cutting temperature. ................................................................. 45

Table 5. The Design of Experiment complete matrix, interactions and effects calculated. .......................................................................................................................... 46

Table 6. The analysis of variance (ANOVA) for maximum temperature......................... 46

Table 7 Average Prediction Error ........................................................................................... 50

Table 8. The NCM electrodes information with different solvent processing and composition ....................................................................................................................... 58

Table 9. The ICP-MS results for the pristine and EOL NCM523. ....................................... 64

Table 10. ICP-MS data for different sintering parameters (lithium excess). ................. 73

Table 11. The cathode powder separation efficiency comparison for different height of stirrer .................................................................................................................................. 81

Table 12. The cathode powder separation efficiency comparison for different size of the cathode sheets ........................................................................................................ 81

Table 13. The cathode powder separation efficiency comparison for different stirring speed.......................................................................................................................... 82

Table 14. The cathode powder separation efficiency comparison for different stirring time duration .................................................................................................................. 83

Table 15. The element content for the LCO powder before and after ammonia leaching m............................................................................................................................ 97
Table 16. The element ratio and lattice parameters of the regenerated sample under different conditions. ................................................................. 100
Chapter 1 - Introduction

1.1 Introduction of LIB and the LIB manufacturing

1.1.1 The development of LIB

During the oil crisis in the 1970s, the breakthrough of the LIB happened as Dr. M. Stanley Whittingham worked on researching conductors and found the energy-rich material, which invented the novel cathode for LIB. The titanium disulphide has spaces for housing lithium ions and allows their intercalation and de-intercalation at a molecular perspective. The anode of LIB was partially made from lithium metal, which can supply enough lithium ions for circulation between cathode and anode. The battery with this electrode combination can deliver great potential but increases the risk of explosion due to the great reactivity of lithium metal. To further increase the cell potential for achieving high energy or power density, researchers have tried to improve the battery components. John Goodenough demonstrated that transition metal oxide, like LiCoO$_2$ (LCO) electrochemically reached as much as four volts in 1980. With Goodenough's invention of LCO as the cathode material, Akira Yoshino invented the rechargeable lithium battery five years later using petroleum coke as the anode instead of lithium metal. Then the lightweight and powerful batteries were presented in human history and they have revolutionized our lives to help build the wireless, fossil-fuel free society. In 2019, LIBs accounted for the highest market share among energy storage devices. In the same year, the Nobel Prize in Chemistry awarded to M. Stanley Whittingham, John B. Goodenough and Akira Yoshino, for their pioneering contribution for the development of LIBs.

With high energy density and powerful dynamics, LIB is continuously expanding its market share for the growing demand of electric EVs and ingratiating the expectation by society to decarbonize the transportation fleet. The world will need to produce more than 700GWh of batteries, which would be more than six times what were produced in 2016, if just a 15% penetration rate of electric vehicles in proportion to all new vehicle sales by 2026. However, the share of EVs in the global auto market is growing at a slower rate than people’s expectation. One of the key reasons is that the unbalanced supply and demand relationship fluctuates the prices in supply chain of raw materials, which limits the
scaling up \textsuperscript{14}. The booming market of LIBs leads to a three-fold increase in the price of lithium and a four-fold increase in that of cobalt between 2016 and 2018 \textsuperscript{15}. Therefore, the critical components in the supply chain of the battery manufacturing is an important strategic resource, which is the cornerstone of large-scale promotion of LIBs. The critical and strategic metal resources such as cobalt, lithium, will be more scarce if they are mined only in a few countries whose trade policies could limit their availability and influence prices \textsuperscript{16}. In addition, environmental impact during the manufacturing process also hinders the development of LIBs. It is believed that the greenhouse gas (GHG) emissions for the manufacturing of a 24 kWh LIB pack applied on BEV are 3.4 metric tonnes of CO\textsubscript{2}-eq (11 kg CO\textsubscript{2}-eq per kg of battery or 140 kg CO\textsubscript{2}-eq per kWh). 45\% of the GHG emissions of the cell manufacturing process are relevant to the use of utilities \textsuperscript{17}. The battery manufacturing process and the cell components from upstream dominate the criteria pollutant emissions including volatile organic compounds (VOC), carbon monoxide (CO), sulfur oxides (SO\textsubscript{x}) and nitrogen oxides (NO\textsubscript{x}) \textsuperscript{17-19}. Hence, the current manufacturing process needs to be further improved to become more eco-friendly.

1.1.2 The manufacturing process of LIB

\textit{Battery assembly process}

A LIB is made up of the classical battery structure components: cathode, separator, anode, electrolyte, and current collectors. While the battery is in discharge, the anode releases Li-ions and the Li-ions would go across the separator to the cathode. When charging, the opposite happens: Li-ions will transit from the cathode part to the anode. The Li-ions can migrate between cathode and anode sides to make the battery cycling practical. In the raw material perspective, the processing technology of the electrode manufacturing should be as follows: active material, binder and conductive additive, are homogeneously mixed in a solvent under the water free atmosphere. Currently the most widely used solvent in commercial battery manufacturing is N-methyl-2-pyrrolidone (NMP) combined with binder of poly (vinylidene fluoride) (PVDF) \textsuperscript{4,20}. The uniformed and smooth suspension should be perfectly coated on the metal foils like the mirror. Aluminum foil is normally used for cathode material while the copper is used for the counter one. To form the electrode in high energy density with superior electrochemical performance, several factors
or parameters will be taken into consideration: the solid/liquid ratio of the suspension, stirring speed or duration, drying temperature, coating thickness and so on. After the drying and vacuum treating, the coating sheet is cut into designed shape for battery assembly. The whole cell assembly contains the electrodes winding with separator, electrolyte fulfilling, sealing, cell formation and examination\textsuperscript{21-23}.

Figure 1 describes the flow chart of the pouch cell battery manufacturing line in our lab. The cathode powder material is mixed with conductive additive and the binder PVDF in the proper ratio. The homogeneous slurry is made with solvent NMP using the vacuum mixing machine. The influence of moisture in the air is excluded during the slurry mixing process. The time duration and the stirring speed should be controlled to ensure that the slurry is in a proper thickness. Then the slurry is coated on the aluminum sheet using the doctor blade. For a consistent thickness of the electrode slice, the scraping speed or force needs to be stable. After air drying in the convection oven, the calendaring process would be conducted on the electrode sheet to flatten the surface and enhance the energy density as well as its physical properties\textsuperscript{24}. Using the die cutting machine, the whole electrode sheets are sheared into proper shapes, which should be compatible with the size of the pouch cases. In the structure of the stacking cell, the cathode and anode sheets are stacked alternatively with the separator separated. Nickel tabs are welded to each electrode current collector by the ultrasonic metal welder. Normally the new made pouch parts are vacuum dried to further exclude the remaining moisture before adding electrolyte. With the designed mold, pouch cell cases are laminated to accommodate the core material. The cells are sealed by the hot sealing machine keeping one side open for electrolyte addition in the glovebox. Then, the vacuum sealing is also conducted in the argon filled glovebox followed by cell formation process employing the battery tester or analyzer.
Cell is the most basic unit of the battery which has the voltage of 3.7V for LCO cell. The connected cells in series or in parallel can form the module of battery, which can provide high voltage and capacity. The jointing of multiple cells needs the battery management system (BMS) to measure the voltage of the module. When the modules are connected in a stackable frame, it is the pack. One or multiple packs can be connected to form a system and a cooling system will be accoupled for avoiding the thermal-runaway problem. Thermal management is one of the biggest problems that impede the development of a LIB system. Although the energy density of the battery pack has been remarkably improved in contrast with the lead acid battery, the compact design of cells would accumulate large amount of heat that deteriorate the cycling performance of the battery system. It is believed that, the elevated temperature condition would facilitate the dynamics of the battery cycling, but the surface reaction between electrolyte and electrode would also be aggravated, causing irreversible lithium ion loss and even safety problems. Similarly, the low temperature condition also deteriorates the cycling performance of the battery. According to the literature, the reason is that the degradation in both bulk and surface of graphite anode. The loss of lithium ions which are plated on the surface of anode triggers the capacity decay. In some cold regions the battery pack must be heated to ensure the normal function. Therefore, a liquid circulation for heat exchanging is required to keep the whole battery system in the appropriate temperature section.
The battery manufacturing process can be regarded as the linear process with parts added in sequential order. Figure 2 below represents the flow chart of the battery pack manufacturing process and the material flow for the 24kWh EV battery pack. The material flow and corresponding energy consumption were analyzed for better understanding the whole battery production. Yuan et al., 4 analyzed the material flow and the energy consumption during the manufacturing process of the LIB pack employing LiMn$_2$O$_4$ (LMO) as the cathode accompanied with graphite anode. This 24 kWh Li-ion battery pack was used in commercial EVs like Nissan Leaf. Based on the Battery performance and cost software (BatPac) 28, the detailed components and their composition weights were presented for research analysis as well as calculation. This 24kWh pack contained 192 single cells with 3.85V working voltage that used (LMO) as cathode material and graphite for the counter one. For the cathode electrode, the ratio of active materials, PVDF binder and the conductive carbon in mass was 89:5:6 while the anode was made of graphite and aqueous binder carboxymethyl cellulose (CMC) at the mass ratio of 95:5. The total N/P ratio was 1.2. As for the electrolyte, the lithiumfluorophosphate (LiFP$_6$) was used as the salt which was dissolved in the combination of ethylene carbonate (EC) and dimethyl carbonate (DMC). The mass of the separator and pouch case was 11g and 39.5g respectively. Current collectors for cathode and anode sheet were 399g. The total mass was 868g. The pack contained 16 modules with insulating polymer spacers inserted and the whole pack was situated in the aluminum tray. For each module, there were 12 cells arranged in series. The BMS and cooling system were also part of the pack whose weight was linearly correlated with the size of the whole pack. The battery pack assembling accessories accounted for around 18% mass fraction of the total battery pack. With all these parts assembled and tested, the battery pack was ready for sale.

For the production process, details of the parameters were also summarized in the literature. The active materials LMO and graphite were separately mixed with binder and additives in the NMP solvent. The graphite slurry was coated on 12 mm-thick copper foil while LMO was coated on 15 mm-thick aluminum foil. The slurry was coated on the aluminum sheet followed by the drying process under 150 °C overnight for evaporating and recycling the NMP. The dried electrode sheet went through the calendaring process and the density of electrode will reach 10 mg/cm$^2$. The prepared electrode sheets would be punched into the
desired shape using the designed mould, then the cathode and anode sheet can be paired and stacked into LIB pouch cells. Multiple pairs of the electrodes were stacked together with and separated by the separator. The electrolyte was added followed by the cell formation process and the pouch cases were then sealed to form the single pouch cell. The quality test would be conducted to evaluate the pouch cells before the pack assembly.

Mass production of LIBs may result in more serious environmental concerns during battery manufacturing and disposal \(^{29,30}\). In fact, 4.1 million kg per year of NMP is used for depositing the cathode layers for a battery manufacturing plant producing 100,000 packs per year of 60 kW, 10 kWh plug-in hybrid vehicle (PHEV) batteries \(^{31}\). NMP is expensive and reprotoxic and has been added to the restricted substances list by the European Commission in 2018. In addition, energy consumed for the NMP solvent evaporation and recovery during the electrode drying process accounts for more than 47% of the energy consumption in the whole LIB manufacturing. It can reduce 25% if the NMP is replaced with water \(^{32}\). The dry room facilities used for the temperature and moisture control during the slurry preparation and coating process occupy another 29% of the total energy \(^{4}\). Therefore, it is favorable to substitute the NMP with harmless solvent during the electrode manufacturing processes for reducing the energy consumption and processing cost \(^{33}\).
Figure 2. The flow chart of the manufacturing process and material flow of the 24kWh Li ion battery pack used in commercial EV.\textsuperscript{2-4}
The energy consumption of the material production

There are various types of cathode material that are widely used. The raw materials for cathode are synthesized through reactions between lithium source and the metal compounds. For cathode material like LCO, it can be made by high temperature calcining cobalt oxide (Co₃O₄) with lithium carbonate under precisely regulated conditions. The nickel rich cathode involves multiple metal elements like nickel, cobalt and manganese for partially replacing cobalt to reduce the cost. The precursor metal hydroxide with required element ratio, which has the similar morphology with the final product, can be synthesized by coprecipitation, sol-gel and spray-drying method. Finally, the cathode powder is synthesized by sintering lithium salt with the cathode precursor. Several factors would influence the characteristics of cathode material including the processing temperature, synthesis time, atmosphere and the particle size as well as pH of the precursors.

The energy consumption for the LIB manufacturing has also been calculated. The software, Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET) model is used to model and calculate the unit energy consumption of the raw material production process. Together with Batpac, the life cycle analysis (LCA) is conducted to calculate the energy consumption of the battery pack manufacturing. The processing energy also contains the energy consumed from ingredient production, processing utilities as well as the transportation cost. It is calculated that the total energy consumption for the cathode material LMO is more than 30 MJ/kg. In addition, the energy consumption for other cathode material production using virgin material has also been calculated. The purchased energy for virgin LCO material is 169 MJ/kg while it for LiFePO₄ (LFP), LiNi₀.₅Co₀.₂Mn₀.₃O₂ (NCM523) and LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (NCA) are 22 MJ/kg, 140 MJ/kg and 162 MJ/kg respectively, as shown in the Figure 3 below. The lithium resource would be mainly from the Li₂CO₃ except for the three-element compounds which use the LiOH. The Li₂CO₃ is produced from Chile where the energy intensity including transportation is 40% less than it from US. Figure 3 (c) and (d) illustrate the energy intensity of NCM and NCA chemistry. The production of three-element material needs the formation of cathode precursor before the final product. Normally, the preparation of cathode precursor derives from metal sulfate with ammonia and NaOH added. The reaction between LiOH and precursor would generate the cathode material. The LCO has the highest energy intensity
among all these materials because the high value of energy harvesting during cobalt oxide obtainment. Meanwhile LCO is also the most expensive cathode material compared with others. That is the reason why most of the recycling technology aims at cobalt recovery.

Figure 3. The energy intensity of cathode active material production and contributions of different components (a) LCO (b) LFP (c) NCA (d) NCM523.

The energy consumption and the contributions of different raw materials are shown in the Figure 4 which includes four types of LIBs with different cathode material. Although the mass and energy consumption of each component vary according to different cathodes, the relative contributions of each battery are in common. The cathode material accounts for 36~48% of life cycle energy consumption of the total battery pack. In contrast, aluminum and copper sheet which are served as current collector contribute 18~ 29% of energy consumption. LFP is the exception due to its low purchased energy. Battery constitution
including the binder, binder solvent, electrolyte and separator contribute minimally to life cycle energy consumption. Although the diversity of battery manufacture gives us many choices in LCA such as BMS and binder use, the model is simplified by some normal assumptions. For example, the BMS is supposed to account for 2.5% of total mass of battery pack. The binder for cathode and anode in different active material should be PVDF.

Figure 4. The life cycle energy consumption of components in LIBs for different cathode materials.¹⁻³
1.2 Overview of LIB supply chain

1.2.1 The critical material flow of LIB supply chain

![Figure 5. The end use of lithium and cobalt element as a percentage of consumption.](image)

Cobalt has a wide application in the development of society, such as the superalloys and hard materials. In recent years, the booming of battery industry has gained growing share of the cobalt use, especially in the cathode materials of LIB for EVs and consumer electronics \(^47\). From Figure 5, the LIBs application of Co accounts for nearly 60% of global Co demand in 2019. The price of Cobalt has experienced a four-fold increase from 2016 to 2018, which directly stimulated the vigilance of the whole industrial supply chain including the battery manufacturer and automakers \(^15\). Although nickel rich and cobalt free cathode materials like NCM333, NCA and LFP have been investigated and applied in EVs to alleviate some of the supply issues, cobalt is still the indispensable element in existing LIBs as its largest demand because the cobalt should be contained more or less \(^48\). The future direction of cathode components is aiming at lowering the cobalt content which can be replaced by other cheaper transition metals such as manganese or nickel \(^49\).

Same as cobalt, lithium is also widely used as the industrial ingredient. The end use of lubricating greases, glasses and ceramics has obtained the largest part of share in end use
With the expansion of the battery market, a structural shift happens to the end use of lithium resource. As Figure 5 shows, the percentage of lithium consumption and end use has greatly inclined to being applied to rechargeable batteries. It can be seen that its market share of material end use has significantly increased from 29% in 2013 to 65% in 2019. Lithium carbonate is the normal form existed for lithium use, which is the main lithium source for synthesizing the battery materials, and has a steady price at around $4000 to $5000 per ton before 2016, but it have gone through the sharply rise then to a price of around $15,000 at 2017 and $17,000 per ton in 2018. From the USGS Mineral Commodity Summaries, the worldwide reserves of lithium are 17 million tons.

Nickel and manganese are being used in manufacturing cathode active material of NCM LIB to replace part of the cobalt and reduce its cost. Nickel can provide high energy and power density while it is cheaper than cobalt. But the Ni$^{2+}$ in cathode material may cause the cation mixing with Li-ions due to the similar radius. Manganese is utilized in the cathode material to enhance the thermal stability and has even lower price than nickel. Aluminum is served as current collector in LIBs for cathode material. It has the high electrical conductivity, good ductility and is electrochemically stable under the working range of voltage.

