Process Development in Synthesis and Recycle of Lithium Ion Battery Cathode Material

by

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the Degree of Doctor of Philosophy

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February 2015, Hong Kong
Authorization

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February 2015
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This is to certify that I have examined the above PhD thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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List of Publications

1. **Journal papers resulting from this thesis:**


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2. **Patent:**

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Process Development in Synthesis and Recycle of Lithium Ion Battery Cathode Material

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Abstract

Li-ion batteries (LIBs) are widely used in portable electronic devices and electric vehicles. LiFePO₄ (LFP) has been one of the most promising cathode materials for LIBs due to its high theoretical specific capacity. This thesis aims at developing a causal table which summarizes the effect of all particle quality factors on battery performance. A critical assessment was performed to validate the causal table by measuring the particle qualities of commercial LFP. One of the LFP sample with small particle size (0.15*0.4*0.6 μm), plate morphology, and around 2.5 wt% carbon coating had the highest specific capacity (164.9 mAh g⁻¹ at 0.1C) and rate capability (88.5% at 1.5 C). With the causal table, desired particles quality can be identified to enhance the battery performance. The particle synthesis methods and their operating conditions are then selected to ensure particles with the desired attributes can be produced. The LFP particles should be designed with a good particle quality to have a good electrochemical performance, including nano-size, rod-like morphology, and uniform carbon coating. The optimal conditions for synthesis of nano-size carbon coated LFP particle by polyol refluxing process is summarized, and the physical properties of four different morphology LFP and the electrochemical performance are measured. The sample with small particle size (140*40 nm), rod morphology, and around 2.9 wt. % carbon coating had the best specific capacity (160.5 mAh g⁻¹ at 0.1C) and rate capability (77.1% at 1.5 C).

Recycling of spent LIBs receives increasing attention in recent years, and chemical precipitation and solvent extraction have been widely applied in the recycling process of spent LIB. Solid-liquid equilibrium (SLE) phase behavior governs the products to be recovered from the precipitation process and can be used to guide and optimize the process. Case studies on the recycling of LiFePO₄ and LiCoₓMn₁₋ₓO₂ have been studied in this thesis to demonstrate how the SLE phase behavior can be used to design the recovery process. The SLE phase behavior can be utilized to determine the optimal operating conditions such as the amount of precipitant to be added to the system. With the insights provided from the SLE phase behavior, new process alternative with solvent extraction can be generated. Process alternative can be compared with the base case process to come up with the optimal process for recycling metal salts from spent LIB.
1. Introduction

1.1. Background

Energy is the lifeblood of modern society, and is the base of our civilization. Global warming, limited fossil fuel resource and air pollution conspir to make the use of renewable energy, together with electric transportation. There is an urging need to design electrical energy storage systems to balance supply with demands, as renewable sources are intermittent, and to power the rapidly developing hybrid electric vehicles (HEVs) or electric vehicles (EVs). Batteries are currently being developed to power an increasingly diverse range of applications, from EV to mobile phones. Despite the new lease of life recently brought by the arrival of nanomaterials, present Li-ion technology falls short of meeting all of the requirements dictated by the large volume of applications linked to renewable energy and electric transportation fields.

![Figure 1-1 Mechanism of Li-ion battery. [1]](image-url)
1.2. Lithium ion battery

Portable electronic devices and EVs are being extensively used with rechargeable lithium ion batteries (LIBs). The mechanism of LIB is shown in Figure 1-1, during discharge, Li ions carry the current from the negative (anode) to the positive electrode (cathode), through the non-aqueous electrolyte and separator diaphragm, and then the electrons go through external circuit leading an output to the load. During charging, an external electrical power source applies an over-voltage (a higher voltage but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The Li ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

The electrochemical reaction of the LIB made of LiCoO$_2$ cathode material is shown in the following equation:

Cathode half-reaction is: \[ LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^- \]  

Anode half-reaction is: \[ xLi^+ + xe^- + xC_6 \rightleftharpoons xLiC_6 \]  

![Figure 1-2 Plot of volumetric energy density against gravimetric energy density for batteries.](image-url)

[2]
LIBs are light, compact, and work with a voltage of the order of 4V with a specific energy ranging between 100Whkg$^{-1}$ and 200Whkg$^{-1}$, shown in Figure 1-2. In its most conventional structure, a LIB contains a graphite anode (e.g. mesocarbon microbeads, MCMB), a cathode formed by a lithium metal oxide (LiMO$_2$, e.g. LiCoO$_2$) and an electrolyte consisting of a solution of a lithium salt (e.g. LiPF$_6$) in a mixed organic solvent (e.g. ethylene carbonate-dimethyl carbonate, EC-DMC) imbedded in a separator felt. In most common cases, these batteries are based on the C/LiPF$_6$ in EC-DMC/LiMO$_2$ sequence and operate on a process as follows:

$$xC_6 + LiMO_2 \rightleftharpoons xLiC_6 + Li_{(1-x)}MO_2, \text{voltage} = 3.7V$$  \hspace{1cm} (3)

![Graphs showing battery market data]

Figure 1-3 The battery market in past 10 years. [3]

1.3. Production and market

LIBs are one of the great successes of modern electrochemistry. These batteries have an established role in the consumer electronic market with no risk of replacement by any other contender and, by intelligent modification of the electrode and electrolyte components, they will
soon dominate the electric automotive transportation and renewable energy storage markets. The potential of these unique power sources makes it possible to foresee an even greater expansion of their area of applications to technologies that span from medicine to robotics and space, making lithium batteries the power sources of the future. Due to the high value of the energy content, LIBs have triggered the growth of the market of popular devices, such as HEVs mobile phones, laptop computers, digital cameras and others. Figure 1-3 shows the battery market development in various applications in past 10 years. Indeed, Li-ion batteries are produced by billions of units per year. Figure 1-4 shows the worldwide annual sales of Li-ion battery and the sales reached over 9000 million USD in 2011.

![Figure 1-4 Li-ion battery sales, worldwide, 2000-2011 [USD million]. [3]](image)

1.4. Cathode materials

In a LIB, the most important and expensive component is the cathode; also, it is the bottleneck for enhancing the performance of a LIB. The key requirements for a material to be successfully used as a cathode in a LIB are as follows. 1) The material contains a readily reducible/oxidizable ion, for example a transition metal. 2) The material reacts with lithium in a reversible manner, which indicates an intercalation-type reaction in which the host structure essentially does not change as lithium is added. 3) The material reacts with lithium with a high free energy of reaction, exhibits high capacity, high voltage, and high energy storage. 4) The material reacts with lithium very rapidly both on insertion and removal. 5) The material should be a good electronic conductor,
preferably as highly conductive as possible. (a) This allows for the easy addition or removal of electrons during the electrochemical reaction. (b) This allows for reaction at all contact points between the cathode active materials and the electrolyte rather than at ternary contact points among the cathode active material, the electrolyte, and the additive electronic conductor (such as carbon black). (c) This minimizes the need for inactive electronic conductor, which take away from the overall energy density. 6) The material should be stable in the battery, i.e., not change structure or degrade, to over discharge and overcharge. 7) The material needs to be at low cost. 8) The material should be environmentally benign and can be recycled.

1.5. LiFePO$_4$ cathode

Since Padhi et al. [4] did their breakthrough work on phosphoolivine polyanionic compound in 1997, LiFePO$_4$ (LFP) has become one of the most promising cathode materials for lithium ion batteries. LFP has a high theoretical capacity of 170 mAh/g, with a flat discharge potential of 3.4 V vs Li/Li$^+$. LFP exhibits other outstanding properties such as better cycling stability [5], superior thermal stability [6], low cost, and environmental friendliness [7]. Consequently, in EVs/HEVs, backup power systems, and other energy storage devices, LFP has fulfilled most of the principal requirements, i.e. non-toxicity, low cost, safety, higher power/energy density, and excellent rate capability and long cycle life [8].

However, LFP suffers two major disadvantages in its application: low electronic conductivity ($\sim 10^{-9}$ Scm$^{-1}$) and a small Li ion diffusion coefficient ($\sim 1.8 \times 10^{-14}$ cm$^2$ s$^{-1}$) [9], resulting in poor electrochemical performance, especially poor in rate capacity. Although it possesses so many advantages, LFP still meets some obstacles for practical application as a cathode material. To improve its electric conductivity, carbon coating around the particles[5, 10, 11] and cation doping into the olivine structure have been performed and high battery capacity results have been obtained [12, 13]. In addition, the synthesis processes were optimized to minimize the particle size and obtain uniform particle size distribution [14]. In order to solve the low diffusivity of Li ion, the formation of LFP particles in sub-micron or nano-size can enhance the electrochemical performance by reducing the transporting path lengths of Li ions and electrons. In addition, decreasing the crystallite size is important for the electrode-electrolyte interface, and may also
reduce the mechanical lattice strain upon Li (de)insertion [15, 16]. Many research groups have focused on the synthesis of LFP in recent years, thus, various synthesis routes were proposed to prepare LFP, such as mechanical alloying [17, 18], sol–gel methods [19, 20], co-precipitation [21], microwave processes [22], hydrothermal routes [23, 24], emulsion drying synthesis [25, 26], a carbothermal reduction method [27], vapor deposition [28], spray solution technology [29], and so forth. It is obvious that morphological control of LFP is becoming increasingly important, as many of the properties are highly shape and size dependent [30, 31]. Given the importance of surface structure and particle morphology on the properties of LFP, knowledge of these features on the atomic level would provide valuable information for understanding electrochemical mechanisms.

1.6. Recycle of spent Li-ion battery

The increased reliance of LIB in electronic equipment also increases the number of spent batteries being disposed to the landfills. The number is expected to grow in the near future due to the faster replacement of the electronic products. However, disposing spent batteries that contain organic electrolyte and metals such as Ni, Co, Cu, and Li lead to serious environmental problems such as soil and underground water contamination [32]. This is also a waste of the valuable metals contained in the LIB batteries. Therefore, recycling LIB batteries not only reduces environmental pollution, but also saves limited metal reserve in the earth. As a result, effective methods and low costs are the objectives in separating and recovering the spent LIB. It will be very interesting to be able to recycle and regenerate the major metal values of spent batteries, in order to benefit the economy, and at the same time, reduce environmental pollution. Some hydrometallurgical and pyrometallurgical processes for the recycling of spent LIB have already been reported or patented, but most of these are in the pilot or laboratory testing phase. In addition, using recycled metal value from spent LIB to prepare LiCoO₂, LiMn₂O₄, LiNiO₂ and related oxides electrode materials is a good way for battery reused. Giving a generic method for guiding and optimizing the recycle process is quite useful in such new recycle area.
1.7. Objectives of the thesis

In this regard, the overall objectives of this work are to study the particle quality effect on the performance of the LIB, and develop an effective quality control process synthesis for LiFePO$_4$ nano-particle, and study the design an effective process for recycle the spent LIB. A causal table of quality control of the synthesis method is developed for guiding and optimizing the production of LFP. In the particle synthesis process development, the condition of wet processes for morphologically-tailored nanoparticles LiFePO$_4$ is optimized. In the recycle process development, the general approach in utilizing SLE phase behavior to design the recycling process and determine its operating conditions is discussed, and followed by case studies to illustrate this general approach. The selective precipitation and liquid-liquid extraction methods for recovery of valuable metal in LIB cathode materials are studied; and these two processes are compared to study their advantages and disadvantage.