Graphite is widely used in the anode of LIBs and it can be found naturally in diversified locations. Meanwhile it can be artificially synthesized in the form of coke (from coal) and charcoal (from wood). The application of graphite in battery just accounts for a small fraction of the graphite production. However, the battery production requires the flake graphite of high purity, which would be more constrained. It is believed that flake graphite only accounts for 30% of the natural graphite produced in China in 2017. The graphite production in North America only account for 3% of the global supply in 2017. Although silicon has been investigated to replace the graphite for the anode material since it owns the extremely high specific capacity, the large expansion of volume during the cycling impedes its replacement of graphite. The eclectic method is to combine graphite and silicon in a seemly ratio but entirely eliminating graphite is nearly impossible in the short term.
Table 1. Summary of 60 kWh NCM523/Graphite battery materials.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Element</th>
<th>Weight percent (kg/kWh)</th>
<th>Cost percent ($/kWh)</th>
<th>Mine production and supply information worldwide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cathode</strong></td>
<td>Cobalt</td>
<td>0.22</td>
<td></td>
<td>14800 tons: 70% Congo (Kinshasa)</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>0.55</td>
<td></td>
<td>2400000 tons: 25% Indonesia, 15% Philippines</td>
</tr>
<tr>
<td></td>
<td>Manganese</td>
<td>0.31</td>
<td>40.77</td>
<td>18900 tons: 31% South Africa, 18% Australia</td>
</tr>
<tr>
<td></td>
<td>Lithium</td>
<td>0.13</td>
<td></td>
<td>95000 tons: 62% Australia, 18% Chile</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>0.22</td>
<td>0.03</td>
<td>63600 tons: 56% China</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td>Copper</td>
<td>0.46</td>
<td>0.08</td>
<td>20400 tons: 29% Chile, 12% Peru</td>
</tr>
<tr>
<td></td>
<td>Graphite</td>
<td>1.1</td>
<td>20.43</td>
<td>1120000 tons: 62% China</td>
</tr>
</tbody>
</table>

1.2.2 Challenges in material supply chain for LIB

Table 1 introduces the elements used in the battery manufacturing and their mining production geological locations. It is known that over 70% of global cobalt production is from the onefold area, the Democratic Republic of the Congo (DRC), which has a long tortuous and complicated history with civil war, internal conflict and infrastructure issues. The heavy geographical concentration of mining and refining, sociopolitical instability and unrest significantly destabilize the cobalt supply. Sun et al., has assessed the material supply risk of the LIB materials, which means the possibility of material supply interruption. The Herfindahl-Hirschman Index (HHI), which represents the market concentration, has been incorporated with the Worldwide Governance Indicator (WGI) to express the risk for different countries administration levels. Then the index HHI-WGI is utilized to represent the supply stability and the cobalt supply is proved to be high risk as well as vulnerability. What makes the matter worse is that cobalt is primarily manufactured from the by-product or co-product of other metals. It is known that around 38% of cobalt was the by-product of nickel production, and 60% was mined from the by-product of copper. Also the production and price of Cobalt would fluctuate with the market of the primary production of nickel and copper.
The challenges of lithium production lie in whether supply can meet the demand rather than if there is enough material \(^{61}\). Lithium has diversity of extraction technologies. Main mining countries like Australia and Chile are obtaining lithium from pegmatite, which also leads to the extraction of other valuable elements like Stannum \(^{62}\). Argentina and the U.S also recover the lithium via evaporation from the brine of salt lakes, in which the co-product potash can be extracted and provides some offsetting revenue \(^{16}\). However, this process requires the drilling and breaking the shell of salt brine which needs to be elevated into evaporation ponds for experiencing 12 to 24-month solar evaporation \(^{63}\). Eventually only 6% of Li content can be extracted to produce the pure Li_2CO_3 for the LIBs \(^{49}\). Meanwhile the process is also extremely water consuming, nearly 500000 gal water per ton of lithium production is needed \(^{64}\), which may destroy the rockbed and bring safety concerns about the local water use. High time consumption for production period, low recovery rate as well as the water intensity of lithium product make the brine evaporation method less preferable, while the hard rock mining of lithium has obtained more market share as the demand of lithium was continuously increasing, although it is much more costly \(^{16}\). The worldwide lithium production increased from 35000 ton in 2016 to 95000 ton in 2018 while Australia, who extracted the lithium by hard mining operation, had a proportion growth from 40% to 62% \(^{65}\). Therefore, to satisfy the explosive demand of lithium due to the EV production, most of the lithium production growth came from the hard rock mining and the cost is bound to rise compared with that from brine evaporation. Furthermore, the geographical concentration of lithium mining is becoming more serious. Therefore, improving the extraction technology of lithium through an efficient and cost saving way is necessary.

1.2.3 The application of Internet of Things (IoT)

*Internet of things*

Internet of Things (IoT), one of the latest information technology (IT), is a new IT revolution supplying a fundamental shift across various fields. The ‘Internet-of-Things’ is served as the umbrella keyword to extend the Web and Internet into the physical world through the devices, sensors with functions of sensing data collection and data processing. To build a more powerful manufacturing plant with strong structural flexibility and
resilience facing marketing risk, IoT makes for mitigating the time delay between the data capture and the action. By linking the digital signal and physical entities, the rapid spreading of real-time interaction skills are necessary to enhance the industrial applications and services for the customers. There are four essential layers in the classical IoT network. First, the sensing layer, which can integrate the ‘things’ or existing hardware like Ratio-frequency identification (RFID) tags, actuators, sensors. The networking layer is responsible for the information transferring across the network. Meanwhile the service layer is to combine the application with service using the middleware. The interface layer is facing the customer and achieve the communication between users and the system.

There are five critical IoT technologies for the data connection and communications. RFID is for verification function, processing trace as well as message passing which is classified into five main classes. People can only write and read information from the passive class 1 tags. Class 2 tags are added with security related functionalities and the class 3 is semi-passive, which can extract the information by the integrated battery and sensors. For the class 4 tags, they can achieve the active communication between different tags while the highest class 5 tags are able to interfere with the back-end networks and control other tags comprehensively. To monitor the whole process, several sensor devices are used to detect the local information, such as the moisture, distance, and speed. This is the Wireless sensor networks, or WSN. It is known that the sensors are widely used in the different fields. For example, the physical scenario in temperature, viscosity, moisture, acceleration and various of forces. In addition, the sensors can be used in industrial processing to control and monitor the parameters like liquid flow, pressure, movement and noise. It can also be integrated into the network to upload the data to receivers like RFID tags. To realize the real-time communication for different things, the middleware can be used to explore the method communicating the sensor devices with tags or actuators. The data detected from the sensors is transferred for being used in the next step. As for the cloud computing, it includes several resources in one sharing platform, which allows all the identified people to get access to it based on their requirements. It is very significant to process the real-time data from the IoT system in high volume and then the decision can be made efficiently for purposing. That is the central theme in the IoT application to solve problems. Furthermore, the IoT systems can have the human and device connected. This interaction
can promote the interflow of the information. The interface between the user and the devices makes it easy to infuse the people’s minds into the machine. In summary, the IoT technologies function cooperatively to realize the accurate data collection, fast data transportation, effective analysis to locate the defects and decision making to improve the whole system.

IoT upgrades the supply chain to a higher level: The ‘things’ are interconnected while the human is involved to achieve the autonomous and smart coordination. To finish the customer order, the supply chain is to transfer the information through the processes and entities and the goal is to deliver the product that can satisfy the customer request. It is also suggested to reduce the cost and time consumption while the product should be kept in high quality. For the supply chain system, it is the linear relationship between the raw material suppliers and the customer. The factories and retailers are located between them to jointly process the plan making, source exploration, production, product delivery and customer feedback or return. Although these commercial behaviors have been around for many years, the systematic and intelligent management is lacking for promoting the industrial ecology. With IoT embedded, the physical objects in the supply chain are effectively connected for data connection and transmission. The industrial company can monitor the manufacturing process and the local things on the manufacture line would sense the characterized data for improving the quality of production. The data can also be shared between the companies if permitted. Therefore, this pattern would vastly enhance the visibility and the data sharing of the manufacturing. When the underlying defect is detected, the IoT system would present its advancement in the reaction agility to make the decision for improving it. The information sharing can promote the real-time control, timely planning and benefit maximization of the supply chain process. The researches on supply chain management aim to promote the function efficiency in the product tracking, process optimization, inventory accuracy and cost-saving.

The application of Cyber-Physical system (CPS) in the supply chain has been investigated by several searchers and it can combine the cloud-based manufacturing (CM) with analogue hardware or digital hardware. The purpose is to make the system fit for scaling up and agile for different applications. Meanwhile, the ubiquitous access,
resource pooling and virtualization are also important for developing the architecture for supply chain flow. The supply chain not only contains the material flow but also the information and value flow. It is significant to cut the expenses and effectively manage the growth of node identity for maximizing the adoption by users and infrastructure 70.

*Challenges of IoT application in supply chain management*

The function of IoT device applications is to make people’s life easier and simpler. The devices can be remotely accessed and controlled and the problems are expected be diagnosed and mitigated remotely. However, this advanced technology proposes higher requests when being applied. Several challenges of the IoT application are listed below:

1) Cybersecurity: It is believed that the security issue is the biggest barrier for the application of IoT. The underlying threats are further amplified by the new conditions when applied to the Website service. The IoT system might be attracted by manufacturers because that the hardwares are distributed separately. IoT devices are then typically interconnected with other devices making it complex to manage device-to-device interactions. This structure also can protect them from vicious data manipulation. Furthermore, the computing power of the system is limited. IoT devices would drain the computing power and the security frameworks would be exponentially exposed to the web attacks. The complexity of the IoT system in the internet would aggravate this issue because the modern security threats may attack the system and spread through the internet to cause the massive loss.

2) Privacy: The IoT devices can collect, transmit and process the data generated from IoT devices. The volumes of the data also include the private information of the users. For example, the living address of the users or owners and their personal habits may be contained. It may not be an intentional data collection with private filch purpose. But these data can expose the private information and can be accessed by the third parties without user consent. The data on the IoT cloud which is shared with others lacks the safeguard procedures and even expropriating users of the right to manage their data 71. Although the policies have been issued to protect the users privacy in IoT system, the enforcement and punishment of the rules are still the barrier to ensure privacy security.
3) Data Management: The amount of data produced by the IoT devices is very massive. Managing data would be difficult for processing, refining, transmission, storage and communication. To handle the data efficiently, it is necessary to build the scalable infrastructures for dealing with the enormous volume of data in high speed increasing.  

4) Lack of Standardization: As a new-born technology which is still under development, engineers around the world are exploring the possibility applying the IoT in different fields under different regulations. The application of IoT would be influenced by local factors such as the customer habits, government policies and even the climate environment. Several multinational governance organizations or alliances, such as OneM2M, IETF, IEEE, ETSI, W3C, are supporting the open solutions for the standards. Currently they are under discussion to reach the agreement which cover different areas of the IoT from the communication to architectures. The system function, product model and the services are required to be standardized. However, standardization means most of the existing strategies will be discarded and it is difficult to calculate the profit of the final norm. With the continuous proliferation of standards, the IoT adoption and application would be further impeded by the fragmentation of standards. This is a real barrier that hinders the interaction or integration of multiple application domains.  

5) Lack of Craftsmanship: The professional skills are needed to design and execute the IoT infrastructures due to the highly complexity and advancement of this emerging technology. Obtaining or building these skills is very difficult by organizations. In these circumstances, it is necessary to supply the proper skills for users or organizations to ensure the efficient application of IoT. These technologies in IoT ecosystem makes for capturing value by connecting the governments, consumers and consumers.  

Therefore, information security and the privacy protection are the core of future IoT technologies. Increasing the transparency is essential to guarantee the trust and security of the IoT system. For the supply chain in battery manufacturing process, the main conflict lies on the cost-saving and the quality control. In contrast with food supply such as cold-chain transportation, which requires the sensor to record the temperature during the whole transportation process and ensure the quality of the product, the battery manufacturing
also involves complicated procedures that are strictly requiring conditions, such as atmosphere, temperature and viscosity. Employing the sensors or devices to monitor the parameters not only can help improve the quality of product but also track the records for fault diagnosis. The integration of IoT with the supply chain of battery manufacturing is a promising research for the near future.

Celia et al., 76 presented a multi-stage framework for collection, assessment, dismantling, recycling and shipment of the EV batteries. The IoT ecosystem was integrated into this framework with suitable communication standards bringing intelligence to the ‘Things’ like containers, pallets and trucks which can transmit data collected by embedded sensors. The Things-levels of hierarchy was established from truck, pallet, container, to battery module levels. Meanwhile the RFID tags were placed on the cover of the battery to trace the information such as the manufacturing date or material composition. The sensors embedded on the pallets can provide the real-time inventory data and improve the transparency and visibility of the system.

The recycling process is becoming a newborn return procedure in supply chain system. Normally the return happens when the product exists the defects which ascribes to the responsibility of manufacturers. When the recycling grows into popularity the return procedure will be inevitable if the products reached their EOL. Then the manufacturer will have two resources of supply chain, one of whom is the conventional supply chain and the other one is the material recycler 77. A closed-loop supply chain and the reverse supply chain model have been built to reduce the excessive dependence on new materials. Both the newmade and remanufactured products would together serve for the input of the supply chain. The lifecycle information of the products are utilized by the proposed model through the IoT technology 78. The direct recycling serves for reusing the battery grade material for supplying the battery manufacturers. It is suggested that the information-sharing platform should be built for electronic waste collection and recycling through the electronic product code 79.
1.3 LIB recycling: state of the art

The booming LIB market not only continuously consumes scarce expensive metals but also brings a rapid growth in battery waste from EOL LIB disposal. Improper disposal of EOL LIBs can generate enormous amounts of waste and poses a significant environment hazard as some components are toxic and carcinogen nature. Thus, economic viability and environmental sustainability should be taken into consideration while the LIB is being developed. It is expected that 41 million EVs will be on the roads worldwide by 2040, which can displace 13 million barrels of crude oil per day. While the use of EVs could relieve the scenario that transportation heavily relies on the fossil-based fuels and lead to the reduction of GHG emissions, the related concern will follow: Where will such a large quantity of batteries go when they retire from EVs? It is well known that the waste LIBs contain both pollutants and valuable metal resources. The growing market of the EVs, accompanied by plentiful batteries in service, will result in the resource shortage of the raw materials in nature including lithium, cobalt and then price swing in the upstream supply chain. The cobalt resource is even considered strategically important as it is widely used in the military. Therefore, the LIBs need a circular economy modeled after that of lead-acid batteries, more than 99% of which are recycled. There are four major objectives for LIBs recycling: Making full use of the valuable elements to create the new profit growth, retaining key resources with the long-term supply chain to avoid the shortage, reutilizing the potential hazards for eradicating environment pollution and capturing the critical materials for national security. However, the current situation is that only less than five percent of the LIBs are recycled. Hence, the effective recycling technology deserves an extensive concern and deep development, which should be faster than the battery retirement.

Currently, the hydrometallurgical and pyrometallurgical methods are the main industrial methods of recycling LIBs. These two approaches are regarded as indirect recycling where the battery components are degraded into elemental constituents thus losing their high value position for resale. To say nothing of the energy consumption or economic cost during the process, the secondary pollution generated from them has already gone against the original intention of the recycling. Promising direct recycling technology is on the
pipeline. It is the recovery, regeneration and reuse of the battery cathode materials directly without breaking down the chemical structure. It is the electrode-to-electrode recycling process which can yield the battery grade materials. Recycling the EOL LIBs is also a potential strategy for narrowing the gap between supply and demand\textsuperscript{16,91,92}. The growing demand of relevant critical materials and the increasing pressure on the environmental impact of solid waste disposal promote more research on the recycling of LIBs. The service life of the EV battery is about 8-10 years\textsuperscript{93}. As it is known that the market of electric vehicles started to boom in 2012, we can expect that the battery packs will reach their EOL in the near future\textsuperscript{47}. The huge inventory of the spent batteries and potential continuous accumulation in the near future will provide sufficient input for the recycling plant, and ideally the metal material extracted from spent batteries will satisfy the demand for batteries production, with the continuously optimization of the recycling technologies. The balanced supply circular chain will form where most of the batteries are manufactured with the recycled material from retired batteries and the metal materials can be repeatedly reused and serve for human development in the long run. Compared with mining products, those cathode material retired from EVs still holds as high as 80% capacity and keeps the crystallized layered structure\textsuperscript{94}. The lithium metal oxide electrode as well as the anode graphite flakes, are in high grade, which are very suitable to be reutilized for battery manufacturing.
1.3.1 Pyrometallurgical process

Nowadays, the recycling routes of LIBs can be classified into pyrometallurgical, hydrometallurgical and direct recycling process. Research is focusing on them to make them more efficient and more environmentally sound. The red line in Figure 6 indicates the pyrometallurgical process, or smelting, which treats the EOL batteries as if they were ore and simply dump them into a high-temperature furnace without pretreatment. It can even process with solid waste, ores and any other types of batteries simultaneously. However, further process is required to refine valuable metals like cobalt, nickel and copper through leaching or solvent extraction methods. Lithium and aluminum recovery are normally given up in the pyrometallurgical process due to the unfeasibility in economic view. As the chemistry of cathode choices has been evolving towards low cobalt content, the pyrometallurgical recycling process with high operate cost and high energy consumption is unfavorable to be the primary LIB recycling technology. Umicore utilizes a unique pyrometallurgical treatment followed by hydrometallurgical processes to recycle lithium-ion and NiMH batteries into three constituent parts: an alloy that contains the valuable metals, a slag fraction that can be later processed for use in construction, and exhaust gases that are later treated with a unique gas cleaning process. Similarly, most
other competitors use LIB recycling to recover metals from the cell (especially cobalt and nickel), which must often be removed from the waste stream to comply with local laws or commercial standard operating procedures \(^\text{97}\). Figure 7 below introduces the details of the pyrometallurgical recycling process.