In chapter 2, the objective is providing a comprehensive study on the effect of LFP particle quality on battery electrochemical performance. Based on the information obtained from the literature, a causal table is developed to summarize the effect of various particle qualities on electrochemical performance. For some of these relations, literature studies provide results pointing to different conclusions and only the general trend is captured in the causal table. A critical assessment is performed in this study to substantiate the causal table. The characteristics of the commercial LFP particles and their electrochemical performances were measured. Particle quality for enhancing the specific capacity and rate capability of LFP particles were identified.

In chapter 3, the optimal conditions for synthesis of carbon coated LFP nano-particles by polyol refluxing process is determined. Also, the morphology of LFP particles is modified by changing the composition of the reacting solution, and comparing their electrochemical performance. The characteristics of the carbon coated LFP (C/LFP) particles, including crystal structure, crystallinity, purity, particle size, morphology, specific surface area, and carbon content in particle coating, were measured. Button cells were fabricated and their electrochemical performances were measured. The optimized synthesis conditions for producing high quality LFP particles were identified.

In chapter 4, the utilization of SLE phase behavior to design precipitation processes is applied to the separation and recovery of metal salts from the cathode materials. Two cathode materials,
namely LiFePO₄ and LiCoₓMn₁₋ₓO₂, are studied in this chapter to illustrate how the SLE phase behavior can be used to design the process and determine the optimal operating conditions of the recycling process. The general approach in utilizing SLE phase behavior to design the recycling process and determine its operating conditions is discussed first, followed by using two case studies to illustrate this general approach.

In chapter 5, the objective is to recover the valuable metal from a spent LiMnₓCo₁₋ₓO₂ cathode material LIBs by solvent extraction and chemical precipitation process. To achieve this objective, selective precipitation and solvent extraction experiments were performed using artificially prepared metal solutions to simulate H₂SO₄ leach liquors, and the performance of the processes based on these two separation technologies was evaluated in terms of metal recovery and metal selectivity. The proposed process in this chapter was then compared with process from chapter 4 to determine the advantages and disadvantages of the proposed process.
2. Critical assessment of particle quality of commercial LiFePO$_4$ cathode material – A causal table for lithium ion battery performance

2.1. Introduction

Rechargeable lithium ion batteries (LIBs) are widely used in portable electronic devices and electric vehicles (EVs). Various studies have been conducted to evaluate the electrochemical performance of LIBs made of different cathode materials. Cathode materials commonly used in LIBs include LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$. LiFePO$_4$ (LFP) has become a popular cathode material after the breakthrough work on phospho-olivine polyanionic compound by Padhi et al. [1]. It has the advantages of high theoretical capacity (170 mAh g$^{-1}$), flat discharge potential of 3.6V vs Li/Li$^+$ [2], long cycle life [3], superior thermal stability [4], low cost, and being an environmental friendly material [5].

However, LFP has two major limitations in battery applications, low electrical conductivity ($\sim 10^{-9}$ S cm$^{-1}$) and small Li ion diffusion coefficient ($\sim 1.8 \times 10^{-14}$ cm$^2$ s$^{-1}$) [6], leading to poor electrochemical performance. Carbon coating on LFP particles [3, 7, 8], and cation doping into the olivine structure of LFP could increase the conductivity to $10^{-2}$ S cm$^{-1}$ [9, 10]. The Li ion diffusion coefficient is an intrinsic material property that cannot be changed. However, the LFP particle size could be reduced to shorten the diffusion paths of Li ions in reaching the electrode-electrolyte interface [11, 12].

Researchers also focus on shortening the Li ion diffusion path by controlling the morphology of the LFP particles. Computational [13] and experimental [14] studies indicated that electron transfer mainly takes place on the ac-plane of the LFP crystal, and Li ion migration prefers to take place via the short one-dimensional channels oriented along the [010] direction (b-axis) of the LFP crystal. When these LFP crystals align in a particle, it is desirable to have the direction of Li ion transport (i.e. b-axis) matched with the shortest side of that particle morphology to reduce the diffusion paths of Li ions to reach the electrode-electrolyte interface [15]. Therefore, for particles of similar weight, particles of thinner morphology such as nanorod and nanoplate are preferred when compared with spherical particles. LFP particles with different morphologies can be
produced by different synthesis methods. For example, LFP nanorods can be synthesized by the surfactant-assisted hydrothermal method [16], while nanoplates can be synthesized by solvothermal and solid-state reaction methods [17, 18]. Other LFP crystal structures such as spherical [12], orthorhombic prism [19], hollow [20], and fiber [21] have also been synthesized.

Although LFP has been used as the cathode material for various commercial LIB products, it is not clear how particle size, morphology, amount of carbon coating, etc. impact one or more aspects of the LIB electrochemical performance. This is a serious omission as products for different purposes have different requirements on electrochemical performance. For example, LFP cathode materials used in LIBs of cell phones or other mobile devices need to have a high specific capacity at a low C-rate, amount of charge per gram of cathode material at a specific C-rate. A C-rate of 1 C represents the battery is able to discharge one cycle in one hour. If the battery is used for EVs or hybrid electric vehicles (HEVs), the rate capability, defined as the percentage of retained specific capacity at different C-rates when compared with a low C-rate (0.1 C or 0.2 C), at high C-rate should be as high as possible for fast charge and discharge. The energy density, nominal battery energy per unit volume, of the battery should also be high for having a longer battery life.

This chapter aims at providing a comprehensive study on the effect of LFP particle quality on battery electrochemical performance such that LFP particles can be tailor-made for having excellent performance in their applications. Based on the information obtained from the literature, a causal table that relates product performance to product attributes is developed to relate electrochemical performance to various particle quality. Note that only the general trend from the literature is captured in the causal table and there might be other studies that provide opposite trends. A critical assessment of different brands of commercial LFP particles is performed to corroborate the relations between particle characteristics and battery performance. The characteristics of the commercial LFP particles, including crystal structure, crystallinity, particle size, morphology, tap density, specific surface area, particle size distribution (PSD), and carbon content in particle coating, are measured. Button cells are then fabricated and their electrochemical performances are measured to illustrate the relations in the causal table. Finally, particle quality that provides the required electrochemical performance can be identified.
2.2. LFP Particles design – Causal table of particle quality on battery performance

In order to tailor-make LFP particles for achieving the desired electrochemical performance required by specific applications, a causal table is presented in Table 2-1 to relate electrochemical performance (first column), including specific capacity, rate capability, energy density, and charge transfer resistance to various particle quality (first row) such as primary particle size, morphology, PSD, particle agglomeration, and carbon coating. Charge transfer resistance refers to the resistance of the electron transfer out of the particle lattice during electrochemical reaction, and is affected by the fabrication method and cathode material used in the battery. Note that cycle life is also an important parameter for battery performance. However, most academic studies do not provide tests with sufficient cycles (> 500) to observe the impact of particle quality on cycle life. A positive sign in the causal table indicates that an increase in particle quality would lead to enhanced battery performance, while a negative sign indicates the reverse.

The second and the third column in the causal table relate battery performance to primary particle size and morphology, respectively. Primary particle size refers to the size of the particles without secondary agglomeration or self-aggregation. Reducing primary particle size increases specific capacity and rate capability, and reduces charge transfer resistance as smaller particles have shorter diffusion paths and larger contact area between electrode and electrolyte for Li ion diffusion [12, 22, 23]. The electron transport from particles to the current collector is also easier for smaller particles. For example, Meligrana et al. [24] showed that that the specific capacity and the rate capability of LFP cathode material increased ~100 % when the particle size decreased from 100 nm to 50 nm. Li ion diffusion can also be enhanced by having particles with thinner morphology such as nanoplates or nanorods, leading to higher specific capacity, higher rate capability, and smaller charge transfer resistance [25-27]. As the particle packing density depends on both particle size and PSD, the increase of the particle size may have a positive or negative effect on energy density. This ambiguity is indicated by a +/- sign in Table 2-1. When the rate capability of a battery is high, the battery can be charged and discharged at high rate; because the retained percentage of specific capacity is acceptable for application at high rate. As the specific capacity is higher, the power of the battery will be larger.

Various studies also observed that particles agglomeration leads to an increase in specific capacity and rate capability, and a decrease in charge transfer resistance [28]. This might be
attributed to an increase in particle-particle contact which enhances Li ion diffusion and electron transfer. Similarly, particles with a wider PSD allows a denser packing and increase in particle-particle contact for having higher specific capacity, higher rate capability, and lower charge transfer resistance. The energy density of the battery can be increased by packing the LFP particles denser in the cathode [23, 29]. This in turn requires LFP particles with a high tap density, which can be achieved by having larger primary particles, more spherical particles, a wider PSD, or forming secondary particles before cathode fabrication. However, the PSD effect on energy density may be ambiguous because the relation between the PSD and packing of the particle still ambiguous in LFP particle.

Carbon coating improves the electrical conductivity of LFP particles and reduces the charge transfer resistance [33]. For synthesis process such as solid state reaction, carbon source is added during the synthesis process. This forms a layer of carbon around particles during particle formation which reduces particle growth. Having smaller particles in turn increases specific capacity and rate capability [34, 35]. Konarova et al. [36] synthesized carbon coated LFP particles which exhibited 96% of the theoretical capacity at 0.1 C. Miao et al. [37] also reported that carbon coated LFP particles had a specific capacity of 155 mAh g⁻¹, which was higher than that of uncoated LFP (135 mAh g⁻¹).

Table 2-1 Causal table for the effect of particle quality factors on battery performance.

<table>
<thead>
<tr>
<th>Battery performance</th>
<th>Particle quality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary particle size¹</td>
</tr>
<tr>
<td>Specific capacity</td>
<td>− [16, 38]</td>
</tr>
<tr>
<td>Rate capability</td>
<td>− [38, 41]</td>
</tr>
<tr>
<td>Charge transfer resistance</td>
<td>+</td>
</tr>
<tr>
<td>Energy density⁵</td>
<td>+/- [44]</td>
</tr>
</tbody>
</table>
Notes:

(1) Primary particle size is directly related to specific surface area, which increases as particle size decreases.

(2) An increase in particle morphology means particles become more spherical (i.e. from nanoplate to sphere).

(3) A positive sign in secondary particles refers to enhanced battery performance if secondary particles are formed.

(4) An increase in PSD refers to a wider PSD.

(5) Energy density is mainly affected by the tap density of the LFP particles. Particle attributes such as size, morphology, PSD, and secondary particle formation affect the tap density.

For other cathode materials, since the crystal structures are different, e.g. LFP is olivine, LiCoO₂ is layer structure, and LiMn₂O₄ is spinal structure, the relations between other cathode particle attributes and battery performance would be different from the one of LFP. As a result, the causal table for LFP cannot applied in other cathode materials. For example, the specific capacity of the button cell made of LiCoO₂ does not increase as the size of cathode particle decrease. Also, the relation between of particle size and rate capability of LiCoO₂ cathode material is not the same as the one of LFP.

2.3. Experiments

2.3.1. Particles characterization

Six commercial LFP particles, labeled as I to IV, were characterized in this study. Crystal structure and crystallinity of these samples were determined by X-ray diffraction, using Cu Kα radiation (λ= 1.54Å) (XRD, Model PW1830 Philips, 2KW, Cu anode, graphite monochromator), to verify whether the phase of the powders were LiFePO₄. The XRD experiment was conducted by steps scanning method with a step interval of 0.02° and a count time of 1s per step. MDI Jade 6.0 software was used to analyze the XRD patterns of the samples. The particle size and particle morphology of the samples were observed by a field emission scanning electron microscope (SEM, JSM-7100F, JOEL). The tap density was obtained by recording the volume before and after tapping.
a measuring cylinder containing LFP particles, until no further change in volume was observed. The PSD was measured by the laser diffraction particle size analyzer (Beckman Coulter, LS13 320), after dispersing the samples in double deionized water. The specific surface area of the samples was measured by the Brunauer-Emmett-Teller (BET) method (Surface Area Analyzer, Beckman Coulter, SA3100). The carbon content on LFP particles was determined by thermogravimetric analysis (TGA) using TA instruments Q50, with a 5 °C min⁻¹ heating rate from 25 to 600 °C, under purified air.

2.3.2. Button cell fabrication

The cathode was prepared by casting slurry onto aluminum sheets. The slurry contained 90 wt% active material (LFP), 2 wt% Kynar polyvinylidene fluoride, and 8 wt% conductive carbon (Super P), being dispersed in N-methyl methyl-pyrrolidone. All materials were used without further treatment. The cathode was then dried at 120 °C for 16 h. The current collector was punched into discs with an area of 1.227 cm² and weighed around 3.5 mg. Lithium metal was used as the anode. 1 M LiPF₆ in a 1:1 (vol/vol) mixture of ethylene carbonate and dimethyl carbonate was used as the electrolyte, and Celgard 2400 microporous membrane was used as the separator. CR2016 type button cells were assembled in an argon-filled glove box.

2.3.3. Electrochemical performance tests

The galvanostatic charge and discharge test was performed between 2.3 and 4.2 V at room temperature with different current densities of 0.1, 0.2, 0.5, 1 and 1.5 C using Neware BTS 3000 (Shenzhen, China). Electrochemical impedance spectroscopy (EIS) measurement was conducted by potentiostatically applying a 10 mV AC voltage from a frequency of 30 mHz to 1 MHz using a CHI 760E electrochemical workstation (Chenhua, Shanghai China). Before the EIS test, the cell was cycled for two times at a rate of 0.1 C. All electrochemical measurements were carried out at room temperature.
2.4. Results and discussion

2.4.1. LFP particles characterization

Crystal structure and crystallinity

The XRD patterns of all samples are shown in Figure 2-1. These patterns were indexed in the space group Pnma reported for LFP particles (ICSD no. 200155) with lattice constants $a = 10.294(2)$ Å, $b = 5.974(1)$ Å, and $c = 4.694(1)$ Å. All samples were confirmed to be single phase LFP as their peaks matched with that of standard LFP. They were also crystalline as the XRD patterns showed sharp peaks with relatively high intensity.

![XRD patterns of six commercial LFP samples.](image)

Figure 2-1 XRD patterns of six commercial LFP samples.
Particle size and morphology

The size and morphology of LFP particles have significant impact on battery performance. SEM images of all LFP samples with 20,000 magnification are depicted in Figure 2-2. The primary particle size and particle morphology were observed from the SEM images and are listed in Table 2-2. The morphology of primary particles were observed to be spherical for samples I and VI, plate for sample II, irregular for samples III and IV, and rod for sample V. Based on SEM images, Sample I (diameter (D) = 0.3-0.5 μm) and sample II (length (L) = 0.6 μm; width (W) = 0.4 μm; thickness (T) = 0.15 μm) were the smallest, while sample VI had the largest primary particle size (D = 1-3 μm). The SEM images also showed that particle agglomeration forming secondary particles was observed in samples I and III.
Figure 2-2 SEM images of the commercial LFP samples.
PSD was measured by laser diffraction, and the D50 and D90 of all samples are also summarized in Table 2-2. Results showed that sample II was small with narrow PSD, while samples IV, V, and VI had a wider PSD. D50 and D90 for samples I and III were significantly larger than those observed in SEM as secondary particles were formed in these samples. Note that the particle size measured by laser diffraction for samples without particle agglomeration was larger than those reported from SEM. This might be attributed to the inaccuracy of laser diffraction for particles smaller than 1 μm and the difference in defining particle size for non-spherical particles between the two methods. Instead of taking the dimensions as the primary particle size in measuring the SEM images, laser diffraction obtained the size by the Mie theory of light scattering and represented it as the volume equivalent sphere diameter.

Table 2-2 Physical properties of different commercial LFP particles.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Morphology</th>
<th>Primary particle size (μm)</th>
<th>Secondary particle formation</th>
<th>PSD (μm)</th>
<th>Tap density (g/mL)</th>
<th>Specific surface area (m²g⁻¹)</th>
<th>Carbon content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D = 0.3-0.5</td>
<td>Yes</td>
<td>7.87</td>
<td>13.50</td>
<td>1.04</td>
<td>19.21</td>
</tr>
<tr>
<td>I</td>
<td>Spherical</td>
<td></td>
<td></td>
<td>1.45</td>
<td>2.80</td>
<td>0.69</td>
<td>22.31</td>
</tr>
<tr>
<td>II</td>
<td>Plate</td>
<td>L = 0.6</td>
<td>No</td>
<td>6.67</td>
<td>10.07</td>
<td>0.98</td>
<td>18.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W = 0.4</td>
<td></td>
<td>2.52</td>
<td>6.27</td>
<td>0.83</td>
<td>12.41</td>
</tr>
<tr>
<td>III</td>
<td>Irregular</td>
<td>L = 0.8</td>
<td>Yes</td>
<td>3.43</td>
<td>7.86</td>
<td>0.90</td>
<td>9.87</td>
</tr>
<tr>
<td>IV</td>
<td>Irregular</td>
<td>L = 2.5</td>
<td>No</td>
<td>3.87</td>
<td>8.78</td>
<td>0.95</td>
<td>7.64</td>
</tr>
<tr>
<td>V</td>
<td>Rod</td>
<td>L = 2.5</td>
<td></td>
<td>0.38</td>
<td>0.78</td>
<td>0.90</td>
<td>2.4</td>
</tr>
<tr>
<td>VI</td>
<td>Spherical</td>
<td>D =1-3</td>
<td>No</td>
<td>3.87</td>
<td>8.78</td>
<td>0.95</td>
<td>7.64</td>
</tr>
</tbody>
</table>

Note:

(1) Primary particle size was the average size of 300 particles measured from SEM images. D = diameter; L = length; W = width; T = thickness.
**Physical properties of LFP particles**

Tap density, specific surface area, and carbon content of the LFP samples are also reported in Table 2-2. Tap density generally increased with primary particle size if no secondary particles were formed in the samples. For samples with similar primary particle size, sample forming secondary particles had a higher tap density. For example, sample I had a tap density 50% higher than that of sample II. A higher tap density generally leads to a higher energy density (by volume) in the battery. The specific surface area of the LFP samples varied from 7.64 to 22.31 m² g⁻¹, and generally increased with decreasing particle size. All LFP samples were coated with a carbon layer and the carbon content varied from 1.4 wt% of the weight of LFP particles for sample III to 4.2 wt% for sample VI.

**2.4.2. Electrochemical properties**

The galvanostatic charge and discharge curves of selected LFP sample (sample II) are shown in Figure 2-3 for selected C-rates (0.1 C, 0.5 C, 1.5 C), and the discharge curves of all samples at 0.1 C are compared in Figure 2-4. The specific capacity at a certain C-rate was obtained from the corresponding discharge curve at a potential of 2.0 V, and are summarized in Table 2-3 for all LFP samples at a C-rate of 0.1 C to 1.5 C. The specific capacity generally dropped with increasing C-rate. Button cell made of sample II cathode material had the highest specific capacity at both 0.1 C (164.9 mAh g⁻¹) and 1.5 C (146.0 mAh g⁻¹), while button cell made of sample VI cathode material exhibited the worst performance at 0.1 C (136.7 mAh g⁻¹), but still had an acceptable specific capacity at 1.5 C (105.4 mAh g⁻¹). Button cell made of sample III cathode material had the lowest specific capacity at 1.5 C (m Ah g⁻¹).
Figure 2-3 Charge–discharge curves (0.1, 0.5 and 1.5 C) of button cell made of Sample II LFP cathode material.

Table 2-3 Specific capacity of button cells made of different LFP cathode materials.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Specific capacity at different C-rate (mAh g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1C</td>
</tr>
<tr>
<td>II</td>
<td>164.9</td>
</tr>
<tr>
<td>I</td>
<td>162.1</td>
</tr>
<tr>
<td>III</td>
<td>160.5</td>
</tr>
<tr>
<td>IV</td>
<td>155.6</td>
</tr>
<tr>
<td>V</td>
<td>152.3</td>
</tr>
<tr>
<td>VI</td>
<td>136.7</td>
</tr>
</tbody>
</table>
Figure 2-4 0.1 C discharge curves of button cells made with different LFP cathode materials.

Table 2-4 Rate capability of button cells made of different LFP cathode materials.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Specific Capacity at 0.1 C (mAh g(^{-1}))</th>
<th>Rate capability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.2 C</td>
</tr>
<tr>
<td>II</td>
<td>164.9</td>
<td>98.0</td>
</tr>
<tr>
<td>V</td>
<td>152.3</td>
<td>98.0</td>
</tr>
<tr>
<td>IV</td>
<td>155.6</td>
<td>97.4</td>
</tr>
<tr>
<td>I</td>
<td>162.1</td>
<td>98.6</td>
</tr>
<tr>
<td>VI</td>
<td>136.7</td>
<td>97.8</td>
</tr>
<tr>
<td>III</td>
<td>160.5</td>
<td>97.3</td>
</tr>
</tbody>
</table>
LFP is particularly suitable to be used at high C-rate as it has a stable olivine crystal structure. The rate capability of all LFP button cells at different C-rates are presented in Table 2-4 as the percentage of retained specific capacity at 0.1 C. As the specific capacity was lower at higher C-rate, the rate capability decreased with increasing C-rate. The button cells made of samples II, V, and IV cathode materials had retained above 80% capacity of 0.1 C when discharged at 1.5 C, which made them suitable to be used in EVs. On the other hand, button cell made of sample III cathode materials had low rate capability at high C-rate, and a more significant drop was observed when the C-rate was above 1 C.

The difference in specific capacity and rate capability for different LFP samples can be attributed to the difference in physical properties of the LFP particles. Although particle size for different particle morphology was hard to compare, experimental results showed that the specific capacity generally increased with decreasing primary particle size at 0.1 C, which agreed with the causal table. For particles of roughly similar sizes, LFP particles with thinner morphology had better performance, as it favored Li ion diffusion. For example, plate-like LFP particles (sample II) had specific capacities larger than that of spherical particles (sample I), especially at high C-rates. Similar conclusion was also achieved by comparing sample V (rod) and sample VI (spherical). Although button cells made of samples I and III had a high specific capacity and rate capability at low C-rate, their specific capacity and rate capability at high C-rate (≥1 C) were lower than other samples. This might be attributed to the low carbon content of samples I and III, resulting in insufficient conductive channels for electron transfer. Although sample VI had the highest carbon content in all samples, its large particle size and spherical in shape resulted in a low specific capacity and rate capability.

The EIS is used to evaluate the charge transfer resistance of button cells made of different cathode materials, and the impedance spectra of all button cells are shown in Figure 2-5. The impedance spectrum is composed of a depressed semicircle and the data points are arranged at decreasing frequency along the real impedance axis (x-axis). The difference between the two intercepts of the semicircle with the real impedance axis represents the charge transfer resistance [45]. Figure 2-5 shows that the charge transfer resistance increased in the order of samples II, I, III, IV, V and IV, which generally agreed with the increasing trend of primary particle size. For particles of roughly similar sizes, particles of thinner morphology (sample II) had a charge transfer
resistance smaller than that of spherical particles (sample I). All these matched with the relations presented in the causal table.