![Figure 7. The flow chart of pyrometallurgical recycling process for LIBs \(^\text{98}\).](image)

1.3.2 Hydrometallurgical process

The hydrometallurgical process is to mechanically shred the LIBs followed by chemical leaching process to dissolve the metal material. The blue line in the Figure 6 represents the hydrometallurgical process which enables the closed loop of battery industry to reproduce the cathode materials. It involves the use of aqueous reagents to leach the valuable metals from electrode materials. It has been proved by previous research that acids combined with reducing agents can dissolve almost all transition metal oxides into solution. For strong inorganic acids like HCl \(^\text{99,100}\), H\(_2\)SO\(_4\) \(^\text{101-103}\) and HNO\(_3\) \(^\text{104,105}\), a high recovery rate can be achieved by excessive acid use. Hydrogen peroxide (H\(_2\)O\(_2\)) was added to accelerate the leaching reaction with less acid utilized \(^\text{106,107}\). In addition, organic acids which are more environmentally friendly have also been validated to be effective for leaching transition metal materials under mild experiment conditions \(^\text{108-110}\). Furthermore, the alkali leaching has been studied recently \(^\text{111,112}\). Ammonia based system can form the stable metal ammonia complexes and fortissimo alkali such as sodium hydroxide can dissolve the cathode current collector to extract the active material \(^\text{113}\). The metal ions could be
separated by various precipitation and solvent extraction methods and recovered as salts for battery raw material\textsuperscript{114}. Compared with the hydrometallurgical process, hydrometallurgy should be more energy and cost saving meanwhile it delivers high metal recovery efficiency\textsuperscript{115}. It has been commercialized by several companies for battery recycling. Recupyl combines the mechanical pretreatment and the hydrometallurgical process for recycling LIBs\textsuperscript{116}. The EOL batteries are shredded and crushed into fines fraction followed by magnetic and density separation under inert gas atmosphere. Lithium is recovered by adding Na$_2$CO$_3$ and H$_3$PO$_4$ and the rest of materials are recovered using hydrometallurgical method\textsuperscript{117}. Such a complexing procedures reveal some fatal issues of hydrometallurgical process, the high liquid solid ratio would generate volumes of solvents waste and additional cost is needed for neutralization.

![Hydrometallurgical Recycling Process](image)

Figure 8. The flow chart of hydrometallurgical recycling process for LIBs\textsuperscript{118}.

1.3.3 Direct recycling process

Process overview

The conventional recycling processes such as pyrometallurgy and hydrometallurgy are becoming undesirable because of the low lithium recovery and high energy input\textsuperscript{15, 119}. Direct recycling processes have attracted more attention since they can restore the cathode powder directly to yield battery grade material. The PVDF binder is currently widely used in the LIB electrodes, NMP is heavily used to dissolve the binder and separate out the
cathode material from the aluminum foil. Undoubtedly, it will exacerbate the environmental and economic problems. Thus, novel methods are in urgent need to eliminate the dependence on this toxic solvent.

The EOL cathode or anode materials can be recovered, reconditioned and reused in the supply chain for remanufacturing without additional processing is known as the direct recycling \(^3\). Theoretically, everything inside the LIBs can be recycled through direct recycling process including the electrolyte, separator, aluminum and graphite \(^{120}\). The main defect or aging mechanism of the degraded cathode material is the loss of lithium ions \(^{121-123}\). The relithiation method is the key point in direct recycling process to restore the electrochemical performance. Solid state sintering has been applied on EOL LCO and LFP to regenerate the cathode materials with performance comparable to pristine ones \(^{124-128}\). This method treats the EOL powder material as if they were the precursor and calcined with lithium source like LiOH. It is similar with the synthesis process in cathode powder production and can comprehensively heal the material. Also a hydrothermal method has been employed to regenerate the spent LCO \(^{129}\). It restores the spent cathode material without lithium quantification process using ICP. Beyond that, LCO has also been tried to use the aqueous pulsed discharge plasma method to regenerate LCO in the mild reaction \(^{130}\). But the electrochemical property is not fully recovered as the first cycle discharge capacity is less than 130 mAh/g in C/5 rate. Electrochemical relithiation has also been employed to insert the lacking lithium ions into the vacancies in layered structure of EOL cathode. Lithium resource can be lithium metal, concentrated lithium solution and even pristine cathode sheet \(^{121,131}\). In addition, the chemical lithiation using lithium iodide (LiI) solution has been applied to LFP \(^{132}\). Hydrothermal method is also an effective way to direct regenerate LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\) (NCM523) \(^{133}\). Recently, the ambient pressure relithiation via eutectic Li-ion molten-salt solution has been successfully executed on NCM523 material \(^{134}\). The green line in the Figure 6 indicates the direct recycling, which owns the least energy consumption or cost among three recycling technologies, is still under development in the pilot-scale stage \(^{95,135,136}\). Its advancements in high recovery rate of critical materials, low process consumption as well as remarkable products drive the trend
to take more effort on developing direct recycling of LIBs. Figure 9 below shows the general processing flow chart of the battery direct recycling process.

Figure 9. The flow chart of the direct recycling process of LIBs.

Table 2: Comparison of the Hydro, Pyro and direct recycling technologies of LIBs.

<table>
<thead>
<tr>
<th></th>
<th>Hydrometallurgical</th>
<th>Pyrometallurgical</th>
<th>Direct recycling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Recovered material</strong></td>
<td>Li_2CO_3, Metals</td>
<td>Ni, Co</td>
<td>Cathode, anode electrolyte</td>
</tr>
<tr>
<td><strong>Feed requirements</strong></td>
<td>Size reduction required</td>
<td>None</td>
<td>Single chemistry required</td>
</tr>
<tr>
<td><strong>Comments</strong></td>
<td>The wastewater needs to be treated</td>
<td>Li, Al cannot be recycled</td>
<td>Recovers battery grade material</td>
</tr>
</tbody>
</table>
The recycling of anode graphite

Recycling the valuable metal materials from EOL LIBs is beneficial in both economy and environment perspective. However, the studies in anode recycling have not drawn enough attention for researchers and recyclers, due to the inexpensive price of the anode material like graphite. Since the anode material only accounts for 11% to 20% of the battery cost, recyclers mainly focus on recovering the cathode materials which accounts for nearly half of the cost. The market price of the graphite in the anode is around $8/kg–$13/kg, and recently a graphite producer Pyrotek has lowered the cost of the battery grade synthetic graphite as low as $5/kg. Meanwhile, graphite has the abundant deposits among the world. The amount of mine production of the natural graphite was around 1,100,000 tons per year over 20 countries around the world. However, it is worth noting that not all kinds of graphite can be used for LIB anode, and only the large flake graphite gains significant interest to be LIB anode in the market. Graphite mines only can produce 90-98% purity flake graphite. The battery grade graphite can be upgraded to 99.5% purity with sphere shape through the purification methods. However, the methods involved in the graphite purification utilizing strong acids and high temperatures under inert atmospheric conditions are not in an environmentally acceptable manner. Thus, the purified graphite prices also will vary depending on the flake size and purity. With the rapid growing demand of flake graphite of high purity used in EVs, it is believed that the recycling and reusing the anode material are indispensable. Furthermore, the anode material from the spent battery contains 5% to 7% of lithium and the spent anode belongs to the hazardous waste. Recycling the anode material can also provide a new source for lithium recovery.

The main valuable components of spent anodes are the graphite material and the lithium residue. The lithium residue in an anode mostly remains in the graphite lattice voids and SEI component in the form of Li$_2$O, Li$_2$CO$_3$, CH$_3$OLi, ROCO$_2$Li and LiF. Among these materials, the CH$_3$OLi, ROCO$_2$Li and Li$_2$O are water soluble, whereas the others are hard to be dissolved in water. Based on this phenomenon, He et al. used the HCl to leach the EOL anode material and achieved the 99.4 wt% efficiency of anode recovery. Similarly, Aravindan et al. shredded the battery followed by magnetic separation, sieving and the fine fraction in a mix of cathode and anode powders were leached out by sulfuric acid using iron pellets catalyst for reaction acceleration. The recovered graphite
material showed great electrochemical performance for both LIBs and capacitors. In addition, Zhang et al., 144 combined the dismantling process with acid washing and the scrapped anode material was shear emulsified in H$_2$SO$_4$ + H$_2$O$_2$ solution. The separated powder went through the heat-treatment in air at 300–600°C and the regenerated graphite can deliver similar capacity to that of the new graphite. A more economical and environmentally friendly reclaim technique was proposed to mechanically separate the spent graphite from Cu current collector and wash it using deionized water for five times. The water treatment would generate hydrogen due to its reaction with residual lithium which helps separate SEI from graphite and reopens the channels for Li-ion transport 145. Sabisch et al., 146 directly reused the prelithiated graphite from EOL LIBs for new battery anodes after immersion of the graphite in organic solvents. The LIB cells produced with recovered anode material this way showed equivalent cycling capacity and lower first cycle capacity loss to virgin graphite anodes.

Apart from directly regenerating the EOL anode material from electrode and reusing it in LIB, we can also produce alternative value-added products (e.g., graphene) from the EOL graphite anode. The anode material was cut into small pieces followed by ultrasound leaching, electrothermal drying to separate the graphite and copper foil. The graphene oxide was synthesized through the improved Hummers method and the graphene oxide dispersion solution was reduced to graphene using vitamin C 147. Zhang et al., 148 fabricated the graphene from the spent anode material using acid leaching and shear mixing processes. It is believed that the battery cycling would result in the lattice expansion and weaken the bonding between graphite layers. The functional groups containing oxygen may impede the aggregation of graphene layers, leading to higher exfoliation efficiency of anode graphite than that of pristine graphite.

The anode graphite from EOL LIBs has also been regenerated for other uses. Liang et al., 149 proposed the new recycling concept for reusing it on sodium ion or potassium ion batteries. Besides, the recovered graphite from spent LIBs was converted to graphite oxide by modified Hummer’s method and used as adsorbent for the methylene blue and congo red dyes from waste water 150. In addition, the anode graphite and separator (PP,
PE) materials have been utilized for the synthesis of polymer-graphite nanocomposite thin films with improved tensile strength and other physical properties.  

1.4 The progress and challenges of LIB direct recycling

1.4.1 The progress of direct recycling process

Table 2 compares these three different recycling technology routes. It can be concluded that the process is evolving from pyrometallurgical process, hydrometallurgical process to the direct recycling. However, there are more difficulties being conquered to make the direct recycling practical. The LIB market in the past has the variety of sizes but most of the cathode chemical is the LCO, which is of high value. Meanwhile the volume of the EOL batteries is not enough to support the recycling plant. The story will change in the future. With the booming market of EVs, volumes of EV batteries manufactured from the same model or from the same supply chain can greatly simplify the operations of recycling processes. Those batteries own the same chemical components and therefore, we do not need to worry about the cross contamination from other batteries with different battery material. Currently most of the cathode materials retired from EOL portable electronics are LCO that is of high value. Nevertheless, there is a trend that nickel-rich cathode is expendingly used in EV batteries. The ratio of Ni: Co : Mn will be 5:2:3, 6:2:2 or even 8:1:1 in the next 10 years and this measure can effectively reduce the cobalt content as well as the cathode cost. The lower value of cathode material would help reduce the price of LIBs, then further popularize the use of LIBs. Meanwhile it gives less incentive to recyclers to deal with the EOL LIBs since recycling is motivated by the high value of waste. Therefore, it is necessary to make the recycling technologies more efficient and cheaper to make up the profit margins. For the direct recycling process, there is no doubt that it would be a promising method and deserves the further development.

In contrast with the incumbent recycling technologies, the direct recycling process maintains the original structure and morphology of battery components through physical and chemical separations, which yield resalable electrode material to the battery manufacturers without additional processing. We have compared the energy consumption, yield value and unit cost of our direct recycling technology with incumbent
pyrometallurgical and hydrometallurgical recycling technologies used by competitors. The direct recycling of several typical LIB cathode materials (LFP, NCM111, NCA for EVs and LCO for consumer electronics) has the lowest energy consumption among the three proposed recycling approaches based on life-cycle analysis using the computation software GREET 2016 [154]. The energy consumption of three different recycling method were compared with the purchased energy which means the energy cost during the production of virgin material. It can be seen from Figure 10 that the purchased energy of LCO and NCM is much higher than it of any recycling methods. The energy consumption of the direct is less than 10 MJ/kg cathode material while for hydrometallurgical or pyrometallurgical process it is at least 5 times higher. Compared with other two methods, the direct recycling has much lower energy consumption of unit active material processed. That is because the process does not decompose the material structure into element level but directly reproduce the battery grade material. The deficiency of lithium can be replenished and other defects caused during battery cycling can be healed. It keeps the original morphology and crystal structures of the particle during the recycling process.
1.4.2 The challenges of direct recycling process

The spent batteries in pyrometallurgical recycling process are poured into the burning tower without any pretreatment and the hydrometallurgical process reduces the sized of the batteries by mechanical shredding and crushing. By contrast, the direct recycling requires the elaborate pretreatment for the EOL batteries since the it can only process one single type of cathode chemistry at a time. In fact, the reality of the current battery market, especially the EOL batteries, are in great amount and assorted varieties. Even the batteries in the same chemistry component, the slight differences during the manufacturing still exist. Therefore, it is necessary to classify the battery into different types according to their cathode chemistries before the recycling process. One favorable information is that most of the batteries are clearly labelled and even have the unique QR code. This would
simplify the classification process, especially when machine learning techniques are applied. After the classification, the single variety of the battery will be separated out and the physical properties like particle size can be consistent and suitable for single use. For example, the smaller particles make for better rate performance and it’s applied to electronics with high rating requirements like unmanned drones\textsuperscript{158}. The high degree of consistency of material properties for the input of recycling plant is the basis of product quality. The more information we know for the product manufacturing, the more convenient for recyclers pretreatment. Therefore, battery classification during the waste collection becomes highly important for direct recycling process. Meanwhile the disassembly of spent LIBs is also a barrier since the cross-contamination between different components would destroy the recycling product if the cathode and anode cannot be effectively separated.

Researchers are exploring the solutions to overcome the barriers. Ideally, the mass-produced commercial batteries are in standard configurations of packs and cells. This feature would enable the design of recycling equipment and the standardization of chemistry reduces need for sort and multiple processes. For classification process, the cell labelling will simplify the recognizing procedure and improve the sorting accuracy. The novel method, Convolutional neural network (CNN), is a deep learning technique that has produced promising results in solving image classification by automatically discovering the representation needed for the task at hand\textsuperscript{159}. For the battery disassembly and separation process, the smart sensors can be employed to monitor the key parameters for the real-time data collection. The intelligent machine learning model will be trained to analyze the real-time data for making decisions to take measurement and mitigate the defects. In summary, it is feasible to separate the material through mechanical pretreatment and directly regenerate it eco-friendly and economically. The utilization of machine learning techniques will defuse the obstacles and make it possible to realize the intelligent manufacturing and recycling.
1.5 Organization of the Dissertation

This dissertation demonstrates a green and sustainable system for LIBs where the batteries are manufactured, harvested and direct recycled to form a closed loop. As shown in Figure 6, the circular model of the manufacturing and recycling system is desired.

The introduction part provides detailed review on the state of art of the battery manufacturing and recycling. The challenges and potential improvements for supply chain of LIB are analyzed. Three recycling processes including pyrometallurgy, hydrometallurgy and the direct recycling process are detailed and analyzed. Comparing with different recycling methods, the direct recycling process has obvious advantage in terms of the high recovery efficiency and low energy consumption.

The second part demonstrates a cyber-enabled and machine learning enhanced battery disassembly system. It improves the safety and efficiency of EOL battery pretreatment, which reduces the difficulty of direct recycling process. The computer vision is used to classify different types of batteries based on their unique characteristics. Combined with the real-time temperature data captured from thermal camera, a data-driven prediction model is built to predict the cutting temperature pattern. Then a close-loop control is implemented to avoid the temperature spike by adjusting the cutting variables before the predicted position. Furthermore, quality control is integrated with computer vision model to detect and mitigate cutting defects.

To avoid hazardous organic solvent being used during electrode manufacturing and recycling, the water-based electrode demonstrates the comparable cycle life and rate performance to the ones from the conventional organic solvent-based processing. The third chapter also introduces that the utilization of water to dissolve the aqueous binder enables the separation of cathode material from the collect collector without organic solvent. The nickel rich cathode compounds including the carbon black are successfully regenerated from the spent electrodes to deliver a comparable electrochemical performance to the pristine one. The direct recycling process has the advancements to regenerate the cathode material from EOL LIBs and yield the battery grade material without decomposing it into
elements. In addition, the systematic investigation on separating cathode powder from aluminum current collector has been completed which can reach 98% of separation efficiency. As for the impurity removal, the acid and ammonia leaching method can help eliminate the cross-contaminated metal impurities in the cathode powder.