![EIS spectra of button cells made of different LFP cathode materials.](image)

Experimental results conducted in this study were comparable to those studies summarized by Gaberscek et al. [46]. They concluded that the battery performance increased as the particle size of the LFP cathode decreased. However, this conclusion is not exactly true as they only considered the average particle size and carbon coating or carbon adding. From the previous study, the electrochemical performance of LIBs highly depends on the LFP particle attributes, including particle size, morphology, etc. Instead of only comparing the particle size, additional particle attributes of the same references are summarized Table 2-5. From the second column, the specific capacity generally increased with decreasing LFP particle size. Similar to the results in Table 2-1, particles with elongated morphology (nanofibers), carbon coating, and agglomeration to form secondary particles had higher specific capacity.
### Table 2-5 Particle quality and battery performance in the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Particle size (μm)</th>
<th>Average particle size (μm)</th>
<th>Morphology</th>
<th>Secondary particle formation</th>
<th>Carbon coating</th>
<th>Specific capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sides et al. [47]</td>
<td>~0.05</td>
<td>0.05</td>
<td>Nanofibers</td>
<td>Yes</td>
<td>Yes</td>
<td>165 at 3C</td>
</tr>
<tr>
<td>Kim et al. [31]</td>
<td>0.02-0.04</td>
<td>0.03</td>
<td>Orthorhombic</td>
<td>No</td>
<td>No</td>
<td>163 at 1C</td>
</tr>
<tr>
<td>Delacourt et al. [16]</td>
<td>0.1-0.2</td>
<td>0.14</td>
<td>Orthorhombic</td>
<td>Yes</td>
<td>No</td>
<td>147 at 5C</td>
</tr>
<tr>
<td>Shin et al. [48]</td>
<td>0.1-0.3</td>
<td>0.15</td>
<td>Irregular</td>
<td>Yes</td>
<td>Yes</td>
<td>119 at 1C</td>
</tr>
<tr>
<td>Kim et al. [49]</td>
<td>0.2-0.4</td>
<td>0.3</td>
<td>Irregular</td>
<td>Yes</td>
<td>Yes</td>
<td>134 at 1C</td>
</tr>
<tr>
<td>Yu et al. [50]</td>
<td>0.2-0.4</td>
<td>0.3</td>
<td>Plate</td>
<td>No</td>
<td>Yes</td>
<td>120 at 1C</td>
</tr>
<tr>
<td>Wang et al. [51]</td>
<td>~0.5</td>
<td>0.5</td>
<td>Irregular</td>
<td>No</td>
<td>No</td>
<td>115 at 1C</td>
</tr>
</tbody>
</table>

#### 2.4.3. Particle quality for mobile devices battery

A high specific capacity is desired for LIBs in mobile devices. Current study showed that small LFP particles (~0.2 μm) with plate morphology had a high specific capacity. Carbon-coated LFP particles with 2.5-4 wt% carbon content increased the electrical conductivity of the LFP particles and retained a high specific capacity during high C-rate discharge. Particles with a wide PSD and with agglomeration to produce secondary particles (~ 5 μm) led to a higher tap density, which in turn increased the energy density of the battery.

#### 2.5. Conclusions

The electrochemical performance of LIBs highly depends on the LFP particle quality. A causal table is presented in this study to relate electrochemical performance to various particle quality. Among the six LFP cathode materials tested in this study, sample II with small particle size (0.15 μm as the diffusion path of Li ion), a plate morphology, and 2.4 wt% carbon coating exhibited the best specific capacity (164.9 mAh g⁻¹ at 0.1 C) and rate capability (88.5% at 1.5 C). Also, the charge transfer resistance measured from EIS was the smallest. On the other hand, sample VI with large particle size and spherical in shape had lower specific capacity and rate capability. All these results matched with the relations presented in the causal table. Therefore, desired LFP particle
quality for good LIBs electrochemical performance targeted for specific applications can be identified. This in turn determines the synthesis conditions required to produce LFP particles with the desired particle quality.
3. Process Development for High Quality LiFePO₄ Cathode Material

3.1. Introduction

Li-ion batteries (LIBs) are widely used in mobile devices such as mobile phones, laptop computers, electric vehicles (EVs), and hybrid electric vehicles (HEVs) due to their high energy density, lightweight, high power density, and long cycle life. Cathode serves as the site for Li intercalation and de-intercalation in batteries and is the major component that affects LIB performance. Various LIBs cathode materials have been extensively studied and include three main crystal structures, namely layered structure (e.g. LiCoO₂, LiNiO₂, LiNiₓMnᵧCo₂O₄), spinel structure (e.g. LiMn₂O₄), and olivine structure (e.g. LiFePO₄, LiMnPO₄, LiCoPO₄). Among these materials, the olivine structure of lithium metal phosphate received more attention because of its stable structure for Li intercalation and de-intercalation. With the breakthrough work on phosphoolivine polyanionic compound in 1997 by Padhi et al. [4], LiFePO₄ (LFP) becomes the popular cathode materials for lithium ion batteries because of its relative high theoretical capacity (170 mAh g⁻¹), a flat discharge potential of 3.6 V vs Li/Li⁺ [52], long cycle life [5], high thermal stability [6], low cost, and being a relatively environmental friendly material [7].

The electrochemical performance of LFP cathode material is closely related with its phase purity, particles size, surface area, particle morphology, carbon content, and so on [53]. For producing LIBs with enhanced electrochemical performance, our previous study summarized the desired product attributes of the LFP particles. Highly crystalline, smaller particles (~200 nm) and particle morphology with a shorter b-axis (nanoplates or nanorods) are preferred as they provide a shorter diffusion path to enhance Li ion diffusion and result in a higher specific capacity and rate capability. As LFP has a low conductivity, LFP particles are usually coated with ~2.5–4 wt% carbon to increase the electrical conductivity, which leads to a higher specific capacity at high C-rate discharge.

Various processes such as mechanical alloying [17, 18], sol–gel [19, 20], co–precipitation [21], hydrothermal [23, 24], solvothermal [54], carbothermal reduction [27], and polyol refluxing [55] have been used to synthesize LFP particles. In order to produce LFP particles with the desired attributes, the conditions of the selected synthesis method should be optimized. Among all
techniques, hydrothermal, solvothermal, and polyol refluxing were widely used to synthesize LFP particle with controllable the particle size and morphology. Particle morphology can be controlled by adding structure-directing agents (surfactants like SDBS [56], CTAB [57]) or templates (KIT-6 and SBA-15 silica template [58], polystyrene polymer [59]) in solid-state, hydrothermal or solvothermal methods. Mathew et al. [60] demonstrated that the LFP particle size can be decreased by shorten the reaction time in polyol refluxing method. Also, Liu et al. [61] used ball-milling-assisted spray-drying method to synthesis a size-controlled carbon coated LFP particle with 200 and 400 nm by adjusting a series of parameters.

The polyol refluxing process is more preferable for LFP particles synthesis, because it does not need to high pressure facility; and it can be used for continual industrial production. The reducing environment in the polyol refluxing process minimizes Fe$^{2+}$ oxidation and produces LFP particles with high purity. Although the high boiling point of the polyol medium requires a high operating temperature, this produces LFP particles with good crystallinity. In the polyol reaction, the polyol medium acts as a solvent as well as a stabilizer to limit particle growth or agglomeration thus can synthesize small size LFP particles. Kim et al. [31] used polyol refluxing process to synthesize high purity, nano-sized (100 nm) LFP particles with excellent battery performance (168 mAh g$^{-1}$ at 0.1 C). Yang et al. [62] concluded that the morphology of the LFP particles were strongly dependent on synthetic parameters such as the composition of the solvent, concentration, and feeding sequence. In LFP particles synthesis, the high purity and crystallinity LFP particles can be obtained by optimizing the Li:P ratio [63], while particle morphology can be controlled by adding surfactants to the polyol medium [56, 57]. The particle size can be controlled by varying the reaction temperature or refluxing time [55]. The optimal carbon content of the carbon coated LFP particle can be achieved by adjust the addition of carbon source [64].

Although the polyol refluxing process has been shown to produce LFP particles with different product attributes, only several studies focused on how to optimize the conditions for producing LFP particles with desired attributes. This study aims at synthesizing nano-sized (100-200 nm) carbon coated (2.5-4 wt%) LFP particles with nanoplates or nanorods (short b-axis) morphology. The LFP particles have to be also of high purity (>99%). The effects of various operating parameters, including mole ratio of Li to P, surfactant added to the reaction, reaction duration, and carbon coating on the product attributes of the LFP particles are studied. The optimal conditions in
synthesizing LFP particles with the desired attributes are selected. The physical properties of these carbon coated LFP particles such as crystal structure, crystallinity, purity, particle size, morphology, specific surface area, tap density, and carbon content in the particle coating are characterized. Finally, button cells are fabricated using these carbon coated LFP particles and their electrochemical performances are measured to verify the LFP particles synthesized under the optimal synthesis condition are with desired product attributes.

3.2. Experiments

3.2.1. Synthesis of LiFePO₄ nano-particle by polyol process

FeSO₄·7H₂O (99%, Sigma-Aldrich) and phosphoric acid (H₃PO₄) (85%, Junsei) were dissolved in the polyol medium tetraethylene glycol (TTEG) (99.5%, Acros Organics) in a mole ratio of 1:1. After complete dissolution in the polyol medium, a specific amount of LiOH (98%, Sigma-Aldrich), dissolving in the same polyol medium, was added to the above polyol solution slowly with strong agitation to prevent the formation of large crystals. Surfactant such as polyvinylpyrrolidone (PVP, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, 99%, Sigma-Aldrich) or polyethylene glycol (PEG, Mw 100,000, Sigma-Aldrich), acted as the structure-directing agent, could be added to the polyol solution in a volume ratio of 1:10 to study its effect on LFP particles morphology. The homogenous solution was stirred with N₂ purging and heated at a rate of 10 °C/min to around 320 °C (the boiling point of the TTEG) for a specific reaction time in a three-neck round bottom flask attached to a reflux condenser. The pH value of the solution was measured before the reaction. After the reaction, the as-synthesized LFP particles were collected by centrifuge. The collected particles were washed with acetone, followed by ethanol to remove impurities. Finally, the precipitates were filtered by nylon membrane under pressure and were vacuum dried at 120 °C for 12 h. The collected powders were then characterized without any heat treatment.

The processing conditions were screened to obtain the best condition for synthesizing LFP particles with the desired product attributes. First, the mole ratio of Li to P was studied to determine the optimal ratio for synthesizing highly crystalline single phase LFP. This was conducted by changing the mole ratio of LiOH and H₃PO₄ (2:1, 2.5:1, 3:1), which lead to different initial pH at different Li:P mole ratios. This range was selected for screening as it provided a weakly acidic
solution which is better for LFP particle synthesis [55, 63]. With the optimal Li:P ratio, the effect of surfactant (PVP, CTAB, PEG) on particle morphology was studied to select surfactants that provided the desired morphology. After that, the reaction was carried out for different duration (3, 6, 12, and 24 h) to select the optimal time for producing particles with desired particle size and product purity. LFP particles with the desired attributes and synthesized under optimal conditions were carbon coated in the next step.

### 3.2.2. Carbon coating on LFP particles

A specific amount of sucrose (99.5%, Sigma-Aldrich), 15 wt% of the weight of LFP particles to be coated, was dissolved in a small amount of water. The synthesized LFP particles were then added to the sucrose solution and the solution was mixed by a magnetic stirrer to ensure complete wetting on the LFP particles. After mixing, the solution was kept at 600 °C under N₂ atmosphere in a tubular furnace for 2 h to obtain the carbon coated LFP nano-particles.

### 3.2.3. Characterization of the LFP particles

LFP particles (before carbon coating) were weighed, dissolved in H₂SO₄, and diluted to measure its purity by inductively coupled plasma optical emission spectrometry (ICP-OES). Crystal structure and crystallinity of the LFP powders were determined by X-ray diffraction, using Cu Kα radiation (λ= 1.54Å) (XRD, Model PW1830 Philips, 2KW, Cu anode, graphite monochromator), to verify whether the phase of powders was LiFePO₄. The XRD experiment was conducted by steps scanning method with a step interval of 0.02° and a count time of 1s per step. MDI Jade 6.0 software was used to analyze the XRD patterns of the products. The particle size and morphology of the samples were observed by a field emission scanning electron microscope (SEM, JSM-7100F, JOEL) and transmission electron microscopy (TEM, JOEL-2010F, 200 kV). The TEM images were also used for analyzing the thickness and the uniformity of carbon coating on the surface of the LFP particles. The tap density was obtained by recording the volume before and after mechanical tapping of a measuring cylinder containing carbon coated LFP particles, until no further change in volume was observed. The specific surface area of the carbon coated LFP particles was
measured by the Brunauer-Emmett-Teller (BET) method (Surface Area Analyzer, Beckman Coulter, SA3100). The carbon content on the coated LFP particles was determined by thermogravimetric analysis (TGA) using TA instruments Q50, with a heating rate of 5 °C min\(^{-1}\) from 25 to 600 °C, under a flow of purified air.

3.2.4. Button cell fabrication

The cathode was prepared by casting slurry onto aluminum sheets. The slurry contained 90 wt% active material (carbon coated LFP), 2 wt% Kynar polyvinylidene fluoride, and 8 wt% conductive carbon (Super P), dispersed in N-methyl methyl-pyrrolidone. All materials were used without further treatment. The cathode was then dried at 120 °C for 16 h. The current collector was punched into discs with an area of 1.227 cm\(^2\) and weighed around 3.5 mg. Lithium metal was used as the anode, a solution of 1M LiPF\(_6\) in a 1:1 (vol/vol) mixture of ethylene carbonate and dimethyl carbonate as the electrolyte, and Celgard 2400 microporous membrane as the separator. CR2016 type button cells were assembled in an argon-filled glove box.

3.2.5. Electrochemical performance tests

The galvanostatic discharge test was performed between 2.0 and 4.0 V at room temperature with different current densities 0.1, 0.5, 1 and 1.5C using Neware BTS 3000 (Shenzhen China). Electrochemical impedance spectroscopy (EIS) measurements were conducted by potentiostatically applying a 10 mV AC voltage over the frequency from 30 mHz to 1 MHz using a CHI 760E electrochemical workstation (Chenhua, Shanghai China). Before the EIS tests, the cells were cycled for two times at a rate of 0.1 C. All electrochemical measurements were carried out at room temperature.

3.3. Results and discussion

3.3.1. Screening of conditions for synthesizing LFP particles with desired product attributes
Li:P mole ratio

The effect of Li:P mole ratio was studied at 2:1, 2.5:1, and 3:1 with the reaction duration fixed at 12 h, and the initial pH values of the solution were 3.4, 4.5, and 6.2, respectively. The crystal structure of the synthesized LFP particles were characterized by XRD and their XRD patterns were illustrated in Figure 3-1. Comparing the XRD patterns of the synthesized particles with that of standard LFP particles (JCPDS#83-2092-Triphyllite), the LFP particles synthesized with mole ratios of 2.5:1 and 3:1 had XRD patterns matched with that of standard LFP particles, but not for particles synthesized with a mole ratio of 2:1. This showed that single phase LFP particles were synthesized with higher mole ratios (2.5:1, 3:1). The intensity of peaks were higher for particles synthesized at a mole ratio of 3:1 when compared with that of 2.5:1, showing that LFP particles with higher crystallinity were synthesized with higher mole ratio. As LFP particles with higher crystallinity exhibit better stability, leading to a longer cycle life, the Li:P mole ratio of the polyol refluxing process was fixed at 3:1 for subsequent experiments.

Figure 3-1 XRD patterns of the LFP samples synthesized in different Li:P mole ratio (reaction time is 12h).
Surfactant for morphology control

Various studies showed that particles morphology can be controlled by adding surfactant to the polyol refluxing process [31, 42, 54]. Three surfactants (PVP, CTAB, PEG) were used in this study, and their XRD patterns and SEM images are illustrated in Figure 3-2 and Figure 3-3, respectively. A control experiment with no surfactant added was also conducted as a comparison. The XRD patterns showed that all samples were single phase LFP, as their peaks matched with the XRD pattern of the standard LFP particles, and were highly crystalline. The SEM images showed that LFP particles with different morphology were produced. LFP particles with rod-like and plate-like morphology were produced when PVP and PEG were used as surfactant, respectively, while irregular LFP particles were produced if CTAB was used as the surfactant. Spherical particles were produced when no surfactant was added. As morphologies with short b-axis (i.e. nanoplate and nanorod) are desired, only PVP and PEG were selected as the surfactant in subsequent experiments.

Figure 3-2 XRD patterns of the LFP samples with different morphology in polyol process (Li: Fe ratio is 3:1, refluxing duration is 6h)
Figure 3-3 SEM images of LFP particles with different morphology by adding surfactants (a) rod-like, (b) irregular, (c) plate-like, and (d) spherical. All scale bars are 100 nm.

**Reaction Duration**

In LFP particle synthesis, the reaction duration affects the size and purity of the synthesized particles. A longer reaction time provides more time for particles to grow. The purity might be lower as more impurities may form during the reaction. The reaction was carried out for different duration (3, 6, 12, 24 h) to observe its effect on particle size, the SEM images of Spherical LFP particles with no surfactant added are shown in Figure 3-4, the average particle size of the LFP particles were increased as the reaction time. Additionally, the SEM images of the rod-like and plate-like LFP particles that synthesized with 3h, 6h and 12h are showed in Figure 3-5. As the reaction time increased in the order of 3h, 6h, and 12h, the particle size of the rod-like LFP were
120(L)\times35(D) \text{ nm}, 140(L)\times40(D) \text{ nm}, and 200(L)\times55(D) \text{ nm} (L \text{ means length, } D \text{ means diameter of the width}); while the size of plate-like particles were 180(L)\times100(W)\times35(T) \text{ nm}, 210(L)\times110(W)\times40(T) \text{ nm}, and 280(L)\times160(W)\times50(T) \text{ nm} (L \text{ means length, } W \text{ means width, } T \text{ means thickness}). From the observation of the SEM images, even when the morphology of the LFP were changed, the average size of the LFP particles also increased as the reaction time.

Figure 3-4 SEM images of spherical LFP sample with different synthesis reaction time (a) 3h, (b) 6h, (c) 12h, and (d) 24h.
Figure 3-5 SEM images of rod-like and plate-like LFP samples with different synthesis reaction time (a) and (d) 3h, (b) and (e) 6h, and (c) and (f) 12h. All scale bars are 100 nm.

Figure 3-6 XRD patterns of the spherical LFP sample synthesized in different reaction duration.
The XRD patterns of spherical LFP particles synthesized at different reaction duration were shown in Figure 3-6. The peaks of all samples (3, 6, 12, 24 h) matched with that of standard LFP particles. The intensity of the peaks was higher when the reaction time was increased from 3 h to 12 h, showing that the crystallinity of LFP particles were also higher. However, the crystallinity became lower for LFP particles synthesized for a longer duration (24 h), as impurities might form if the reaction was conducted for too long. With the XRD patterns and SEM images, a reaction duration of 6 h was optimal in synthesizing LFP particles of different morphology (nanorods, nanoplates, spherical) with the desired particle size and purity, and the dimensions of these LFP particles are summarized in Table 3-1.

Table 3-1 Physical properties of different morphology LFP particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Primary particle size (nm)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Purity (%)</th>
<th>Morphology</th>
<th>Tap density (g/mL)</th>
<th>Carbon content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140(L)*40(D)</td>
<td>27.98</td>
<td>99.3</td>
<td>Rod</td>
<td>0.64</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>210(L)*110(W)</td>
<td>22.55</td>
<td>99.4</td>
<td>Plate</td>
<td>0.67</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>120(D)</td>
<td>25.47</td>
<td>99.1</td>
<td>Spherical</td>
<td>0.67</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Notes: The primary particle size is directly measured from SEM pictures with around 300 particles, the size is the average of the measured sample. In this column, D means diameter, T means thickness, W means width, and L means length.

Summary

After the screening experiments, the optimal conditions for synthesizing LFP particles with desired attributes were obtained. The Li:P mole ratio was optimized at 3:1 for having single phase LFP particle with high crystallinity. PVP and PEG could be added to produce nanorods and nanoplates LFP particles, respectively, and a reaction time of 6 h was enough to synthesize particles with the desired size and crystallinity. On top of particle size and morphology, other particle properties that are important for cathode preparation in button cell fabrication are also summarized.
in Table 3-1. Spherical LFP particles synthesized with no surfactant added are also presented for comparison. The purity of all samples were measured by ICP-OES and were > 99%. The tap densities of LFP particles of different morphology were similar (0.64 - 0.67 g cm\(^{-3}\)), and the specific surface area of the LFP samples varied from 22.55 to 27.98 m\(^2\) g\(^{-1}\). All these LFP particles were carbon coated and fabricated as cathode in button cells for electrochemical tests.

### 3.3.2. Carbon coating

Carbon coating was conducted for LFP particles with the desired size and purity, and of different morphology (nanorods, nanoplates, spherical). As the conductive carbon layer was partially crystalline and the LFP particle was crystalline, the carbon layer could be differentiated from the LFP particle in high resolution TEM images. The TEM images of carbon coated spherical LFP particles are depicted in Figure 3-7. From these images, the size of the LFP particles was around 50-200 nm, similar to that obtained from SEM images, and the carbon coating was uniform and its thickness was around 4 nm. TGA analysis showed that the carbon content of all carbon coated LFP particles was roughly the same, from 2.9% to 3.2%, as illustrated in Table 3-1 for different samples.