When scaled up, the fourth chapter introduces that the degraded cathode material can be directly regenerated by the optimized relithiation thermal synthesis (RTS) method to deliver the homogeneous cathode powder of high quality. The pilot-scale test can successfully recycle and resynthesize the LCO powder in large quantity. In summary, the green and sustainable battery manufacturing system is built and scaled up to the pilot test with recycled product delivering good electrochemical property and cycling performance. The integration of machine learning technologies makes the elaborate dismantling process safer and more efficient.

My research work proposes the circular ecosystem for LIBs and provides the primary results for the battery production and the waste treatment. The competitive electrochemical performance has been achieved in both manufactured and recycled cathode material. It provides a potential path toward green and sustainable manufacturing of LIBs, which enables lower battery cost and much less environmental impact.
Figure 11. The green and sustainable closed loop model for battery manufacturing and direct recycling process.
Chapter 2 - EOL battery disassembly for the direct recycling

All these three recycling methods have their respective benefits and drawbacks. In comparison to the hydrometallurgical and pyrometallurgical recycling processes, the direct recycling is still under the development at the lab pilot scale. The barriers or research directions for the direct recycling of LIBs include the classification according to different chemistries and the efficient and safe preprocessing for battery disassembly. The first step of the direct recycling process is the discharge and disassembly. The existing preprocessing uses mechanical processes like crushing and shredding to expose the high valuable electrode materials for subsequent hydrometallurgical and pyrometallurgical processes. These processes have disadvantages such as the lack of lithium recovery, high output of liquid hazardous waste for wet crushing, and high energy input. Since the output of direct recycling is the battery grade material, one of the challenges is to precisely separate out the electrode material and purify the segregated materials. Tremendous amount of impurities like copper, aluminum is introduced into the EOL cathode material in the conventional crushing method, which makes the downstream recycling process much more difficult. Manual disassembly is not practical because the workers would be exposed to toxic substances in the spent batteries and the risk of battery explosion. Therefore, the automatic disassembly without human intervention is preferred to take over the pre-processing of EOL battery. Recently, some researchers have attempted to automate the disassembly of the EV battery system at module/pack level using robots. At individual pouch cell level, we have demonstrated the prototype machinery that can dismantle the packaging of the mimic 2Ah LIB pouch cell and automatically sort various cell components.

In order to further improve the precise disassembly, we plan to advance the demonstrated disassembling platform to CPS which integrates computing, communication and control to achieve collaborative and real-time interaction through feedback loops of interaction between computational processes and physical processes. Machine learning-based data-driven approaches have demonstrated tremendous impact in a number of aspects involving
image recognition and could potentially enhance the performance of CPS [170]. In the vision-based automatic disassembly system, components can be categorized into two types: main components and fasteners [171]. Typical fasteners are screws, cables and snap-fits, which need to be detected and removed to eliminate the constraints of the main components. Gil et al. [172] used region-based and edged-based template matching to detect the screws on the cover of the battery from toy. Then a robot with eye-in hand camera automatically disassembled the cover of batteries. For the main components, vision detection was performed using a model-based approach to identify the geometrical shapes. Jorgensen et al. [173] used the neural networks for shape recognition of televisions and Buker et al. [174] combined the contour, gray value, and knowledge-based recognition to build the vision architecture which detected vehicle wheels and determined the exact position and pose of their bolts. Different battery cells have unique characteristics in terms of the color, geometry and size, which can be categorized using the machine learning technology. Furthermore, direct recycling requires destructive cutting to open the hermetic sealing of the cell meanwhile keep the stacking/winding structure. This mechanical cutting would inevitably generate heat which may cause the decomposition of the electrolyte salt LiPF$_6$ as well as damage the active material in cathode [175, 176]. The machine learning approach can predict and take measures to control the temperature under certain threshold by analyzing the historical data.

In this chapter, we demonstrate a cyber-enabled and machine learning enhanced battery disassembly system, in which the computer vision is used to classify different types of batteries based on their unique characteristics. Combined with the real-time temperature data captured from thermal camera, a data-driven prediction model is built to predict the cutting temperature pattern. Then a close-loop control is implemented to avoid the temperature spike by adjusting the cutting variables before the predicted position. Furthermore, quality control is integrated with computer vision model to detect and mitigate cutting defects.
2.1 System architecture

The process flow chart of the battery disassembly system is described in Figure 12. The first step of the process is to classify the battery according to its brand and determine its length in order to choose the appropriate machine settings for cutting. During the cutting process, there is a safety concern when temperature spikes. For this reason, it is necessary to monitor the temperature and prevent the spike from happening by adjusting the machine settings. Finally, after the cutting finishes, we use computer vision to assess the quality of the cut.

Figure 12. The process flow chart for the cyber-enabled and machine.

Convolutional neural network (CNN) is a deep learning technique that has produced promising results in solving image classification by automatically discovering the representation needed for the task at hand \cite{159}. In this work, CNN image classification is used for both battery type classification and cutting quality control. For temperature monitoring, our goal is to predict the position of temperature spike and prevent it through feedback mechanisms to the machine. The control rules are derived based on the Design of Experiment results. For temperature spike prediction, we are using Long short-term memory \cite{177}, which is a deep learning framework well suited for making predictions based on time series data.
Figure 13. (a) The cell cutting station prototype equipped with thermal camera. (b) A cell phone battery with hard aluminum case. (c) The side view of the fastened pouch battery and blade. (d) Thermal camera view of the cell and the cutting blade during the cutting process.

The cutting station is built in the hood with ventilation (Figure 13a) consisting of the step motor to feed the batteries into the bandsaw and the thermal camera mounted on the side. The spent phone battery (Figure 13b) was shorted till the voltage is below 0.5V. The shorting process can deactivate the batteries to release the residual energy for safe disassembly. Figure 13c illustrates the orthogonal cutting of the battery with the saw blade. The thermal image of the cutting process is shown in Figure 13d.
2.2 Vision-based battery classification

Image classification is one of the domains that deep learning performs substantially better compared to traditional methods. In this work, the CNN image recognition is applied in the battery classification for the spent LIB recycling process. In the real recycling process of spent batteries, the application scenario is more complicated: 1) The number of battery types and sizes would be much more multitudinous. 2) The surface damage and deformation of the spent batteries will increase the difficulty of classification. 3) As a massive amount of the spent batteries needs to be treated, higher requirements are put forward for the speed and efficiency of classification. CNN is widely used in the image-recognition field due to its outstanding classification capability. It has a great advantage in that both filters and classifiers for optimal feature extraction are automatically acquired from training data. In contrast, the optimal filters must be manually determined by intensive experiments for conventional supervised learning-based techniques such as support vector machine (SVM) and multi-layer perceptron (MLP). Therefore, the CNN method is chosen for the battery classification. While classifying four classes has lower data requirements and complexity, it is sufficient to show how the full system works.

We aim to classify four common types of batteries Samsung (97*41mm), Samsung (62*57mm), iPhone (94*38mm) and iPhone (105*49mm) by training a CNN classifier. A CNN consists of series of convolution, activation, and pooling feature extraction layers for automatically learning features followed by fully connected classification layers to classify an input image into desired categories. We have resized the input images to 100*100 to reduce the time of training. There are some hyperparameters in a CNN model determining the network structure and settings including the learning rate, number of epochs, batch size, depth of the network, etc. Hyperparameter tuning is the problem of finding the best set of model parameters based on the classification results of validation dataset before training starts. We have used Bayesian hyperparameter tuning for this purpose.

The database included the 300 gray scale images from each of the battery types. The batteries were fully shorted before the image collection. 150 images from the database were used for training, 100 images for validation to tune hyperparameters, and the remaining 50
were used for testing. Based on the Bayesian hyperparameter tuning result, the hyperparameters are set as follows: Filtersize 3, Initial learning rate 0.0055, Momentum 0.85, Minibatch size 21, and L2 Regularization 2.71e-07. Figure 14a shows CNN architecture adapted for battery type classification. Max stands for Max pooling and Avg is the Average pooling layer.
Figure 14. (a) CNN architecture for battery type classification and its confusion matrix (b) Battery type classification confusion matrix (c) Some test images together with their predicted classes and the probabilities of those classes.
Based on the confusion matrix shown in the Figure 14b, the instant online battery type classification has an accuracy of 99.5% on the test images, which is reliable when applied to the real battery identification process. As you can see, the classification only confuses small and large iPhones. Such errors can be eliminated given having fixed point of view. Some of the test results are listed in Figure 14c.

After the classification, we can label each image based on its brand and size, which can be used to derive the actual size of the batteries. The width of the batteries is needed for normalizing the position data used in spike temperature prediction. All we need to do is to measure the battery size only once per category (only four times). One way to automatically measure the size of the object is through computer vision by calibration using a reference object \(^{180}\). The reference object should be of the known dimension and should be easily detected. An object that meets these two criteria is a coin placed at a known place in the image. As we know exactly the shape, size and placement of the coin (i.e., the location of the pixels that represents the coin), we can use it to find the pixels per metric of the image which is the ratio of the object width in the image to its actual width. We will first detect all the objects in the image using canny corner detection. Afterward, knowing the placement of the reference object (the coin), we can infer the size of all other detected objects using the found pixel per metric result. It is important to note that this method works under the assumption that we have a perfect 90-degree view. Figure 15 shows the result of this approach applied on the battery images.
2.3 The temperature spike control

2.3.1 Investigation of factors that influence the processing temperature

The maximum spike temperature is considered as an important parameter to be monitored during the disassembly process. The electrolyte salt LiPF$_6$ decomposes near 70°C according to the Equation 2.1 and generate toxic products such as HF and PF$_5$. Some electrolyte solvents have the even lower flash point (Table 3).

\[
\text{LiPF}_6 + H_2O \rightarrow HF + PF_5 + LiOH
\]  

(2.1)

Therefore, the temperature during the disassembly process needs to be strictly monitored and controlled. Using the Design-of-Experiment method, the impact of different parameters on the maximum cutting temperature was investigated. The Samsung batteries with hard aluminum shells were fixed on the step motor by a clamp. The location of cutting was the front edge of the cell that carries the electrode tabs to keep the internal electrode-separator-compound (ESC) structure intact. Factors that affect the maximum cutting temperature are cutting speed (A), feed rate (B) and tooth density of the blade (C). Each
factor affecting cutting temperature is considered at low and high levels and shown in Table 4.

Table 3. The key temperature points of the electrolyte components.

<table>
<thead>
<tr>
<th>Electrolyte component</th>
<th>Flash point</th>
<th>Boil point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Carbonate (EC)</td>
<td>150°C</td>
<td>243°C</td>
</tr>
<tr>
<td>Diethyl Carbonate (DEC)</td>
<td>33°C</td>
<td>126°C</td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>17°C</td>
<td>90°C</td>
</tr>
<tr>
<td>Ethyl Methyl Carbonate (EMC)</td>
<td>26.7°C</td>
<td>104°C</td>
</tr>
</tbody>
</table>

Table 4. The factors for the cutting temperature.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Name</th>
<th>Units</th>
<th>Low level (-)</th>
<th>High level (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cutting speed</td>
<td>ft/min</td>
<td>536</td>
<td>820</td>
</tr>
<tr>
<td>B</td>
<td>Feed rate</td>
<td>mm/min</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>C</td>
<td>Tooth density</td>
<td>tooth per inch (TPI)</td>
<td>14</td>
<td>24</td>
</tr>
</tbody>
</table>

The results of the experiments were listed in Table 5, including the effect of the factors and their interactions. It can be observed that the cutting speed, feed rate, as well as the tooth density have significant positive effects on the cutting temperature. The analysis of variance (ANOVA) in Table 6 indicates that the actual F of 17.06 is bracketed by the critical value for 0.1% and 1% risk. We can say that we are more than 99% confident that the maximum spike temperature is significantly affected by factor A, B and C. Among all the three factors, the tooth density and the cutting speed can be reduced to the minimum within the scope of conditions to lower the processing temperature. The confliction lies on that lowering the feed rate could decrease the cutting temperature but it also loses efficiency (i.e., number of batteries treated per minute). Therefore, the feed rate needs to be controlled in an optimized strategy to realize the balance between efficiency and safety.
Table 5. The Design of Experiment complete matrix, interactions and effects calculated.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Main effect</th>
<th>Interaction effect</th>
<th>response Y (max T)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Effect  11.075  11.575  10.525  0.225  0.325  1.675  5.075

Table 6. The analysis of variance (ANOVA) for maximum temperature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares (SS)</th>
<th>Df</th>
<th>Mean Square (MS)</th>
<th>F value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>734.82</td>
<td>3</td>
<td>244.94</td>
<td>17.06</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>A</td>
<td>245.31</td>
<td>1</td>
<td>245.31</td>
<td>17.08</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>B</td>
<td>267.96</td>
<td>1</td>
<td>267.96</td>
<td>18.66</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C</td>
<td>221.55</td>
<td>1</td>
<td>221.55</td>
<td>15.43</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Residual</td>
<td>57.43</td>
<td>4</td>
<td>14.358</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>798.52</td>
<td>7</td>
<td>114.074</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3.2 Prediction of temperature spike position

Temperature spike is a primary safety concern during the battery cutting. Based on the temperature evolution data collected by thermal cameras, this temperature spike often happens near the end of cutting. Figure 16 shows some examples of the temperature evolution patterns during the cutting process. Our goal is to predict the location of this spike in order to implement preventative measures by adjusting the parameters of the machine through a closed loop control system. Long short term memory (LSTM) is a widely used time series prediction method introduced to solve the vanishing/exploding gradient problem of recurrent neural networks (RNNs) and is capable of learning long-term dependencies. LSTM replaces all the hidden units in RNN with LSTM cell and introduces a new element called cell state, which is a vector that goes through the LSTM cells at each of the next time steps to be modified. The LSTM unit has built-in mechanisms (gates) deciding how much of the past cell state to throw away (forget gate), how to update the old cell state using new inputs (input gate), and how to filter the final cell state to present as the output (output gate). Figure 17a shows the structure of LSTM cell and its internal diagram.
Figure 16. Examples of the temperature patterns during the cutting process.
Figure 17. (a) The block diagram of LSTM cell. (b) LSTM model structure for temperature spike position prediction.
In order to use LSTM for temperature spike prediction, we first need to find the fitting data format and model structure. The data consists of temperature and its corresponding position (since the battery moves at constant feed rate, the position is in proportional with time series) as well as the machine settings for the cut. The first step was to convert the list of numbers in time series into the appropriate format for supervised learning, which is a list of inputs and their corresponding outputs. Since the temperature spikes often happen at the end of the signal, we divide the whole cutting process into ten sections and developed the model to predict the temperature at the last 10% of the data series using the first 10% and find the position for the spike based on this prediction. This way we gave the machine and the control system plenty of time to adjust the parameters when it gets to the range of the spike position. We used a sliding window of 10 time steps to crop out both temperature and position time series and assigned to it a corresponding time point at the last 10% of the series. Therefore, the time series input has the shape of (10,2). In addition to the temperature time series data, we are feeding the machine settings consisting of speed and feed rate as other inputs to the model. Figure 17b shows the structure used for temperature spike position prediction. After searching the hyperparameter space, we configured the LSTM to have 30 neurons, batch size of 2 and epoch of 100. The averaged prediction error over all the data using different indexes is reported in Table 7.

<table>
<thead>
<tr>
<th>Table 7 Average Prediction Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Square Error</td>
</tr>
<tr>
<td>Mean Absolute Error</td>
</tr>
<tr>
<td>Bias</td>
</tr>
</tbody>
</table>
Figure 18. (a). The comparison of LSTM prediction results with experiment results. The red line indicates the predicted results while the green line shows the experiment data. (b). The comparison of the spike temperature with and without closed loop control.

Figure 18a shows the model prediction results on the last 10% of the cutting duration. The LSTM prediction model was integrated into the disassembly system to analyze the real-time temperature data and the control system accurately decreased the feed rate based on the prediction results, e.g. the predicted position where the temperature spikes. The predicted maximum temperature is lower than the experiment data, but the precise position of the temperature spike is more important since it determines when the measure would be taken. Figure 18b compares the temperature evolution patterns during the battery cutting process with and without the integrated closed loop control. It can be observed that the maximum spiking temperature significantly reduced at the end of the cutting when the closed loop control is employed. The cutting speed, tooth density and feed rates without and with control are 536ft/min, 14 TPI, 60mm/min and 10mm/min, respectively.

2.3.3 Closed loop control system

Figure 19a describes the structure of the closed loop control system. The step motor is connected to the board (SparkFun Stepoko), which is able to connect the computer to accept stepper motor commands. The real-time temperature evolution data during cutting process with respect to the battery position are recorded by thermal cameras (Micro-epsilon TIM300) and analyzed by the deep learning prediction model. We use an in-house Matlab code to transfer data to the predictive model and implement the control command to the
hardware. It bridges the real-time interaction between computational processes and physical processes. When the battery position approaches the predicted position, the motor speed would be instantaneously decreased to effectively eliminate the temperature spike. The model predictive control feedback system is shown in the Figure 19b. Compared with other control methods, the model predictive control can achieve the behavior prediction ahead of time and overcome the response delay to control the machine parameters precisely. It also balances the cutting time and process temperature to maximize the efficiency while ensure the safety.