![Figure 3-7 TEM images of carbon coated spherical LFP particles.](image)
3.3.3. Electrochemical performance tests

The galvanostatic discharge curves of LFP samples of different morphology (nanorods, nanoplates, spherical) at selected C-rates (0.1 C, 0.5 C, 1 C and 1.5 C) are shown in Figure 3-8. The specific capacity at a certain C-rate was obtained from the capacity corresponding to the lowest potential (2.0 V) of that discharge curve, and are summarized in Table 3-2 for the LFP samples at a C-rate from 0.1 C to 1.5 C. The specific capacity generally dropped with increasing C-rate. Button cell using nanorods LFP particles as cathode material had the highest specific capacity at both low (160.5 mAh g\(^{-1}\) at 0.1C) and high C-rate (123.7 mAh g\(^{-1}\) at 1.5C), while button cell using spherical LFP particles as cathode material exhibited the worst performance at low (153.4 mAh g\(^{-1}\) at 0.1 C) and high C-rate (103.5 mAh g\(^{-1}\) at 1.5C). The rate capability of the LFP button cells, defined as the retention percentage of the specific capacity at 0.1 C, at C-rates higher than 0.1 C are also summarized in Table 3-2. As the specific capacity was lower at higher C-rate, the rate capability decreased with increasing C-rate. Button cells using nanorods and nanoplates LFP particles as cathode materials had rate capability above 75% at high C-rate (1.5 C), while button cells using spherical LFP particles as cathode material had lower rate capability at high C-rate (67.5% at 1.5 C) and a more significant drop was observed when the C-rate was higher than or equal to 1 C.
Figure 3-8 Discharge curves (0.1, 0.5, 1C and 1.5C) of button cells made of different morphology LFP cathode material.
Table 3-2 Specific capacity and rate capability of button cells made with different morphology carbon coated LFP cathode materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific capacity (mAh g(^{-1}))</th>
<th>Rate capability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 C</td>
<td>0.5 C</td>
</tr>
<tr>
<td>Rod</td>
<td>160.5</td>
<td>148.0</td>
</tr>
<tr>
<td>Plate</td>
<td>153.5</td>
<td>140.7</td>
</tr>
<tr>
<td>Spherical</td>
<td>153.4</td>
<td>139.8</td>
</tr>
</tbody>
</table>

The EIS is used to evaluate the charge transfer resistance of button cells made of different cathode materials, and the impedance spectra of all button cells are shown in Figure 3-9. The impedance spectrum is composed of a depressed semicircle and the data points are arranged at decreasing frequency along the real impedance axis (x-axis). The difference between the two intercepts of the semicircle with the real impedance axis represents the charge transfer resistance \[45\]. Figure 3-9 shows that the charge transfer resistance was the smallest for button cell using nanorod LFP particles as cathode material, while button cell using spherical LFP particles as cathode material had the largest resistance. Button cells with a larger resistance also had to a lower specific capacity at all C-rates (Table 3-2).
The results reported in this chapter matched with the causal table developed in our previous study which summarizes the effect of particle attributes on electrochemical performance. In general, particle morphology of thinner structure such as nanoplate and nanorod (i.e. shorter b-axis) has a higher specific capacity, a higher rate capability at high C-rate, and a smaller charge transfer resistance. In this chapter, button cells using nanorod and nanoplate LFP particles as cathode materials had a performance better than that using spherical LFP particles.

3.4. Conclusion

High quality cathode material can fulfill many requirements on the electrochemical performance for LIBs in many areas. LFP is one of the popular high quality cathode materials that can be synthesized with controllable size and morphology. A poly refluxing process is used to synthesis the morphologically-tailored LFP particles and illustrate their electrochemical performance. After
screening of the synthesis conditions, the single-phase high purity LFP nano-particles with four morphology (rod, irregular, plate, and spherical) were synthesized. With the carbon coating process, a uniform ~4 nm thick carbon layer was coated on the surface of the LFP nano-particles. In the button cell tests, the rod-like LFP sample with around 140*40 nm particle size, 2.9% carbon coating exhibited the best specific capacity (160.5 mAh g⁻¹ at 0.1C) and rate capability (77.1% at 1.5 C). Also, the charge transfer resistance measured from the EIS was the smallest. On the other hand, the spherical LFP samples with larger particle size (120 nm) and spherical shape had lower specific capacity and rate capability, despite the same purity and same amount of carbon was coated on the particles. With this study, desired high quality LFP particles can be produced by determining the synthesis conditions.
4. Process Development for the Recycle of Spent Lithium Ion Batteries by Chemical Precipitation

4.1. Introduction

Lithium ion batteries (LIB) become the major power supply for electric vehicles and portable electronics such as mobile phones and laptops due to their high energy density, high capacity, and lightweight [65]. This results in an increased LIB consumption in recent years. A global production of 4.5 billion cells of LIB that worth 9.3 billion USD was reported in 2011 [66]. The annual production of LIB is expected to reach 6 billion cells in 2015, equivalent to an energy production of around 50GWh [3]. The increased reliance of LIB in electronic equipment also increases the number of spent batteries being disposed to the landfills. The number is expected to grow in the near future due to the faster replacement of the electronic products. However, disposing spent LIB that contains organic electrolyte and metals such as Ni, Co, Cu, and Li leads to serious environmental problems such as soil and underground water contamination [32]. This is also a waste of the valuable metals contained in the batteries. Therefore, recycling spent LIB not only reduces environmental pollution, but also saves limited metal reserve in the earth, and reduces the reliance of lithium import in many countries as around 80% of Li are produced from Argentina, Chile, and China [67].

LIB contains various components such as cathode plate, anode plate, electrolyte, and polymer separator. Among these components, cathode materials that contain Li and other metals are the most valuable for recycling. However, only limited companies such as AEA Technology (UK), SNAM (France), Toxco (Canada), and Umicore (Belgium) have developed processes for recycling valuable metals from the cathode. In the recycling process of cathode materials, metal ions are first dissolved from the cathode plate, followed by separating and recovering metal salts from the solution in various steps. Acids such as dilute HCl [68], HNO₃ [69, 70], and H₂SO₄ [71, 72] could be used to dissolve metal ions from the cathode plate. H₂O₂ is usually added in this process to increase its rate and to convert metals such as cobalt and manganese to the divalent state [70, 71]. The dissolved metal ions are then separated and recovered by various processes such as electrochemical process [71], chemical precipitation [73, 74], and solvent extraction [72]. Among
these recovery techniques, chemical precipitation is commonly employed. The metal salt recovered from the precipitation process can be a mixed metal oxide such as LiCoO$_2$ or a compound containing single metal salt such as Li$_2$CO$_3$ [72, 75]. However, it is not easy to control the target products to be recovered from the precipitation process. The major reason is that the operating conditions for these precipitation processes are determined by trial and error, without considering the solid-liquid equilibrium (SLE) phase behavior that governs the chemical precipitation process. Without understanding the phase behavior of these systems, compound other than the target compound may be recovered from the precipitation process. Or, the target compound would coprecipitate with other metal salts, leading to a reduced purity of the compound recovered from the process or a more complicated process is required to further separate the mixed metal compounds. Even if the target compound is precipitated, the operating conditions may not be the optimal, leading to a lower recovery in the precipitation process or excess usage of chemicals. The process developed based on trial and error is also very specific, meaning that the process may not be applicable even if the same cathode material, but with a different composition is recycled. One example would be the ratio of Co and Mn is changed from 1:9 to 9:1 in LiCo$_x$Mn$_{1-x}$O$_2$ cathode material.

The utilization of SLE phase behavior to design precipitation processes is well-developed in the literature. Wibowo and Ng [76] developed a unified procedure, which relies on the representation of basic operations such as chemicals addition and solvent removal as movements on the phase diagram, for synthesizing separation process based on crystallization or precipitation. This procedure has been applied to synthesize separation process for systems involving chiral compounds [77, 78], solid solutions [79], fullerenes [80], amino acids [81], and proteins mixture [82]. The same idea can be applied to the separation and recovery of metal salts from the cathode materials. Two cathode materials, namely LiFePO$_4$ and LiCo$_x$Mn$_{1-x}$O$_2$, are studied in this chapter to illustrate how the SLE phase behavior can be used to design the process and determine the optimal operating conditions of the recycling process. The general approach in utilizing SLE phase behavior to design the recycling process and determine its operating conditions is discussed first, followed by using two case studies to illustrate this general approach.
4.2. General approach in designing the recycling process

The recycling process of cathode materials typically comprises a leaching process and a series of selective precipitation process that provides separation and recovery of target metals. For each precipitation process, the SLE phase behavior of the components involved in that process governs the component(s) to be recovered from the process and the corresponding recovery. It also dictates the optimal operating conditions for the precipitation process. Therefore, the first step in designing the precipitation process is determining the SLE phase behavior for a system consisting of the components involved in the precipitation process. SLE phase behavior can be conveniently visualized using a phase diagram. Such a phase diagram is usually high-dimensional as the system of interest consists of many molecular and ionic species. The representation of the SLE phase behavior of an electrolyte system using a high-dimensional phase diagram has been studied by previous researchers [83, 84]. The number of independent coordinates $F$ required for a complete graphical representation of the isothermal-isobaric phase behavior of electrolytic systems is represented by the following equation:

$$F = m + n + s - 2$$

where $m$ represents the number of simple cations present in the system, $n$ the number of simple anions, and $s$ the number of non-dissociating molecular species or solvents. Among these independent coordinates, the system contains $m-1$ cationic coordinates, $n-1$ anionic coordinates, and $s$ solvent coordinates. Since it is impossible to visualize the phase diagram in its entirety when the dimensionality is larger than 3, various projections and cuts can be made to reduce its dimensionality. A projection is produced by not explicitly plotting the effect of one or more intensive variables on the phase behavior, whereas a cut is generated by plotting the phase behavior at fixed values of one or more intensive variables. Each variable that is fixed or not explicitly considered reduces the dimensionality of the original phase diagram by one. Various types of projections are applied in this study, including combining various coordinates in the phase diagram, lumping one or more of the components that would not precipitate in the process into another component, and taking a Jänecke projection by normalizing the composition with respect to the solvent.
In order to utilize the SLE phase behavior for process design and determination of operating conditions for the precipitation process, an experimental plan is devised to systematically determine the required solubility data. As mapping out the whole phase diagram by measuring solubility requires a huge experimental workload, only the most important parts of the phase diagram will be studied in order to guide and optimize the design of the whole recycle process. For example, in a process for precipitating Fe salts from recycled LiFePO$_4$ cathode powders, only FePO$_4$ or Fe(OH)$_3$ would precipitate as they are much less soluble than their Li counterparts. Therefore, the SLE phase behavior measurements are focused only on the crystallization regions of Fe salts, and not on the crystallization regions of Li salts.

Figure 4-1 Experimental setup for solid-liquid equilibrium (SLE) measurement.

The experimental setup shown in Figure 4-1 was used to conduct these solubility data measurements. Instead of using cathode materials recycled from spent LIB, a synthetic feed with
a similar composition was prepared. The feed was dissolved in a certain volume of solvent inside a jacketed glass vessel, which was then sealed with a stopper and its outer jacket was connected to a water bath (Huber, model Unistat 360 HT) by two Tygon tubes to control the solution temperature. A specific volume of the precipitant was added to the solution mixture to precipitate metal salts, and the mixture was agitated with a magnetic stirrer (Heidolph Instrument Company, model MR 3001). After equilibration for 240 min, the mother liquor and the precipitated solids were separated by vacuum filtration.

The pH of the mother liquor was measured with a pH/mV meter (Model Mettler-Toledo AG SevenGo2, Switzerland) and concentration of metals such as Li$^+$ and Fe$^{3+}$ in the mother liquor were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES) (Model Varian 725-ES, Australia). For experiments where the concentration of anions such as PO$_4^{3-}$ are important, they were measured by an ion chromatography (Model 881 Compact IC pro, Switzerland). The standard solutions were provided by High-Purity Standards, ISO 9001:2008 99.998%, and diluted in double deionized (DDI) water with a resistivity of 18.2 MΩ cm$^{-1}$ at room temperature. Collected solids were washed with DDI water, dried in an oven and weighed by an electronic balance. Depending on the information required on the collected solids, various analysis could be performed. To confirm the metals concentration in the solids, 0.02 g collected solids was dissolved in 50mL 0.1 M H$_2$SO$_4$ and analyzed by ICP-OES. To confirm the identity of the precipitated solids, thermo-gravimetric analysis (TGA) (Model TGA Q50, US) or powder X-ray diffraction (XRD) system (Model PW1830 Philips, 2KW, Cu anode, graphite monochromator) was conducted. XRD was also conducted in cases where the crystallinity of the precipitated solids is required.

The SLE phase behavior study serves two purposes. First, it provides the rationale behind the separation processes, which were mostly developed by trial and error. For example, the fact that only a particular salt precipitates out when a precipitant is added to a mixture containing various ions can be attributed to the feed point being located inside the crystallization region of that salt. Second, the SLE phase diagram also provides opportunities to further optimize the process. For example, the optimum amount of precipitant that has to be added can be determined by identifying the boundaries of the crystallization region of the desired salt. In some cases, insights from the SLE phase behavior can lead to new process alternatives that would not have been identified otherwise.
These process alternatives could then be compared with the base case process to determine the most effective process flowsheet and the corresponding operating conditions. These ideas of using SLE phase behavior to optimize the recycling process of spent LIB are illustrated below using two case studies, with LiFePO$_4$ and LiCo$_x$Mn$_{1-x}$O$_2$ as the cathode material to be recycled.

4.3. Case Study I: Recycle of LiFePO$_4$ cathode material

With the rapid development of electric vehicles which mostly use LiFePO$_4$ as the cathode material in the batteries, the recycle of LiFePO$_4$ becomes important [85, 86]. Based on similar recycling processes from the literature [68, 73], the base case process for recycling LiFePO$_4$ from spent LIB is illustrated in Figure 4-2. For any recycling process, spent LIB has to be fully discharged first. The batteries are then dismantled manually to remove plastic or steel casing. The components inside the batteries such as anode plate, cathode plate, separator sheet, and electrolyte are then separated. In the cathode plate, the cathode material is adhesively attached to an aluminum foil by a binder. It can be separated from the foil by dissolving the binder with a solvent such as N-Methyl-2-pyrrolidone (NMP). The cathode material LiFePO$_4$ is then collected after filtration. As the structure of the cathode particles is destroyed after hundreds of charging and discharging cycles, the cathode material cannot be reused directly for battery fabrication and has to be recycled as metal salts and re-synthesized as cathode material. As cathode material LiFePO$_4$ is not soluble in water, it is dissolved in an acidic solution. Literature suggested that it can be completely dissolved in 120 min by adding 4 mol/L H$_2$SO$_4$ containing 2 vol% H$_2$O$_2$ at 60°C [68]. The mass of solvent added is 8 times that of the cathode material to ensure complete dissolution, while H$_2$O$_2$ serves as an oxidizing agent [87] to increase the efficiency of dissolution by converting Fe$^{2+}$ to Fe$^{3+}$. After the dissolution process, Li and Fe are separated and recovered in subsequent steps by selective precipitation. As Li salts are much soluble than Fe (III) salts, Fe is recovered in the first precipitation process, followed by recovering Li in the second precipitation process. In order to guide the design of the precipitation process and optimize the operating conditions, it is important to understand the SLE phase behavior of the relevant system.
4.3.1. Precipitation process for Fe recovery

Conceptual phase behavior

After the dissolution process, Fe is recovered in the first precipitation process by adding NaOH to the acidic solution of LiFePO$_4$. Therefore, the overall feed to the precipitation process contains Li$^+$, Fe$^{3+}$, Na$^+$, H$^+$, OH$^-$, SO$_4^{2-}$, and PO$_4^{3-}$. Complex ions such as HPO$_4^{2-}$ and H$_2$PO$_4^{-}$ are not considered since they are assumed to completely dissociate into simple ions for plotting purposes. The corresponding phase diagram has 5 independent coordinates, including 3 cationic coordinates and 2 anionic coordinates as determined by Eqn. 1. There is no solvent coordinate for H$_2$O because H$^+$ and OH$^-$ are both present in the system. To visualize such a high-dimensional phase diagram, its dimensionality can be reduced by lumping Na$^+$ into H$^+$ and SO$_4^{2-}$ into PO$_4^{3-}$, as the sodium and sulfate salts have relatively high solubility and would not precipitate in this process. This results in a simplified 3-dimensional conceptual phase diagram, as illustrated in Figure 4-3. Projected
components are labelled on the corresponding vertices of the phase diagram with a smaller font size. The surfaces in the diagram represent the solubility surfaces of anhydrous FePO$_4$(s), FePO$_4$·2H$_2$O(s), Fe(OH)$_3$(s), Li$_3$PO$_4$(s), and LiOH(s) at a certain ratio of H$^+$/Na$^+$ and SO$_4^{2-}$/PO$_4^{3-}$. Underneath these surfaces there are regions of single, double, or triple saturation that are located on top of each other. Some of these regions are identified in Figure 4-3. Depending on which region the composition of a mixture ends up falling, one or more solid species may crystallize out. Since the precipitation process will be conducted at a relatively high water content, FePO$_4$ is expected to always crystallize as a dihydrate (FePO$_4$·2H$_2$O) rather than its anhydrous form. For this reason, regions involving anhydrous FePO$_4$ are not marked on the diagram. At different H$^+$/Na$^+$ or SO$_4^{2-}$/PO$_4^{3-}$ ratios, the compartment boundaries will be different, and there may also be saturation regions for NaOH, Na$_3$PO$_4$, Na$_2$SO$_4$, Fe$_2$(SO$_4$)$_3$, and Li$_2$SO$_4$, which would overlap with the depicted regions in this projection.

Figure 4-3 3-dimensional conceptual phase diagram for the precipitation process of Fe recovery in case study I.
To further reduce the dimensionality, the solvent edge (H$_3$PO$_4$-H$_2$O) is projected onto the Li$_3$PO$_4$-LiOH edge to give a two-dimensional diagram as shown in Figure 4-4. Each crystallization compartment corresponds to the precipitation of the component with bold and larger fonts in that vertex. Other components are labelled for completeness, but they will not be precipitated in this step. Note that FePO$_4$·2H$_2$O is located on the plane of FePO$_4$·Fe(OH)$_3$-H$_3$PO$_4$-H$_2$O in Figure 4-3, and so that the projection of solvent edge onto Li$_3$PO$_4$-LiOH edge results in a point of FePO$_4$·2H$_2$O located in the interior of the diagram. Li$_3$PO$_4$ and LiOH, which are much more soluble than FePO$_4$·2H$_2$O and Fe(OH)$_3$, have very narrow saturation regions on the right hand side of the diagram. Consequently, unless the feed contains very little Fe, FePO$_4$·2H$_2$O and Fe(OH)$_3$ will always precipitate out first, while their Li counterparts will only co-precipitate after the Fe content in the solution is low enough to reach the corresponding saturation regions. Nonetheless, it is important to identify the saturation region boundaries, which dictate the recovery of pure Fe salts before there is co-precipitation of either Li$_3$PO$_4$ or LiOH. Note that Figures 4-3 and 4-4 are not drawn to scale; they are only a sketch to illustrate the relative solubility of the different species and to clearly identify their saturation surfaces. Readers unfamiliar with SLE phase diagram representations can refer to Wibowo and Ng [76] and Wibowo [88] for more detailed explanations.

The process path of the Fe precipitation is also shown on Figure 4-4. The numbers on the process paths correspond to stream numbers in Figure 4-2. The feed after the dissolution process (point 10) is located in the interior of the diagram as it contains OH$^-$ from water (which is assumed to completely dissociate into H$^+$ and OH$^-$ for plotting purposes). With the addition of NaOH, the process point moves to point 12 and FePO$_4$·2H$_2$O precipitates out, producing a mother liquor with a composition indicated by point 15 which is located on the boundary between FePO$_4$·2H$_2$O and Li$_3$PO$_4$ compartments. Alternatively, a larger amount of NaOH can be added to the feed, so as to move point 12’ inside the precipitation region of Fe(OH)$_3$. The mother liquor composition after precipitation is given by point 15’, located on the boundary between Fe(OH)$_3$ and LiOH compartments. Note that depending on the solvent content, the mixture may also fall inside the region where both FePO$_4$·2H$_2$O and Fe(OH)$_3$ precipitates out. As illustrated in Figure 4-3, this region is located underneath the saturation regions of FePO$_4$·2H$_2$O and Fe(OH)$_3$, so that it does not appear in the projection in Figure 4-4. The maximum recovery of pure Fe in any form can be determined by looking at the identity of the multiple saturation points27, 28. In Figure 4-4, S1 and S2 are identified to be incongruent and congruent multiple saturation point, respectively. Therefore,
the maximum recovery of pure Fe (in any form) is achieved by regulating the addition of NaOH so that the mother liquor composition (point 15’) is located at the congruent multiple saturation point S2. Although it is feasible to recover Fe either as FePO$_4$·2H$_2$O or Fe(OH)$_3$, precipitating Fe as FePO$_4$·2H$_2$O is preferred as it has a higher economic value compared to Fe(OH)$_3$, and less amount of NaOH is required to precipitate FePO$_4$·2H$_2$O. The maximum recovery of pure FePO$_4$·2H$_2$O will be achieved if point 15 is located at point S1.

Figure 4-4 Projection of H$_3$PO$_4$-H$_2$O edge onto Li$_3$PO$_4$-LiOH edge in the conceptual phase diagram for the precipitation process of Fe recovery in case study I.
Experimental methods

Rather than attempting to map out the entire five-dimensional SLE phase diagram, which would require a large number of data points, experiments are focused on the expected path taken by the process as NaOH is added to the acidic solution of LiFePO$_4$. Instead of actual cathode materials from spent LIB, Li$_3$PO$_4$ and FePO$_4$ (FePO$_4$·2H$_2$O, Fe 29%), both purchased from Sigma-Aldrich and used without further purification, served as the ingredients of a synthetic feed. A mixture of Li$_3$PO$_4$ (0.039g) and FePO$_4$·2H$_2$O (0.187g) was dissolved in a jacketed glass vessel containing 100 mL of 0.08 M H$_2$SO$_4$ (95-97%, Merck). This produced a mixture with Li:Fe mole ratio of 1:1 as in the acidic solution of LiFePO$_4$, although the Fe:P ratio was different. A specific volume of 2M NaOH solution, prepared by dissolving NaOH pellets (ACS reagent, ≥97.0%, Sigma-Aldrich) in DDI water, was added to the solution mixture to cause precipitation. The mother liquor and the precipitated solids were then separated by vacuum filtration. The pH and concentrations of Li$^+$, Fe$^{3+}$, and PO$_4^{3-}$ in the mother liquor were measured. The solids were dried in a vacuum oven to remove solvent. A sample of the solids was dissolved in H$_2$SO$_4$ and analyzed by ICP-OES to measure the concentrations of Li$^+$ and Fe$^{3+}$, so as to confirm whether any Li was precipitated together with Fe. The identity of the collected solids were also analyzed by TGA to determine whether it is Fe(OH)$_3$ or FePO$_4$·2H$_2$O.