2.4 Vision based quality control of cutting cross-section

In this section, we attempt to detect defective cuts using convolutional neural network. The two classes of cuts are clean cut and defective cut. The database includes around 1100 RGB images with resolution of 640*480 from each label turned to gray scale and resized to the resolution of 150*200. 900 images from the database were used for training model, 100 images for validation to tune hyperparameters and the rest were used for testing. Based on the Bayesian hyperparameter tuning results, the best found hyperparameters for classifying quality of the cuts are: Filtersize 6, Initial learning rate 0.0051, Momentum 0.81, Minibatch size 22, and L2 Regularization 1.01e07. Figure 20a shows CNN architecture adapted for battery type classification. Based on the confusion matrix shown in the Figure 20b, the clean or defective cut classification had the accuracy of 90.5%. Some tests of the recognition results are listed in the Figure 20c.
Figure 19. (a) The structure of the closed loop model predictive control system (b) The model predictive control feedback system.
Figure 20. (a) The input image of defect cutting and CNN architecture adapted for cut quality classification. (b) Cutting quality classification confusion matrix. (c) Some test images together with their predicted classes and the probabilities of those classes of the quality control.
2.5 Conclusion

This work has demonstrated a cyber-enabled and machine learning enhanced battery disassembly system. The spent LIBs went through the classification and size measurement by trained computer vision model. The selected battery pouch cells with hard aluminum shell were used as test articles to demonstrate the effectiveness of the CPS system. Combined with the real-time temperature data captured from thermal camera, a data-driven prediction model was built to predict the location of the temperature spike. Then based on DOE results, the feed rate was precisely controlled to slow down before reaching the predicted position to avoid the temperature spike. Furthermore, quality control is integrated with computer vision model to detect and mitigate the cutting defect. The CPS paradigm established for disassembling process can be used to improve the safety and quality control of other unit operations in the battery recycling process.
Chapter 3 - Green manufacturing and direct recycling of LIBs

In this chapter, we report a green manufacturing process for LIB production and recycling where NMP was replaced by water in electrode fabrication and black mass (mixture of carbon black and active material) was separated from the current collector and recovered by dissolving the water-soluble binder in water. The active material was separated from carbon black and relithiated to generate battery grade material. This process enables numerous advantages and benefits in both economy and environment: 1) lower LIB manufacturing cost by eliminating NMP enabling ~2% cost reduction in the battery pack and $3-6 million savings in capital investment from removing the entire emission control and solvent recovery system \(^{32}\); 2) recovering black mass without using any organic solvents and direct recycling of the active material compound, which reduces the recycling cost and environmental impact while generating value-added compounds compared to elements. In comparison, organic binder was burned out in pyrometallurgical recycling and active material was separated from carbon black using NMP in hydrometallurgical recycling \(^{183}\); 3) reducing life cycle CO\(_2\) equivalents emission for a 10 kWh battery by 1000 kg \(^{184}\). Excellent electrochemical performance was achieved from the water-based processed electrodes used in this work and comparable performance was obtained from the recycled materials. This methodology provides a green, sustainable process for LIB manufacturing and recycling if some underlying challenges can be resolved.

3.1 Water-based electrode manufacturing and direct recycling process

Switching from NMP-based to water-based processing in fabricating composite cathodes \(^{185-187}\) has attracted great interest in the last decade. Although there are still challenges in realizing water-based processing for NCM cathodes, i.e. Al corrosion from high pH of the aqueous slurry \(^{188}\) and poor mechanical integrity in thick cathode \(^{189}\), great progress has been demonstrated, e.g. excellent cycle life \(^{32, 190}\). When successful, the water-based processing can significantly facilitate binder removal and recovery of black mass in the
recycling process. In direct recycling, the binder removal process is particularly challenging. For conventional EOL LIBs with PVDF binder, toxic solvents such as NMP and dimethylformamide (DMF) are needed to re-dissolve the binder and extract the active cathode materials in the black mass. Using water for the binder removal process will not only minimize the negative environmental impact caused by organic solvents, but also significantly reduce the cost for the binder removal unit operation. Meanwhile using water instead of an organic solvent eliminates the solvent regeneration and reuse unit operation that further simplifies the overall process.

3.1.1 Water-based electrode manufacturing

Pouch cells (~1.6 Ah) were assembled with NCM523 and graphite electrodes fabricated from NMP and water-based processing, respectively. The NMP-processed electrodes were used as a baseline to validate the performance of the water-based processed ones and were not used for recycling. The electrode fabrication and calendering processes followed the standard procedures reported in our previous work. Aluminum foil was treated by corona plasma at 4.4 J/cm² to enhance slurry wetting on the current collector substrate. Table 8 lists the detailed electrode information. The electrode balance (negative/positive ratio) ratio was around 1.2. The electrolyte was 1.2 M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC in 3/7 wt), Celgard 2325 was used as the separator, and the electrolyte amount was 1.2 times the total pore volume of electrodes and separator. Electrochemical cycling took place between 2.5 V and 4.2 V. Pouch cells went through 4 formation cycles at C/20 (1C=1.6 A) charging and discharging rates followed by rate capability or cycle life testing, respectively. For rate capability testing, the pouch cells were charged at C/5 until 4.2 V followed by constant voltage charge until the current dropped to C/20. Discharge rates ranged from C/10 to 2C. Cycle life testing was evaluated at 0.2C/-0.2C, 0.33C/-0.33C, and 1C/-2C, respectively. Most of the cycle life testing was performed at 25 °C, but some cycles occurred at 30 °C due to a change in temperature setting in the environmental chamber, which is specified in the experimental results. Two sets of cells were tested. One went through rate performance test followed by cycle life test at 1C/-2C. The other went through cycle life test at 0.2C/-0.2C or 0.33C/-0.33C. The pouch cells had at least 20%
capacity fade. The NCM523 cells with water-based processed electrodes aged for months at room temperature before being recycled (referred as EOL).

Table 8. The NCM electrodes information with different solvent processing and composition \(^32\).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Solvent</th>
<th>Electrode Composition</th>
<th>Porosity</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCM523-NMP</td>
<td>NMP</td>
<td>NMC532/Denha CB/5130 PVDF in 90/5/5 wt%</td>
<td>37%</td>
<td>12.5 mg/cm(^2)</td>
</tr>
<tr>
<td>NCM523-Water</td>
<td>Water</td>
<td>NMC532/Denha CB/CMC/PVDF Latex in 90/5/1/4 wt%</td>
<td>36%</td>
<td>12.5 mg/cm(^2)</td>
</tr>
<tr>
<td>A12-NMP</td>
<td>NMP</td>
<td>A12/C65 CB/9300 PVDF in 92/2/6 wt%</td>
<td>33%</td>
<td>6.5 mg/cm(^2)</td>
</tr>
<tr>
<td>A12-Water</td>
<td>Water</td>
<td>A12/C65 CB/CMC/SBR in 92/2/2/4 wt%</td>
<td>34%</td>
<td>6.5 mg/cm(^2)</td>
</tr>
</tbody>
</table>

3.1.2 Degradation analysis of the LIB cathode material

From the literature, the mechanisms of the electrode degradation include the formation of the films on the surface of electrode, blocking of pores for the Li-ion diffusion, disintegrations, or cracks in the electrode coating \(^{195-197}\). Cathode material degrades due to the Li-ion loss, transition metal dissolution, particle cracks, surface reconstruction layer, and decomposition of electrolyte \(^{198-200}\). To investigate the main factor that causes the cathode material degradation, the cells with pristine NCM as cathode and graphite as anode are cycled at \(-10\) °C, \(25\) °C and \(50\) °C. The coin cells are firstly cycled at \(25\) °C for three cycles with the current rate of C/5 (1C = 2.8 mAh) and then cycled at 0.667C followed by hybrid pulse power characteristic (HPPC) loops. Figure 21 (a) shows the cycling data at different temperature conditions. It can be observed that the higher discharge capacity is obtained in the \(50\) °C cycling than cells at \(25\) °C and \(-10\) °C at the beginning. Negligible capacity decay is found for the \(25\) °C cycling over 400 cycles while the cycling at \(-10\) °C degrades quickly at the first 20 cycles. The cell impedance at three different temperatures is measured at around 3.8V from HPPC sequences. As shown in the figure 21 (b), the impedance of cells at three different temperatures are compared. The impedance gradually
increases for the cells cycling under 50 °C, while the cell impedance is relatively more stable at 25 °C. The impedance of cell at -10 °C is extremely high and the cell capacity degrades quickly. It is believed that cycling at elevated temperature (higher than 30 °C) aggravates side reactions between the electrolyte and cathode, leading to severe Li-ion loss. While cycling at the low temperature, the degradation of the graphite anode and the Li-ion loss triggered by irreversible lithium metal plating on anodes jointly cause the capacity decay.

Figure 21 (a) The cycling data of the discharge capacity for cells at different temperatures. (b) The impedance measured at 3.8V for cells cycled at different temperatures. (c) The voltage profile of the relithiation process for the EOL NCM electrode at C/10 rate.

The cycled coin cell is dismantled to obtain the EOL cathode disc. After DMC wash to remove the residual electrolyte, the EOL cathode disc is used for another coin cell with lithium metal as the anode. The half-cell is discharged to re-intercalate the Li-ions into the layered structure of EOL NCM electrode. The voltage profile of the relithiation process is illustrated in the Figure 21 (c). The coin cells are assembled with relithiated NCM electrode, EOL NCM electrode and the pristine NCM electrode as the cathode respectively while the
graphite is served as the anode. The electrochemical cycling data at 25 °C with a current of 0.667C is shown in the Figure 21 (d). The direct relithiation process can greatly improve the reversible capacity of the EOL NCM electrode. It proves that the capacity loss is primarily caused by the Li-ion loss. Meanwhile, the capacity loss of the EOL NCM cannot be fully restored to deliver the same irreversible capacity as the fresh electrode. This result gives indication to the direct recycling process. To fully regenerate the cathode structure as well as the capacity, the heat treatment is required in the direct recycling process.

![Diagram](image)

Figure 22. The process flow chart of the direct recycling process for the water-based cathode electrode.

3.1.3 The direct recycling of water-based electrode

Figure 22 shows the schematic flow chart of the closed loop recycling process where the EOL cells were discharged to 2.5 V at C/5 before being recycled. The pouch cells were first discharged to 2 V and then fully shorted below 0.5 V for safe disassembly. After deactivation, the cathode sheets were separated from the other cell components and thoroughly rinsed in dimethyl carbonate (DMC) to remove the electrolyte. Since water-soluble binders were used in the electrodes, the cathode sheets were then sonicated in DI water for 2-5 minutes in the electrode/H₂O ratio of 3g/50ml. After the sonication, the EOL cathode material was washed off from the aluminum current collector and suspended in water. The aqueous suspension composed of EOL cathode material and a small amount of
carbon additives was then centrifuged to separate the cathode materials out. The extracted EOL cathode material was dried and its Li/transition metal (Li/TM) ratio was quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X-Series). The EOL cathode material was mixed with LiOH·H₂O using the agate mortar and pestle. For the amount of LiOH powder added, a mixture with a Li/TM ratio of 1.05 was added for the stoichiometry of final product. The mixtures were pressed into pellets and sintered at 700°C for 6 h under air at a ramping rate of 10 °C/min in a muffle furnace.

The annealed pellets were ground and mixed with other components in NMP to prepare a cathode slurry (80 wt% active material/10 wt% TIMCAL carbon/10 wt% PVDF (MTI corporation). The homogeneous slurry was coated onto an aluminum foil and dried at 100 °C overnight in a vacuum oven. Half coin cells were assembled in an argon-filled glove box with a lithium metal chip as the counter electrode, 1M lithium hexafluorophosphate (LiPF₆) in a mixture of EC and dimethyl carbonate (DMC) with 3:7 volume ratio as the electrolyte, and Celgard 2325 as the separator. Electrochemical tests were performed on LAND battery tester using CR2032 coin cells. The crystal structure of the materials was investigated by X-ray Diffraction (XRD) using a PANalytical X’Pert Pro multipurpose diffractometer equipped with Cu-Kα radiation and X’Celerator detector. The morphology of the samples was examined by Environmental Scanning Electron Microscopy (SEM, FEI Quanta 600 FEG).

3.2 Experiment results of the water-based electrode and the recycled material

3.2.1 Electrochemical performance of pristine materials

Rate capability and cycle life was compared between NMP/PVDF baseline cells and cells with water-processed electrodes (NCM523 cathodes and graphite anodes) with three replicates for both tests. As shown in Figure 23a and 23b, the NMP- and water-processed electrodes exhibited excellent reproducibility and rate performance. When normalized to the capacity at C/20, the rate performance was identical up to 1C. When further increasing discharge rate, the water-based processed electrodes showed slightly lower performance and higher cell to cell variation. A similar phenomenon has been observed with NCM811,
and it was attributed to a difference in binder coverage rather than structural changes to the active material. The cycle life testing shown in Figure 23c was started at 25 °C in an environmental chamber where the temperature was raised to 30 °C later to meet testing requirements for other projects, but the capacity was normalized to the initial value at the same rate. The NMP cells were cycled at 0.2C/-0.2C at 25 °C before the temperature was increased to 30 °C at the 530th cycle, which resulted in a 4% increase in capacity. The water-processed electrodes were cycled at 0.33C/-0.33C to reach 1000 cycles in a shorter time, and it is seen in Figure 23c that their capacity initially faded at a higher rate. However, the fade rate subsequently decreased after 50 cycles, and the capacity retention was the same for both sets of cells at the 668th cycle. Considering the water-based cells were cycled at higher rates, their cycling performance can be considered superior to the NMP-based cells. It was found that the water-based cells retained 80% capacity after 864 cycles.

Cycle life at higher charge/discharge rates was also performed, and it was found that the water-based cells degraded quickly initially and slowed down afterwards, as was the case for the lower cycling rates. The capacity retention was same for both sets of cells after 600 cycles before the temperature was increased to 30 °C for the water-based cells. Based on the trend of the capacity retention curves up to the point of the temperature change, the water-based cells were on track to have better capacity retention through 1000 cycles.
Figure 23. Electrochemical performance comparison. (a) Rate capability of the baseline NMP/PVDF cells; (b) rate capability of the cells with water-processed electrodes; and (c) comparison of cycle life between NMP/PVDF baseline cells and cells with water-process.  

The chemical compositions of the pristine and EOL NCM523 are listed and compared with the target values in Table 9. The Ni fraction was normalized to 0.5 and other elements were scaled by the same factor. The experimental values of the pristine NCM523 agreed well with the target values, which validate the effectiveness of ICP-MS. The EOL NCM shows a ratio of Li to transition metal of 0.687, which was attributed to the capacity fade. In addition, the significant loss in Li content in the EOL sample indicates significant degradation to the NCM cathode.
Table 9. The ICP-MS results for the pristine and EOL NCM523.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Li</th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
<th>Li/Transition Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual</td>
<td>Target</td>
<td>Actual</td>
<td>Target</td>
<td>Actual</td>
</tr>
<tr>
<td>Pristine NCM</td>
<td>0.99</td>
<td>1.000</td>
<td>0.500</td>
<td>0.500</td>
<td>0.204</td>
</tr>
<tr>
<td>EOL NCM</td>
<td>0.684</td>
<td>-</td>
<td>0.500</td>
<td>0.500</td>
<td>0.196</td>
</tr>
</tbody>
</table>

3.2.2 Structure of NCM523

Figure 24 shows the XRD patterns for the pristine NCM523, the Li$_x$Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ EOL LIBs, and recycled NMC523. All materials were indexed to the α–NaFeO$_2$ (space group: R 3m) with no observed impurity peaks. Compared to the pristine material, the merging of the (108) and (110) peaks in the EOL Li$_x$Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ pattern indicated a lithium deficiency and the degradation of the layered structure of the EOL battery cathodes$^{203}$. The (104) peak shifted to a lower angle after cycling corresponding to an increase in the c lattice parameter due to electrostatic repulsion between the oxygen layers in the Li deficient state$^{204}$. The XRD pattern of the recycled NCM523 matched that of the pristine sample, indicating full restoration of the crystal structure. Its XRD pattern shows a higher intensity ratio $I_{003}/I_{104}$ than that of the EOL as well as the pristine material, indicating less Li/Ni cation mixing in the recycled material, which is of great advantage to intercalation/deintercalation of Li-ions and its good electrochemical properties$^{205}$. 
Figure 24. Comparison of XRD patterns for pristine NCM523, Li$_x$Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ in EOL pouch cells, and recycled NCM523.
The SEM images in Figure 25 show the evolution of the cathode materials before and after recycling. Figure 25c and 25d show the EOL cathode materials washed from the current collector, and the observed agglomeration is possibly due to some binder residuals. The recycled materials in Figure 25e and 25f show well-distributed and enlarged particles in contrast to the EOL powder. Compared to the pristine powder shown in the Figure 25a and 25b, the EOL and recycled powders had more small particles, which could be due to the
fracture of secondary particles during calendering and cycling \(^{206}\). This change will likely lower the tap density of powder and affect the quality and performance of the recycled powder. More optimization on the annealing process is required to better reconstruct particle morphology.

3.2.4 Electrochemical behavior

The electrochemical performance of the recycled NCM523 cathode particles was evaluated in the voltage range of 2.7-4.2 V at 0.2C as shown in Figure 26. For direct comparison, a baseline electrode was coated with pristine NCM523 and identical formulation (NMP) and coating process. The recycled NCM523 showed stable cycling and comparable electrochemical performance with that of the pristine one, although its charge-discharge curve indicates higher hysteresis with slightly lower capacity. The irreversible capacity loss is mainly caused by kinetic inhibition except the initial capacity loss \(^{207}\). Therefore, detailed structural characterization and recycling process optimization are needed to further improve the electrochemical performance of the recycled NCM523, but these promising preliminary results demonstrate the feasibility of the direct recycling of the NCM cathode materials. Since the Ni-rich NCM cathodes are less stable in water than Co-rich ones, one of the strategies to optimize the aqueous recycling process is to use high salt concentration aqueous solutions or other solvent during the washing process \(^{208, 209}\).
3.3 Method optimization

The experimental results indicate that it is feasible to develop the direct recycling process for water-based cathode materials although the electrochemical performance can be further improved. From the literature, the immersion of NCM523 material in water for aqueous processing would cause the surface degradation \(^{210}\). The surface lattice structures of NCM523 would suffer from an irreversible transformation from the pristine rhombohedral phase to the mixture of spinel and rock salt phases. The formation of rock salt phase, which is ionically insulating, may result in sluggish kinetics and deteriorates the capacity.
retention. In addition, the water processing or immersion would result in the formation of lithium-based compounds like LiOH and Li$_2$CO$_3$ over the particle surface. The surface compounds would impede the Li-ion de/intercalation and deteriorate the electrochemical performance. In addition, the alkaline pH of the aqueous slurry caused by the surface compounds may result in corrosion of the aluminum collector during coating of the electrode.

The aqueous processing of the electrode washing process in the direct recycling requires the soaking, sonication, centrifuge or filtering separation and drying. To maximumly prevent the material degradation or the formation of the lithium compounds over the particle surface, the process has been optimized by reducing the materials exposure to water. The method is improved by integrating the organic solvent washing process between the centrifuge separation and the drying step. Ethanol or alcohol is employed due to its solubility in water and high volatility. After ethanol wash for several times, the material slurry was nearly dehydrated and the heating process is conducted under the vacuum atmosphere to avoid the further degradation by the moisture. The electrochemical results show an improved capacity as well as first cycle irreversibility, which is better than commercial ones. Figure 27 compares the 1st cycle voltage profile of the recycled NCM523 with the commercial material. The irreversible capacity of the recycled NCM523 material is reduced and the hysteresis or polarization is even lower than commercial powder. In addition, the recycled NCM523 with improved washing process shows higher cycling stability than the water washed material. This result indicates the direct recycling of nickel rich cathode material using water can deliver the regenerated material with competitive performance in contrast to the commercial material.
There are two methods liberating the electrode powder materials from the current collector. The electrode particle can be separated out through the thermal decomposition process to burn off the binder. Alternatively, solvent washing assisted with sonication can be used to dissolve the binder and liberate the electrode particles. To investigate their influence on the surface evolution of NCM523 cathode powder, materials retrieved by both methods were characterized. Figure 28 and Figure 29 illustrate the Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) results of the EOL cathode powder obtained from 400 degree C heating and water washing process respectively. It can be observed that the EOL cathode powder from water washing process has less carbon material than it from 400 °C heating while both samples show similar particle morphology. Since the water washing process with centrifuge separation can partly separate the carbon black from cathode materials.
Figure 28. (a), (b) and (c) SEM images of the EOL NCM523 powder after 400 °C heating in air for 1 hour. (d) EDS mapping of element distribution.
To resynthesize the stoichiometric cathode material, the amount of lithium addition is an important factor for the sintering process. The complicity lies on the fact that lithium is added based on ICP data to quantify the Li/Transition Metal ratio and the lithium will evaporate during the long-time sintering process. Table 10 shows the variation of Li/Transition Metal ratio with the increasing lithium addition. For 850 degree C sintering for 12 hours, the Li/Transition Metal ratio is approaching 1.0 with the increasing of lithium excess from 0% to 10%. The Li/Transition Metal ratio of 1.0 means a stoichiometric resynthesizing and it would be the index to represent the expected element composition.
Table 10. ICP-MS data for different sintering parameters (lithium excess).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li/Transition Metal ratio</th>
<th>Ni</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTI NCM523 powder</td>
<td>1.0</td>
<td>5</td>
<td>1.99</td>
<td>2.85</td>
</tr>
<tr>
<td>850C 12h sintered NCM523 with 0% Li excess</td>
<td>0.913</td>
<td>5</td>
<td>2.10</td>
<td>2.86</td>
</tr>
<tr>
<td>850C 12h sintered NCM523 with 2% Li excess</td>
<td>0.930</td>
<td>5</td>
<td>2.15</td>
<td>2.85</td>
</tr>
<tr>
<td>850C 12h sintered NCM523 with 5% Li excess</td>
<td>0.952</td>
<td>5</td>
<td>2.09</td>
<td>2.91</td>
</tr>
<tr>
<td>850C 12h sintered NCM523 with 10% Li excess</td>
<td>0.995</td>
<td>5</td>
<td>2.03</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Figure 30. The ThermalGravimetric Analysis of the aqueous EOL NCM523 through 400°C heating and water wash under oxygen or nitrogen atmosphere.

Figure 30 indicates the Thermal Gravimetric Analysis of the aqueous EOL NCM523 through 400 °C heating and water wash under oxygen or nitrogen atmosphere. It can be concluded that the thermal stability of NCM523 in nitrogen should be worse than that of in oxygen atmosphere. It may be caused by the fact that oxygen-free environment provides kinetics for oxygen release to form the oxygen non-stoichiometry material. The oxygen
deficiency is responsible for the instability during heating process and generating oxygen and resulting in the weight loss. The future work requires the comprehensive characterizations on those sample materials including X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM) and Raman spectroscopy to investigate the surface evolution and the influence of different processes.

In conclusion, the direct recycling process for the water-based cathode material has been improved using the optimized method. The ethanol washing process helps reduce the exposure of NCM523 powder to the water and enhances the electrochemical performance. Two methods liberating the electrode powder materials from the current collector are considered. Powder sample from these two methods show similar morphology in SEM images. The oxygen-free environment during the heating process triggers the oxygen release and leads to the weight loss.

3.4 Preliminary study of the anode graphite recycling

In the direct recycling process, the anode graphite needs to be separated from cathode material. Graphite in anode will be the byproduct when the cathode metal oxide is obtained in the direct recycling process. Based on the literature review, the preliminary experiment is conducted to synthesize value added product graphene. The spent battery is fully shorted, the anode electrodes are separated and rinsed in DMC to remove the remaining electrolyte. Graphite powder is obtained from copper substrate by sonicating in deionized water followed by centrifuge. As shown in the Figure 31, the graphite powder from EOL LIBs keep the original morphology.
Following the Hummer’s method$^{213}$, the graphite oxide (GO) is synthesized from the spent graphite (SG). The NaNO$_3$, KMnO$_4$ and Concentrated H$_2$SO$_4$ are used to oxidize the SG. Additional water and 30% H$_2$O$_2$ are added to obtain the GO powder. The GO powder is then reduced to the reduced graphite oxide (rGO) using Vitamin C as the reducing agent. After washing several times, the rGO can be extracted through centrifuge and vacuum drying. Figure 32 shows key experiment steps of the oxidation and reduction reactions.

Figure 32. (a) The solution turned brown after the oxidation process. (b) The solvent turned black during the reduction process.
The characterization is carried out for the SG, GO and the rGO. According to the XRD pattern in the Figure 33, the unchanged diffraction peaks of graphite after battery cycling means the SG keeps the original crystal structure. The peaks of the GO and rGO are consistent with the literature results. These results prove that the graphene is successfully synthesized. Furthermore, to prove the single or few layer structure of the synthesized graphene, the Transmission Electron Microscope (TEM) is conducted for the rGO sample. As shown in the Figure 34, the TEM images represent that the rGO sample is typically in the structure of thin layer. It can be observed that some of the sheets are folded together while some wrinkles exist in the sample. From the preliminary experiment results, synthesizing the graphene using the spent graphite anode is a feasible route to recycle and reuse the graphite material.
3.5 Conclusions

A green manufacturing and direct recycling process are proposed where the organic NMP solvent is replaced by water during electrode fabrication and recovery of black mass during battery recycling. It is demonstrated that the water-processed electrodes exhibit comparable electrochemical performance to the ones from NMP-based processing. The cathode powder is successfully recovered from the spent electrodes, relithiated and restored to stoichiometry, delivering comparable capacity to the pristine material. While there are still many challenges remained to be resolved, this process provides a potential path toward green and sustainable manufacturing of LIBs, which enables lower battery cost and much less environmental impact.

Figure 34. The TEM images of the synthesized graphene material (rGO).
Chapter 4 - Scaling up the direct recycling of cathode material

In this chapter, a scalable direct recycling approach relithiation thermal synthesis (RTS) is developed which is simple and non-destructive to generate the high-capacity cathode materials with great cycling performance. LiOH·H$_2$O is served as the lithium replenisher and react with lithium deficient Li$_x$CoO$_2$ in the high temperature to generate the cathode material with desired stoichiometry. In contrast with the Li$_2$CO$_3$, the LiOH is dissolvable in water. Hence, the Li$_x$CoO$_2$ powder mixing with LiOH solution can achieve the more homogeneous particles with well distributed LiOH. In addition, the melting point of LiOH is around 450°C, which is close to the decomposition temperature of the PVDF binder. The liquated LiOH could further spread over the particles to tie up the cathode particles. The HF formed during the heat treatment would be captured with LiOH before it reacts with the surface of the cathode particles. In addition, to optimize the condition for the sintering process, the lab scale experiments are explored to validate the temperature and lithium addition issue. Then the pilot test is executed to scale up the approach. Some improvement measures like the air flowing to the furnace, the two-step powder mixing process are also adopted to form the uniform powder material with high crystallinity and correct stoichiometry. The properties of the restored LCO are characterized. It shows that the LCO recycled from spent LIBs has the comparable properties with the commercial LCO. This method successfully realizes the direct regeneration of LCO in Kg-level and plays a guiding role for the mass production of direct recycling in industry.

4.1 Lab scale experiment of LiCoO$_2$ direct recycling

4.1.1 Battery deactivation and separation

The spent batteries from drones were collected and the modules were manually dismantled into pouch cells. A novel shorting method was used to fully release the residual energy of the cell. The discharge platform was made by mixing the graphite flakes with oil in proper ratio. Dipping the cell leads into the conductive slurry, for only 6 hours, the cell can be fully shorted from 3.7V to 0.5V. Compared with the brine shorting method, this non-
volatile graphite slurry can achieve fast shorting, reuse, avoiding the leads corrosion and cell leakage. Furthermore, the anode graphite material from spent LIBs can be directly reutilized to build up the shorting platform which is a potential route to realize the anode recycling.

The separated LCO cathode sheets are washed assisted with sonicating in the NMP. The LCO active material and conductive carbon black are separated from the aluminum substrates and LCO powder in the obtained suspension would precipitate to the bottom of the tank as the LCO powder has four times more density than NMP. Pumping out the upper NMP liquid and drying the bottom precipitation, the EOL Li$_x$CoO$_2$ powder can be collected. Thermogravimetric analysis was tried to quantify the impurities like polymer binder and carbon in the powder material.

4.1.2 The mechanical separation of cathode powder from aluminum substrate

To investigate the optimized parameters to efficiently separate the cathode powder from the aluminum substrate, a systematic study is conducted to wash off the cathode using mechanical method. The variable speed mixer with the PTFE blender is used to agitate the aluminum sheets without striking them like the stir bar is doing. The idea with the stirring is to create a downward flow pattern that then mixes the aluminum sheets. The experiment device is depicted in the Figure 35.
Figure 35. (a) The EOL cathode sheet after being shredded into 1cm square flakes. (b) The variable speed mixer to separate the cathode powder from aluminum sheet using NMP solvent.

To begin with, the cathode flakes are uniformly mixed and sampled for the benchmark group. This group of flakes is weight and the coating material was manually wiped off, leaving the clean aluminum substrate for mass measurement. The mass ratio of the latter one over the former part would be the ideal ratio of the 100% separation efficiency. Based on this data, the ratio obtained from the following experiments can be compared with it for evaluation. The weight of the cathode coating accounts for 87.4% of the total electrode sheet.

Several parameters are tested including the liquid/solid ratio, size of the flakes, solvent temperature, stirring speed and time duration, etc. The beaker used for container is a typical cylinder-shaped which is suitable to scale up. Table 11 compares the washing efficiency of different height of the blender. The experiments are conducted with the constant stirring speed (1000rpm), same time duration (10 minutes) at 35 °C. The electrode flakes are cut into 1*1 cm².
Table 11. The cathode powder separation efficiency comparison for different height of stirrer

<table>
<thead>
<tr>
<th>The height of stirrer (cm)</th>
<th>Mass before stirring (m₁/mg)</th>
<th>Mass after stirring and drying (m₂/mg)</th>
<th>The separation efficiency (m₁-m₂)/m₁*0.874</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>896</td>
<td>473</td>
<td>54%</td>
</tr>
<tr>
<td>2</td>
<td>930</td>
<td>280</td>
<td>80%</td>
</tr>
<tr>
<td>1.5</td>
<td>915</td>
<td>165</td>
<td>94%</td>
</tr>
<tr>
<td>1</td>
<td>966</td>
<td>190</td>
<td>91%</td>
</tr>
<tr>
<td>0.5</td>
<td>940</td>
<td>231</td>
<td>86%</td>
</tr>
<tr>
<td>Theoretical separation</td>
<td></td>
<td></td>
<td>100%</td>
</tr>
</tbody>
</table>

It can be observed that the washing separation process reaches the highest efficiency when the height of the blender is at the 1.5cm above the bottom of the beaker. Meanwhile it provides the integrated aluminum sheets without being damaged or curled. Besides, the size of the sheet has also been investigated based on the previous optimized condition. Table 12 lists the experiment results for the separation performance of different size of sheet. The experiments are conducted with the constant stirring speed (1000rpm), same time duration (30 minutes) at 35 °C. The electrode flakes are cut into 1*1 cm².

Table 12. The cathode powder separation efficiency comparison for different size of the cathode sheets

<table>
<thead>
<tr>
<th>Size of sheet</th>
<th>Mass before stirring (m₁/mg)</th>
<th>Mass after stirring and drying (m₂/mg)</th>
<th>The separation efficiency (m₁-m₂)/m₁*0.874</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5*0.5cm</td>
<td>975</td>
<td>189</td>
<td>92%</td>
</tr>
<tr>
<td>1*1cm</td>
<td>982</td>
<td>140</td>
<td>98%</td>
</tr>
<tr>
<td>2*2cm</td>
<td>1743</td>
<td>289</td>
<td>95%</td>
</tr>
<tr>
<td>Theoretical separation</td>
<td>1202</td>
<td>151</td>
<td>100%</td>
</tr>
</tbody>
</table>
From the results listed above, we can conclude that the 1*1 cm flakes had the best separation performance. Meanwhile, the stirring speed is studied ranging from 800 to 1500 rpm. To shorten the time consumption, it only took 10 minutes for each batch. All other parameters are kept unchanged. Table 13 lists the experiment results of the separation performance under different stirring speed. The experiments are conducted with the constant stirring speed (1000 rpm), same time duration (10 minutes) at room temperature (around 15 °C). The electrode flakes are cut into 1*1 cm².

<table>
<thead>
<tr>
<th>Stirring speed (rpm)</th>
<th>Mass before stirring (m₁/mg)</th>
<th>Mass after stirring and drying (m₂/mg)</th>
<th>The separation efficiency (m₁-m₂)/m₁*0.874</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1036</td>
<td>694</td>
<td>38%</td>
</tr>
<tr>
<td>1000</td>
<td>892</td>
<td>447</td>
<td>57%</td>
</tr>
<tr>
<td>1200</td>
<td>1047</td>
<td>489</td>
<td>61%</td>
</tr>
<tr>
<td>1400</td>
<td>1080</td>
<td>631</td>
<td>47%</td>
</tr>
<tr>
<td>1500</td>
<td>1055</td>
<td>674</td>
<td>41%</td>
</tr>
</tbody>
</table>

Theoretical separation 100%

From the experiment results, it can be concluded that the separation performance would reach the maximum point when the stirring speed is at around 1200 rpm. The reason is that the lower speed could not generate enough wave impact to peel off the powder material from aluminum sheet while the cathode flakes would collide the inner face of the beaker to become curled if the stirring speed is too high. Therefore, the medium speed at around 1200 rpm would be the best parameter. Furthermore, the stirring time duration is also investigated to explore the plateau where the efficiency did not change with the increasing of time. Table 14 below lists the experiment results of the separation performance for different stirring time duration. The experiments are conducted with the constant stirring speed (1000 rpm) at 35 °C. The electrode flakes are cut into 1*1 cm².
Table 14. The cathode powder separation efficiency comparison for different stirring time duration

<table>
<thead>
<tr>
<th>Stirring time (minutes)</th>
<th>Mass before stirring (m₁/mg)</th>
<th>Mass after stirring and drying (m₂/mg)</th>
<th>The separation efficiency ((m₁-m₂)/m₁*0.874)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>947</td>
<td>241</td>
<td>85.3%</td>
</tr>
<tr>
<td>15</td>
<td>892</td>
<td>176</td>
<td>91.8%</td>
</tr>
<tr>
<td>20</td>
<td>874</td>
<td>160</td>
<td>93.7%</td>
</tr>
<tr>
<td>30</td>
<td>939</td>
<td>148</td>
<td>96.5%</td>
</tr>
<tr>
<td>40</td>
<td>962</td>
<td>145</td>
<td>97.1%</td>
</tr>
<tr>
<td>50</td>
<td>943</td>
<td>142</td>
<td>97.1%</td>
</tr>
</tbody>
</table>

Theoretical separation 100%

Based on the experiment results above, it can be observed that the separation efficiency is approaching the stable plateau when the time duration was above 30 minutes. It means that the time duration would only influence the results in the first half hour. The washing efficiency may reach its limitation if other conditions stayed unchanged. It is believed that the higher temperature is conductive to dissolve the binder and wash off the powder material. For security, the temperature is strictly controlled to be under 50 °C since the flash point of NMP is not too high (around 90 °C)\(^{215}\). To avoid the evaporation of the NMP solvent during the heating, the aluminum cup is made to cover the beaker and the whole device should be conducted in the ventilated hood.
In summary, the optimized condition for the cathode powder separation would be the 1.5cm height of the blender, 1200rpm and 30-minute stirring under elevated temperature. The efficiency can be as high as 98% which means nearly all the powder material can be collected while the aluminum sheet is clean to use. This systematic investigation provides a simple and effective method to separate out the cathode powder from the aluminum sheet. The design of the apparatus demonstrates a model which can be scaled up for industrial use of the battery direct recycling. For the aluminum sheets after washing, Figure 36 demonstrates their shape and surface morphology for different experiment conditions. The effective separation leads to the sliver surface of without black powder attached.

4.1.3 The novel relithiation thermal synthesis process

The proper amount of LiOH·H₂O is dissolved in the water to form the concentrated LiOH solution and spent cathode material powder is added into agate mortar for fully blending. More ethanol is employed to adjust the thickness of the slurry. Assisted by stirring and heating, the liquid evaporates while the LCO powder is uniformly covered with LiOH film. Then the relithiated LCO is pressed into pellets followed by sintering process at different temperatures for 12 hours with a ramping rate of 5°C min⁻¹. Figure 37 illustrates the whole process of direct regeneration of cathode material by RTS method.
Figure 37. Process flow chart for the close-loop recycling process by RTS method.

4.1.4 Material characterization and method analysis

The morphology of the LCO powder is observed by using an SEM (FEI Quanta 600 FEG). By X-ray Powder Diffraction method, the powder crystal structure was examined employing Cu, Kα radiation. The element type of the cathode material is identified by Handled X-ray Fluorescence Analyser (HITACHI X-Met8000). The compositions of Li and Co was quantified by using Inductively Coupled Plasma-Mass Spectra (ICP-MS, Thermo Electron X-Series). To evaluate the electrochemical performance, the regenerated LCO and commercial LCO powder are mixed with Timical carbon in 5 wt% PVDF/NMP solution at the active material of 80 wt%. The well-mixed slurry is casted on aluminum foils using doctor blade followed by drying at oven for overnight. The electrode discs are cut in diameter of 0.5 inch with the mass density of around 10mg cm⁻².
The well prepared cathode material serves as the cathode to assemble the 2032-type coin cells with the lithium metal foil as the anode, 1M LiPF6 salt dissolved in the electrolyte of diethyl carbonate and ethylene carbonate (DEC:EC = 1:1 wt). The Celgard membrane was used for the separator. The coin cells are made under argon filled glovebox and cycling tested using LAND tester. Two voltage ranges are tested: 3-4.2V and 3-4.45V. The cells go through the formation process under current rate of C/5 for two cycles and then 1C rate test for the rest.

4.2 Optimization of the direct recycling process for scaling up

4.2.1 Mechanism of Relithiation Thermal Synthesis of the LCO

The mechanism of the capacity decay of LCO/graphite cell system is mainly caused by the loss of active lithium inventory and the lithium plating on the surface of electrode during the cycling life. Meanwhile the power fade happens to the high-power battery accompanied with the impedance rise. For the re-lithiation and sintering process, it is speculated that the following reactions would occur:

\[
Li_xCoO_2 + (1 - x)LiOH + \left(\frac{1-x}{2}\right)O_2 \rightarrow LiCoO_2 + \frac{1-x}{2}H_2O
\]

\[
Li_xCoO_2 \rightarrow \frac{1-x}{3}Co_3O_4 + xLiCoO_2 + \frac{1-x}{3}O_2
\]

\[
4Co_3O_4 + 12LiOH + O_2 \rightarrow 12LiCoO_2 + 6H_2O
\]

Where \(x\) (0.5<\(x\)<1) is the mole number of Li in the cathode. \(Li_xCoO_2\) starts to release oxygen at 220°C and forms \(Co_3O_4\), which later reacts with \(LiOH\) to form LCO again. The RTS process can replenish the Li-ions loss to reach the stoichiometric ratio of material and eliminate the structure defects.
4.2.2 Factors on Relithiation Thermal Synthesis of the LiCoO$_2$

*Lithium addition factor.*

In order to investigate the impact of the amount of lithium excess addition on the properties of recycled cathode material, three groups of the pelletized LCO after re-lithiation are sintered under 900°C for 12 hours in the air. (Li/Co ratios were of 0% excess LCO, 2% excess LCO and 5% excess, abbreviated as 0%E LCO, 2%E LCO and 5%E LCO respectively) Excessive lithium is added to investigate and make up the lithium loss due to evaporation during the high temperature sintering process. After regeneration, the Li/Co ratios were 0.986, 1.007 and 1.021 for each group respectively, which increases with the increasing initial lithium addition and the 2%E LCO has the Li/Co ratio closing to the stoichiometry.

The electrochemical and cycling test results for LCO regenerated with different lithium addition are presented in the Figure 38. The initial discharge capacities for 3-4.2V under C/5 rate for 0%E LCO, 2%E LCO and 5%E LCO are 152.7, 148.0 and 142.9 mAh/g, while it for commercial sigma LCO was 145.5mAh/g. For 3-4.45V cycling, the first cycle discharge capacity under C/5 rate for 0%E LCO, 2%E LCO and 5%E LCO were 190.8, 190.6 and 185.4mAh/g, while it for commercial sigma LCO is 186.1mAh/g. For the 1C rate cycling performance, the 2%E LCO performs the best stability in 3-4.2V and it can realize the 80% capacity retention after 230 cycles. It proves the better rate performance of the regenerated LCO than it of the commercial one. Combining with other characterization results, the detailed results for samples regenerated from different experiment conditions are analyzed.
Figure 38. The charge/discharge voltage profiles of sintered recycled cathode materials with 0%, 2% and 5% Li excess and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 0%, 2% and 5% Li excess and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.

Temperature factor

For the optimized sintering temperature to resynthesize the LCO, the pelletized LCO after re-lithiation (2%E LCO) were sintered at 750°C, 850°C and 900°C for 12 hours in air (abbreviated as 750C LCO, 850C LCO and 900C LCO) with other condition unchanged. The results show that the Li/Co ratios of 750C LCO, 850C LCO and 900C LCO are 1.019, 1.012 and 1.007. The Li/Co in the final sintered products decreases with the increasing sintering temperature, indicating that more lithium or lithium-compounds are evaporated at higher sintering temperature. The electrochemical performance for samples with
different conditions of sintering temperature is compared in the Figure 39. The initial discharge capacities under C/5 rate for 750C LCO, 850C LCO and 900C LCO were 149.8, 145.6 and 146.1 mAh/g for 3-4.2V, while it for commercial sigma LCO is 145.5mAh/g. For 3-4.45V cycling, the first discharge capacity under C/5 rate for 750C LCO, 850C LCO and 900C LCO are 185.3, 185.7 and 190.6mAh/g, while it for commercial sigma LCO is 186.1mAh/g. The 1C cycling data showed that 850C_LCO had better cycling performance between 3-4.45V.

Figure 39. The charge/discharge voltage profiles of sintered recycled cathode materials with 750C, 850C and 900C sintering and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 750C, 850C and 900C sintering and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.
4.2.3 Product characterization for lab scale

The regenerated material from all the groups of samples are characterized. Table 12 lists the Li/Co elemental ratio based on the ICP-MS element quantification test. The lattice parameters of recycled LCO from different experimental conditions are also included. The XRD pattern in Figure 40 indicates that the Li₄CoO₂ powder still maintains a crystal structure although its peaks are not as sharp as regenerated material. All the samples could be indexed to the α–NaFeO₂ (space group: R3m) with no observed impurity peaks. The 003 peak shifts to the lower angle after cycling, corresponding to an increase in the c lattice parameter due to electrostatic repulsion between the oxygen layers along c directions in the lithium deficiency state. The 003 peak shifts back toward higher angles after regeneration, with decreased lattice a and c, which means the tighter packing of atoms and the recovery of the pristine crystal structure.

The scan electron microscopy images of the recycled LCO particle morphology are displayed in Figure 41. It can be observed that the morphology of the LCO powders keeps in consistent with samples regenerated under different conditions, except for the one with excessive 5% Li addition (Figure 41d). It proves that too much lithium may cause the particle agglomeration. The Figure 41e, f and c demonstrate that increasing the sintering temperature in air results in an expected increase of shrinkage, decrease of porosity and specific surface area, which is consistent with the literature. In addition, there are some small particles (residual Li₂O) attached to the surface of the EOL LCO, but these small particles decrease gradually after sintering. As the calcination temperature rises to 850°C, there small particles disappear completely.

The electrochemical performance of the regenerated LCO samples under different conditions are also compared (Figure 38 and Figure 39). It shows that the LCO sintered with 2% excess Li performed the best stability in 1C cycling among all the tested cells. The first discharge capacity is higher than commercial LCO in both 3-4.2V or 3-4.45V voltage range. It is worth noting that the sintered LCO with 5% lithium excess shows the inferior cycling performance in both discharge capacity and cycling stability. That’s because too much excessive lithium may cause the agglomeration in part of the particles, which deteriorates the electrochemical performance. The regenerated LCO sintered with
0% excess Li still shows slight lithium deficiency from ICP result. The lithium deficient particle may have intercalation reaction when the counter electrode supplies enough Li-ions. The performance would be worse if it is in the full cell. Hence, the improved capacity and cycling stability in the half cell are not convincing.

For the temperature factor, the 850°C sintered LCO shows the best cycling stability in 3-4.45V under 1C rate. This result also corresponds to the literature for LCO synthesis that calcination at high temperature >800°C is required to produce High Temperature LCO, which possesses alternating planes of Co$^{3+}$ and Li$^+$ cations in the hexagonal ABCABC oxygen packing, providing superior electrochemical properties in LIBs. Also in another literature, 850°C calcination for more than 12 hours would be the optimal parameters which can regenerate LCO material since it supplies the optimized diffusion property. This conclusion also proves the facticity of our work. The enlarged XRD pattern (Figure 40(c)) indicates the 850 E_LCO owns the sharp 104 peak with narrowest full width at half maximum (FWHM), which is also described in the literature that the decreases of FWHM reflect the increased crystallinity.

Lithium deficient Li$_x$CoO$_2$ also accompanies with phase transitions during cycling. For 3-4.2V cycling, layered LCO transforms to cubic spinel LiCo$_2$O$_4$ when x varies between 0.5 and 1.0. The spinel Co$_3$O$_4$ is also formed besides LiCo$_2$O$_4$ when the x is lower than 0.5. The deterioration of high polarization that would result in the capacity fading is associated with the phase transition to form the low Li-ions conductivity of the spinel LiCo$_2$O$_4$ and Co$_3$O$_4$ phases. Furthermore, the slight dissolution of cobalt happens when the Li$_x$CoO$_2$ is charged beyond 4.2V vs. Li/Li$^+$. As a result, the rigorous 3-4.45V cycling can reflect more characteristics of the material than 3-4.2V cycling. Nearly all the regenerated LCO material exhibits the better cycling stability than the commercial LCO. That’s because the smaller particle size of distribution makes for a better rate performance. Our recycling approach well maintains the original morphology of the cathode material after regeneration and the particle size ranges less than 10µm while it of commercial powder is 15-25 µm (Figure 41).
Figure 40. The XRD patterns of EOL cathode material, commercial LCO from Sigma and the recycled LCO (a) with different Li addition and sintering temperatures in the lab scale, (b) and (c) the enlarged view of Figure (a) for lab scale experiment. (d) The 0% excess Li addition sintered LCO in pilot experiment batch, (e) and (f) the enlarged view of Figure (c).
4.2.4 Liquid leaching for impurity removal

Water or acid leaching

The water or acid leaching after sintering process has been investigated to explore the method eliminating the residual lithium. It would be useful when the lithium addition is superfluous. Theoretically, the extra lithium would remain on the surface of the recycled cathode powder as the lithium salt. Li$_2$CO$_3$ is partially soluble in water and the weak acid can easily clear up the excessive lithium. Therefore, I tried to wash the LCO with water or acetic acid and tested the electrochemical performance of processed material. The cathode material is identified as Li$_{x}$CoO$_2$ (LCO) by ICP-MS where the Li/Co ratio is around 0.93. In order to investigate the impact of the water/acid washing on the final recycled products, the EOL cathode material Li$_{x}$CoO$_2$ is first mixed with LiOH using water and ethanol with the mole ratios of LiOH/Li$_{x}$CoO$_2$ to be 13%. Then the powder mixture is sintered at 850 °C for 12 hours in air (abbreviated as 13% LCO). Then the powder is washed by water and 5 vol% acetic acid respectively. The ICP results show that the Li/Co ratios of the 13% LCO, water washed 13% LCO and acid washed 13% LCO are 1.066, 1.022 and 0.97. This result indicates that the acid leaching makes for eliminating the residual lithium salt. To
resynthesize the LCO of stoichiometry, the experiments need to be improved by optimizing the concentration of the acid and the liquid/solid ratio during the leaching process.

Figure 42. The XRD patterns of EOL cathode materials, sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma.
Figure 43. The charge/discharge voltage profiles of sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials with 13% Li addition, water/acid washed 13% sintered LCO and as-purchased LCO from Sigma at 1C rate between (c) 3-4.2V and (d) 3-4.45V.

From the electrochemical data and 1C rate cycling results in Figure 43, the recycling material after washing process, either by water or acid, would have the better cycling stability than powder without washing, even better than commercial ones. Combining with ICP and XRD results, the washing process did help improve the properties of material. But it does not fully replenish the defects as the performance was not perfect enough. To optimize the recycling process, the systematic research is required to dig into parameters including the sintering temperature, time duration, water or acid washing procedure, acid
concentration and excessive amount of lithium, etc. It is known that the synthesis of the cathode material of lithium metal oxide includes the sintering process to synthesize the lithium salt with metal oxide. Normally the excess lithium will be added to ensure all the lithium vacancies can be filled in and compensate the evaporation loss during high temperature sintering. For the lithium remained in the particles, engineers may wash the synthesized powders with water to remove the extra lithium and adjust the pH followed by the second calcination process to finalize the product. To comprehensively restore and regenerate the cathode material in the direct recycling process, water or acid wash is a feasible measure to exclude the impurities and improve the quality of material. Except for the acid wash, the alkali leaching is also useful to remove the impurities in battery recycling. For example, the strong alkali like sodium hydroxide can dissolve and leach out the impurity aluminum from cathode materials \(^{224,225}\).

*Ammonia leaching*

One of the barriers of the direct recycling process is the cross contamination between the cathode and anode materials. To regenerate the cathode metal oxide, the contamination of copper from the anode substrate would deteriorate the properties as well as performance. Currently, the recycling of LIB employs the mechanical dismantling tools for crushing the cells and reducing their size \(^{226-229}\). The debris of current collector may mingle with the cathode materials and an effective method is needed to purify the metal debris. Ammonia is an effective solvent which can capture the copper to clean up the impurities \(^{230-232}\). The equations below explain the mechanism of ammonia leaching of copper:

\[
Cu + \frac{1}{2}O_2 = CuO \quad (4.4)
\]

\[
2Cu + \frac{1}{2}O_2 = Cu_2O \quad (4.5)
\]

\[
Cu_2O + 2NH_3 + H_2O = 2Cu(NH_3)^{2+} + 2OH^- \quad (4.6)
\]

\[
CuO + 4NH_3 + H_2O = Cu(NH_3)_4^{2+} + 2OH^- \quad (4.7)
\]
The experiments are conducted using 3 wt% ammonia solution to leach the cathode powder recovered from spent battery. The EOL LCO powder was mechanically cut followed by separation process. One batch of the powder (sample 7) went through the NMP wash to obtain the LCO powder while the second batch (sample 1-6) was from the previous batch but a 1-hour 500 °C heating process in air was added. The powder before and after ammonia leaching are analyzed by X-ray fluorescent (XRF) analyzer to quantify the impurity content.

Table 15. The element content for the LCO powder before and after ammonia leaching m.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature</th>
<th>Air flow</th>
<th>Co (wt%)</th>
<th>Al (wt%)</th>
<th>Cu (wt%)</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder before leaching</td>
<td>81.9%</td>
<td>3.9%</td>
<td>13.22%</td>
<td>EOL LCO powder from NMP wash, 500 °C heating in air and ball milling of electrode flakes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30 minutes</td>
<td>RT</td>
<td>NO</td>
<td>88.21%</td>
<td>2.64%</td>
<td>8.63%</td>
</tr>
<tr>
<td>2</td>
<td>60 minutes</td>
<td>RT</td>
<td>NO</td>
<td>89.93%</td>
<td>2.72%</td>
<td>6.84%</td>
</tr>
<tr>
<td>3</td>
<td>60 minutes</td>
<td>RT</td>
<td>YES</td>
<td>90.75%</td>
<td>2.66%</td>
<td>6.23%</td>
</tr>
<tr>
<td>4</td>
<td>90 minutes</td>
<td>RT</td>
<td>NO</td>
<td>92.68%</td>
<td>1.96%</td>
<td>5.13%</td>
</tr>
<tr>
<td>5</td>
<td>90 minutes</td>
<td>60C</td>
<td>NO</td>
<td>91.91%</td>
<td>2.05%</td>
<td>5.16%</td>
</tr>
<tr>
<td>6</td>
<td>60 minutes</td>
<td>RT</td>
<td>NO</td>
<td>91.17%</td>
<td>1.84%</td>
<td>6.65%</td>
</tr>
<tr>
<td></td>
<td>wash twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powder before leaching</td>
<td>94.12%</td>
<td>1.14%</td>
<td>3.14%</td>
<td>EOL LCO powder from NMP wash</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60 minutes</td>
<td>RT</td>
<td>NO</td>
<td>98.06%</td>
<td>0.92%</td>
<td>0.17%</td>
</tr>
</tbody>
</table>

The experiment data was summarized in the Table 15. It can be concluded that limited amount of copper impurity in cathode metal oxide material can be leached out using ammonia leaching. For example, the sample 7 with around 3 wt% of copper impurities can be completely removed. Comparing sample 2 with the sample 3, it can be observed that the air flow does not greatly influence the leaching efficiency although the mechanism equations indicate the oxygen is involved in the reaction. In addition, by comparing
between the sample 1 and 4, it can be concluded that increasing the time duration from 30 minutes to 90 minutes can further reduce the copper content. These results prove the feasibility of the method to remove the copper impurity in LCO cathode. However, one thing needs to be noted that the leaching may lose effect when the EOL cathode flakes have already gone through the high temperature heat treatment. Although the heating process would help separate the cathode powder materials from the aluminum substrate, it may also cause the phase transition of the cobalt which leads to the cobalt dissolving during the ammonia leaching process.\textsuperscript{233}

4.3 Pilot scale experiments and assessment

4.3.1 Product characterization for pilot scale

The XRD pattern in Figure 41 demonstrates that the better crystallization has been formed after regeneration with 2-step mixing. The decreased $a$ and $c$ as well as the FWHM signify the tighter packing of atoms compared with the EOL cathode material, which confirms the increased crystallinity. The SEM images clearly display the morphology and particle sizes of the sintered sample (Figure 44). The rough surface with some groups of particle aggregation was shown in the Figure 44 (b). That is caused by the inhomogeneity of sintering condition as the bottom part of the 500g powder bears higher pressure than the upper part. Higher pressure between powders would reduce the particle spacing and then improve the Li-ions diffusion but also results in the excessive growth of the particle in the bottom of the crucible. When the material is sintered twice with double mixing, the better morphology and electrochemical performance are exhibited that the particle size in the Figure 44 (c) is relatively smaller than Figure 44 (b) meanwhile the particle shows clean and smooth surface. The ICP data also proves the advancement of the method. The Li/Co ratio for the one-time sintering sample is 1.012 while it of the twice mixing sintering is 1.005, which is nearly in stoichiometric. Therefore, the twice mixing strategy does improve the quality of the LCO while it also provides the constructive thought to increase the uniformity of the lithium diffusion by using stirring apparatus or the rotating furnace.
Figure 44. The SEM images of (a) EOL cathode materials, (b) 500g large batch sintered LCO under 850°C with 0% of excessive lithium, (c) 500g large batch, 500°C heated&mixed and 850°C sintered LCO with 0% Li excess. (d) commercial sigma LCO.
Table 16. The element ratio and lattice parameters of the regenerated sample under different conditions.

<table>
<thead>
<tr>
<th>Batch</th>
<th>Sample</th>
<th>Li/Co ratio</th>
<th>(a)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab scale</td>
<td>EOL Li(_x)CoO(_2)</td>
<td>0.89</td>
<td>2.7845</td>
<td>14.0650</td>
</tr>
<tr>
<td></td>
<td>Commercial LiCoO(_2)</td>
<td>1.0</td>
<td>2.8398</td>
<td>14.0305</td>
</tr>
<tr>
<td></td>
<td>750 °C 2% lithium excess</td>
<td>1.016</td>
<td>2.7874</td>
<td>14.0164</td>
</tr>
<tr>
<td></td>
<td>850 °C 2% lithium excess</td>
<td>1.012</td>
<td>2.7932</td>
<td>13.9572</td>
</tr>
<tr>
<td></td>
<td>900 °C 2% lithium excess</td>
<td>1.007</td>
<td>2.7939</td>
<td>13.9498</td>
</tr>
<tr>
<td></td>
<td>900 °C 0% lithium excess</td>
<td>0.986</td>
<td>2.7863</td>
<td>14.0179</td>
</tr>
<tr>
<td></td>
<td>900 °C 5% lithium excess</td>
<td>1.021</td>
<td>2.7849</td>
<td>14.0157</td>
</tr>
<tr>
<td>Pilot scale</td>
<td>EOL Li(_x)CoO(_2)</td>
<td>0.93</td>
<td>2.8147</td>
<td>13.9846</td>
</tr>
<tr>
<td></td>
<td>0% lithium excess, double mix</td>
<td>1.005</td>
<td>2.8173</td>
<td>13.9574</td>
</tr>
<tr>
<td></td>
<td>0% lithium excess</td>
<td>1.012</td>
<td>2.8352</td>
<td>13.9569</td>
</tr>
</tbody>
</table>

4.3.2 The improved relithiation thermal synthesis process of the LCO in pilot scale

When directly scaled up to the pilot scale (kg level per batch), the 850°C pellet sintering with 2% of excessive Li could not produce the LCO powder as good quality as 10g batch. As shown in the Figure 45, the first discharge capacity for 3-4.2V cycling is only 90 mAh/g which is much lower than theoretical capacity of the LCO (140mAh/g). Meanwhile the 3-4.45V discharge capacity is still low either. The sintering condition desiderates the improvements to satisfy the large-scale sintering needs.
Figure 45. The charge/discharge voltage profiles of the 850°C 2% lithium excess sintered recycled cathode materials in small batch (black line) and pilot large batch (red line) sintering and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V.

Compared with lab scale sintering, the large pellet is much thicker and it would impede the air from penetrating into the material. Then the anaerobic condition is formed which may cause the redox reaction between graphite and LCO under high temperature \(^{234}\). That is why the sintered pellet was too tough to crack. Hence, the large batch sintering requires the loose powder format with abundant passway for air diffusion rather than compact pressed pellet. The powder in the crucible is scratched into small grids which can create enough space for air permeation. In addition, the compressed air is aerated into the muffle furnace to supply sufficient air atmosphere for crystallization reaction. Furthermore, the evaporation loss can be ignored in the scale-up calcination. Hence, no excessive lithium is added in the large batch powder sintering process with air flowing.

In the Figure 46, it can be observed that the 1\(^{st}\) cycle discharge capacity of the regenerated cathode material is 149.7 and 186 mAh/g for 3-4.2V and 3-4.45V respectively. However, further improved is required since the capacity retention is below 80% after 80 cycles in 1C rate. Another issue for the scaled-up sintering process, is the powder homogeneity in terms of the Li/Co ratio and the particle size distribution. As the particle spacing in the powder sintering is larger than it in pellet, lithium diffusion and distribution should be less sufficient than lab scale pellet sintering. For a more even product, the LCO after mixing...
with LiOH is firstly calcinated at 500 °C for 3 hours, then the powder is taken out and mixed again with blender. The well-mixed powder is sintered at 850°C for 12 hours with the air blowing in. The improved strategy did work. For 3-4.2V cycling under 1C rate, it could maintain the capacity retention of 80% after 160 cycles, which is the twice of it for the sample without double mixing. The 3-4.45V cycling, in which the original discharge capacity under C/5 rate is 187.6mAh/g, while the commercial LCO is 182.2mAh/g. For the 1C rate performance, the capacity retention drops to 80% after 90 cycles, which is around 30% higher than commercial LCO.

Figure 46. The charge/discharge voltage profiles of sintered recycled cathode materials with 0% Li excess addition, 0% Li excess with double mixing and as-purchased LCO from Sigma at C/5 rate cycling between (a) 3-4.2V and (b) 3-4.45V. The cycling performance of sintered recycled cathode materials above at 1C rate between (c) 3-4.2V and (d) 3-4.45V.
4.4 Conclusion

In summary, an effective direct recycling procedure to regenerate the EOL Li$_3$CoO$_2$ by RTS process has been developed. Above all, this approach could fully recover the electrochemical properties of the material and the cycling stability is even better than commercial LCO powder. When scaled up for the pilot test, our approach is further improved to synthesize the comparable powder materials. The powder sintering method with air flowing and double mixing is conductive to the homogeneous lithium content and particle size distributions in the final product. The first discharge capacity of the recycled material is 143 and 186.7mAh/g, for 3-4.2V, 3-4.45V respectively. It also shows great cycling stability as the regenerated LCO maintains the 80% capacity retention for 1C rate cycling after 160 and 90 cycles, for 3-4.2V and 3-4.45V respectively. Our strategy exhibits the simply, non-destructive and eco-friendly technology route to recycle the spent LCO cathode in industrial-scale and deliver the products in high electrochemical performance.
Chapter 5 - Summary and Perspective

In this work, the green and sustainable LIB manufacturing and recycling system has been built, which provides the primary results toward future battery industry infrastructure design. The significance lies on the fact that there is no toxic solvent being used during manufacturing as well as recycling processes and the competitive electrochemical performance has been achieved in both manufactured and recycled material. To prove the feasibility that this system can be applied into real industry, the whole process has been scaled up to pilot test. With optimized procedures, the pilot test can deliver the repaired cathode powder material of high quality in large amount. The battery in EV is expected to replace the internal combustion engine for reducing the dependence on crude oil. Our research is dedicated to overcoming the challenges and promote the course of development. Recycling will be the downstream industry of battery manufacturing to mitigate the environment issue and protect the valuable resources. If the close loop industry chain can be formed, especially with the direct recycling technology, the battery material will be reproduced to supply the manufacturing with minimum cost but high recovery or utilization rate. Then the recycling is also the upstream industry of the battery manufacturing. In a word, recycling plays a significant role to expedite the circular industry as well as economy.

The future life will be full of opportunities. Battery recycling will play an even more significant role in the future as more and more long-range EVs are put in market. Recycling cannot just start from the EOL of battery but the design of the battery before manufacturing. It is important to consider the EOL of battery when the product is at the under development. Standardizing battery chemistries as well as the sizes makes for the deconstruction of the outer layers of battery when it is to be recycled. Then obtaining the valuable materials inside would become easier. The standardization of battery pack makes for routinizing the recycling process and reducing the cost.

The current design of LIB is the result of years of constant optimization. The special structure conduces to the maximum of energy density as well as power density. But the inner material can be explored and replaced. Like the binder, the low cost is desirable, but
we also expect to be easier to be reclaimed. Ideally, we can find the novel binder with special deliquescent substance that can easily decompose the adhesion effect and quickly get the high value material. The solid-state battery is under investment to be commercialized in the future. It is necessary to take the recycling factor into consideration when the next generation of battery is designed. In this way the recycling process will be conducted much easier.

To build a better circular economy system, the cost or energy consumption or the GHG emission needs to be further reduced. As we know that cell manufacturing is the key contributor accounting for 45% of the GHG emission. Battery production line and recycling plant still owns room to be further squeezed with the improvement of technology. More effective sensors can be employed to monitor the steps and calculate the preferred parameters to improve the efficiency. Meanwhile the big data system will share all the battery information including the fault diagnosis to explore the better flow path of manufacturing as well as recycling by cloud computing. With these promising technologies, the CPS can be built to realize the most efficient circular chain.

Furthermore, the recycling industry still needs the support and incentive from the government to issue related policies. Only in this way people can roll up their sleeves unscrupulously to the recycling research and explore the method to overcome the difficulties. A closed-loop battery ecosystem makes for building the circular economy which can benefit the battery manufacturers, consumers as well as recyclers. Meanwhile the it is environmentally friendly. With the increasing of inventory of EVs, batteries are going to enter their EOL to be recycled from now on. Comparing various recycling processes to different chemistries and designs should be carried out even as the eventual design and material composition of those batteries remain unknown. Based on our analysis, this green manufacturing and direct recycling system is promising although the further improvement is needed. The challenges we meet are complex rather than the question in specific field. Therefore, the cross-disciplines corporation is desired. Especially the intelligent method like image recognition and prediction tools. Meanwhile, the automation equipment also needs to be designed for replacing the worker to deal with the toxic chemicals and eliminate the threats for human. In addition, the material science experts
need to fully restore the material with great energy density and power density. Even for some new inventions that can replace the LIBs for energy storage, recycling will be the everlasting topic when the product is being used.

At last, the future life in high electrification and intelligence for human beings can be expected soon. A green and sustainable manufacturing system for battery enables the eco-friendly cities to be powered by renewable energy and the energy storage infrastructure can be manufactured, reused and recycled without secondary pollution. Such an efficient and green energy supply can provide security and high-quality services for people's urban life. The direct recycling method can resynthesize the material with comparable performance to pristine one and achieve the circular economy to provide opportunities for all the people, with access to basic services, energy, housing, transportation and more. The carbon emission can be heavily reduced through the improved technologies. With a good ecological environment, people can live in harmony with the nature. All these efforts on recycling process will help sustainably tackle urgent resource needs and enhance strategic security on a global scale.
Figure 47. The green and circular model of the future city.
Reference


109


37. Yue, P.; Wang, Z.; Peng, W.; Li, L.; Chen, W.; Guo, H.; Li, X., Spray-drying synthesized LiNi0.6Co0.2Mn0.2O2 and its electrochemical performance as cathode materials for lithium ion batteries. *Powder Technology* **2011**, *214* (3), 279-282.

38. Lee, S.-W.; Kim, H.; Kim, M.-S.; Youn, H.-C.; Kang, K.; Cho, B.-W.; Roh, K. C.; Kim, K.-B., Improved electrochemical performance of LiNi0.6Co0.2Mn0.2O2 cathode material synthesized by citric acid assisted sol-gel method for lithium ion batteries. *Journal of Power Sources* **2016**, *315*, 261-268.


41. Hua, C.; Du, K.; Tan, C.; Peng, Z.; Cao, Y.; Hu, G., Study of full concentration-gradient Li(Ni0.8Co0.1Mn0.1)O2 cathode material for lithium ion batteries. *Journal of Alloys and Compounds* **2014**, *614*, 264-270.


49. Weimer, L.; Braun, T.; vom Hemdt, A., Design of a systematic value chain for lithium-ion batteries from the raw material perspective. *Resources Policy* 2019, 64, 101473.


84. Chagnes, A.; Pospiech, B., A brief review on hydrometallurgical technologies for recycling spent lithium-ion batteries. *Journal of Chemical Technology & Biotechnology* **2013**, *88* (7), 1191-1199.


87. Lv, W.; Wang, Z.; Cao, H.; Sun, Y.; Zhang, Y.; Sun, Z., A critical review and analysis on the recycling of spent lithium-ion batteries. *ACS Sustainable Chemistry & Engineering* **2018**, *6* (2), 1504-1521.


91. Alves Dias, P.; Blagoeva, D.; Pavel, C.; Arvanitidis, N., Cobalt: demand-supply balances in the transition to electric mobility. *European Commission, Joint Research*


117. Sonoc, A.; Jeswiet, J.; Soo, V. K., Opportunities to improve recycling of automotive lithium ion batteries. *Procedia CIRP* 2015, 29, 752-757.

118. Dunn, J. B.; Gaines, L.; Barnes, M.; Sullivan, J. L.; Wang, M. *Material and energy flows in the materials production, assembly, and end-of-life stages of the automotive lithium-ion battery life cycle; Argonne National Lab.(ANL), Argonne, IL (United States): 2014*.


133. Shi, Y.; Chen, G.; Liu, F.; Yue, X.; Chen, Z., Resolving the Compositional and Structural Defects of Degraded LiNi0.5Co0.2Mn0.3O2 (0 < x < 1) via Eutectic Solutions for Direct Regeneration of Lithium-Ion Battery Cathodes. *ACS Energy Letters* **2018**, *3* (7), 1683-1692.

134. Shi, Y.; Zhang, M.; Meng, Y. S.; Chen, Z., Ambient-Pressure Relithiation of Degraded LixNi0.5Co0.2Mn0.3O2 (0 < x < 1) via Eutectic Solutions for Direct Regeneration of Lithium-Ion Battery Cathodes. *Advanced Energy Materials* **2019**, *9* (20), 1900454.


137. Graphite Anode Materials for Lithium-ion Batteries.

138. USGS.GOV Graphite Statistics and Information.


171. Lambert, A. J. D.; Gupta, S., Disassembly modeling for assembly, maintenance, reuse, and recycling. **2004**.


196. Stiaszny, B.; Ziegler, J. C.; Krauß, E. E.; Schmidt, J. P.; Ivers-Tiffée, E., Electrochemical characterization and post-mortem analysis of aged LiMn2O4–Li (Ni0. 5Mn0. 3Co0. 2) O2/graphite lithium ion batteries. Part I: Cycle aging. *Journal of Power Sources* 2014, 251, 439-450.


of aged lithium-ion batteries: Disassembly methodology and physico-chemical analysis techniques. *Journal of The Electrochemical Society* 2016, 163 (10), A2149.


212. Bichon, M.; Sotta, D.; Dupré, N.; De Vito, E.; Boulineau, A.; Porcher, W.; Lestriez, B., Study of Immersion of LiNi0.5Mn0.3Co0.2O2 Material in Water for Aqueous Processing of Positive Electrode for Li-Ion Batteries. *ACS Applied Materials & Interfaces* **2019**, *11* (20), 18331-18341.