Results

The concentrations of Li$^+$, Fe$^{3+}$, and PO$_4^{3-}$ remaining in the mother liquor after adding different volumes of NaOH solution as precipitant are summarized in Table 4-1, both in ppm and as a percentage of their feed concentrations (69.4, 558.5, and 1266 ppm, respectively). The results clearly showed that the concentration of Fe$^{3+}$ remaining in the mother liquor decreased as more NaOH was added, while the Li$^+$ concentration remained more or less the same. Meanwhile, PO$_4^{3-}$ concentration in the mother liquor initially decreased with NaOH addition, but increased when more than 7.5 mL NaOH was added. The results also indicated that the amount of solids collected in the experiments reached a maximum upon addition of 7.5 mL NaOH solution.
Table 4-1 Experimental results of adding different volumes of NaOH to the precipitation process for Fe recovery in case study I.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (NaOH) Volume (mL)</th>
<th>pH</th>
<th>Mother Liquor (ML)</th>
<th>Solid Weight (g)</th>
<th>Li(^+) Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Fe(^{3+}) Concentration (ppm)</th>
<th>% remained in ML</th>
<th>PO(_4^{3-}) Concentration (ppm)</th>
<th>% remained in ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>1.77</td>
<td>63.0</td>
<td>47.7</td>
<td>96.3%</td>
<td>9.0%</td>
<td>417.8</td>
<td>35.0%</td>
<td>0.147</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>2.02</td>
<td>62.5</td>
<td>14.6</td>
<td>95.9%</td>
<td>2.8%</td>
<td>332.6</td>
<td>28.0%</td>
<td>0.152</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>2.15</td>
<td>62.4</td>
<td>8.07</td>
<td>96.2%</td>
<td>1.5%</td>
<td>313.3</td>
<td>26.5%</td>
<td>0.157</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td>3.40</td>
<td>61.3</td>
<td>0.12</td>
<td>94.9%</td>
<td>0.0%</td>
<td>302.4</td>
<td>25.7%</td>
<td>0.158</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>5.44</td>
<td>61.4</td>
<td>0.07</td>
<td>95.5%</td>
<td>0.0%</td>
<td>418.0</td>
<td>35.7%</td>
<td>0.143</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.5</td>
<td>8.29</td>
<td>61.1</td>
<td>0.44</td>
<td>95.5%</td>
<td>0.1%</td>
<td>704.8</td>
<td>60.4%</td>
<td>0.133</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>11.3</td>
<td>60.6</td>
<td>0.13</td>
<td>95.2%</td>
<td>0.0%</td>
<td>1154</td>
<td>99.4%</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>12.5</td>
<td>60.7</td>
<td>0.11</td>
<td>96.3%</td>
<td>0.0%</td>
<td>1146</td>
<td>99.6%</td>
<td>0.111</td>
<td></td>
</tr>
</tbody>
</table>

As the recovery of Li in the mother liquor is less than 100%, the collected solids (20 mg) were dissolved in 50 mL sulfuric acid solution to check whether Li was precipitated together with Fe. The concentrations of Li\(^+\) and Fe\(^{3+}\) in samples 3, 5, 6 and 7 were measured and summarized in Table 4-2. Since the measured Li\(^+\) concentration in all solid samples was negligible, it can be concluded that Li did not precipitate in the Fe recovery step and the difference between the Li\(^+\) concentration in the mother liquor and the feed was mainly due to the experimental error of samples dilution and the accuracy of the ICP-OES measurement.

Table 4-2 Experimental results of dissolving 20 mg of recovered solids in 50 mL of 0.1M H\(_2\)SO\(_4\)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Li(^+) concentration (ppm)</th>
<th>Fe(^{3+}) concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.00</td>
<td>146.4</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>150.4</td>
</tr>
<tr>
<td>6</td>
<td>0.03</td>
<td>168.9</td>
</tr>
<tr>
<td>7</td>
<td>0.04</td>
<td>199.0</td>
</tr>
</tbody>
</table>
Next, the identity of selected samples was determined by TGA to identify whether the precipitated solid was FePO$_4$·2H$_2$O or Fe(OH)$_3$. The results shown in Figure 4-5 show that the weight loss trend of samples 1 and 4 are very similar to that of FePO$_4$·2H$_2$O, while the trend for sample 7 is very similar to that of Fe(OH)$_3$. The TGA results are consistent with the experimental results summarized in Table 4-1. By taking mass balance (comparing the decrease in Fe and PO$_4^{3-}$ concentration from their initial values), the molar ratio of Fe to PO$_4^{3-}$ in the solids can be calculated. The results indicate that samples 1-4 are practically pure FePO$_4$·2H$_2$O, samples 7-8 are pure Fe(OH)$_3$, and samples 5-6 are mixtures of both.

The understanding of the SLE phase behavior helps to rationalize the data collected from the experiments. Upon addition of NaOH, the mixture first entered the compartment of FePO$_4$·2H$_2$O. The results of ICP measurement and TGA analysis suggested that FePO$_4$·2H$_2$O was precipitated in increasing amount from sample 1 to sample 4, as indicated by the increasing weight of solids collected and the decreasing PO$_4^{3-}$ concentration in the mother liquor. Almost all Fe was
precipitated when 7.5 mL of NaOH solution has been added (sample 4) and the mother liquor contained only a minute amount of Fe. When more NaOH was added in samples 5 and 6, the PO$_4^{3-}$ concentration in the mother liquor increased, accompanied by a decrease in the weight of collected solids. This is because the mixture entered the double saturation region of FePO$_4$·2H$_2$O and Fe(OH)$_3$, in which the precipitated FePO$_4$·2H$_2$O partially dissolved and precipitated as Fe(OH)$_3$, which has a lower molecular weight than FePO$_4$·2H$_2$O, resulting in the decreasing weight of the collected solids. With even more NaOH added, the mixture entered the compartment of Fe(OH)$_3$. Therefore, the solid was pure Fe(OH)$_3$ and all PO$_4^{3-}$ ions remained in the mother liquor. As most of the Fe had precipitated by then, further addition of NaOH did not cause much more precipitation, hence the same amount of solids collected. In summary, the experimental data showed that adding 7.5 mL NaOH as precipitant was the optimal condition for recovering Fe as FePO$_4$·2H$_2$O. Further addition of NaOH only converted FePO$_4$·2H$_2$O to Fe(OH)$_3$ and did not increase the Fe recovery.

![Solubility diagram](image)

Figure 4-6 Solubility data of the phase behavior for the Fe precipitation process in case study I (Numbers refer to the corresponding sample in Table 4-1).
By plotting compositions of feed point and mother liquor on the phase diagram, the precipitation regions of FePO$_4$ (as FePO$_4$·2H$_2$O), Fe(OH)$_3$, and a mixture of the two salts can be roughly identified. As the points were located so close to the edges of the phase diagram, the phase diagram was enlarged as shown in Figure 4-6 for easier visualization of the data points on the phase diagram. Samples 1 to 4 are located in the pure FePO$_4$·2H$_2$O region, resulting in mother liquor compositions (points 1’ to 4’) on the solubility surface of FePO$_4$·2H$_2$O. Samples 7 and 8 are located in the pure Fe(OH)$_3$ region, and the corresponding mother liquor compositions (points 7’ and 8’) are on the solubility surface of Fe(OH)$_3$. Points in between (samples 5 and 6) lie on the double saturation region where both FePO$_4$·2H$_2$O and Fe(OH)$_3$ precipitate out. Note that the boundaries of the region shift as the mixture composition progresses through different H$^+$/Na$^+$ ratio upon addition of different amount of NaOH and water.

**Process optimization – reducing water content**

The amount of water used for dissolving the feed powder has a direct impact on the amount of wastewater generated from the process, as well as the outcome of the precipitation process. This is illustrated in Figure 4-7, which is a cut of the three-dimensional SLE phase diagram (Figure 4-3) passing through the line connecting FePO$_4$·2H$_2$O and Li$_3$PO$_4$ vertices and a point along the H$_3$PO$_4$-H$_2$O edge (representing a mixture of H$_3$PO$_4$ and H$_2$O). Note that all components that would not precipitate (with smaller fonts in Figure 4-3) are omitted for clarity in this figure. Depending on the amount of water in the system, the overall mixture after adding the precipitant can be located in the region where only FePO$_4$·2H$_2$O precipitates (point a), in a double saturation region where FePO$_4$·2H$_2$O precipitates together with Li$_3$PO$_4$ (point c), or right on the boundary between the two regions (point b). If the mixture is in the FePO$_4$·2H$_2$O region (point a), the remaining liquid after precipitation will have a composition on the saturation curve of FePO$_4$·2H$_2$O, as indicated by point 1. On the other hand, a mixture in the mixed solids region (point c) will give a liquid composition at the double saturation point (point 2) and a solid composition as given by point 3. Since the Fe content in the liquid increases from point 2 to point 1, the yield of FePO$_4$·2H$_2$O decreases as more water is present in the system. Meanwhile, too little water will lead to a lower product purity due to co-precipitation of Li$_3$PO$_4$. Therefore, the highest yield of pure FePO$_4$·2H$_2$O will be obtained if the overall mixture is located at point b. Note that depending on the composition of the triple
saturation points and the ratio of $\text{H}_3\text{PO}_4$ to $\text{H}_2\text{O}$ in the solvent, the cut in Figure 4-7 may contain a region of three solids co-precipitating. The simplest behavior has been assumed for the sake of clarity in illustrating the effect of solvent volume on the outcome of the precipitation process.

![Diagram](image)

*Solid is a mixture of $\text{FePO}_4\cdot2\text{H}_2\text{O}$ and $\text{Li}_3\text{PO}_4$*

Figure 4-7 A cut from the 3-dimensional conceptual phase diagram in Figure 4-3.

In order to demonstrate the effect of water content in the precipitation process, additional experiments were conducted by dissolving the feed powder in different amounts of solvent, with varying water content but the same amount of acid (8 mmol of $\text{H}_2\text{SO}_4$) in all experiments. In each experiment, 7.5 mL of 2M NaOH solution (the optimum amount as determined above) was added as precipitant to recover Fe and the experimental results are summarized in Table 4-3. It can be clearly seen that with decreasing amount of water in the system, more solid precipitated out from the solution, although the increase was very small because the recovery of Fe was already close to 100%. In order to find out whether any Li had precipitated along with $\text{FePO}_4\cdot2\text{H}_2\text{O}$, all collected
solids were dissolved in 100 mL sulfuric acid and their composition were measured by ICP. The experimental data in Table 4-3 indicates that the solid recovered was pure FePO$_4$·2H$_2$O. In summary, 25 mL of water provided the highest yield in the experiments. As there was no Li coprecipitation yet, it is possible to further reduce the water content, but no further experiments were conducted in this study.

Table 4-3 Experimental results on the effect of water content on Fe recovery in case study I.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>H$_2$O (mL)</th>
<th>Solid Weight (g)</th>
<th>Ions concentration after dissolving all solids in 100mL acid</th>
<th>Li$^+$ (ppm)</th>
<th>Fe$^{3+}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>0.163</td>
<td></td>
<td>0.05</td>
<td>556.3</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.162</td>
<td></td>
<td>0.02</td>
<td>557.5</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>0.161</td>
<td></td>
<td>0.01</td>
<td>560.2</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.159</td>
<td></td>
<td>0.00</td>
<td>565.6</td>
</tr>
</tbody>
</table>

4.3.2. Precipitation process for Li recovery

After recovering Fe, the next step is to recover Li by adding Na$_3$PO$_4$ as the precipitant. As nearly all Fe was recovered in the first precipitation process, the solution contains only very little amount of Fe. Assuming that Fe is absent in this precipitation process, the solution mixture consists of H$^+$, Li$^+$, Na$^+$, SO$_4^{2-}$, PO$_4^{3-}$, and OH$^-$, resulting in an isobaric-isothermal phase diagram with 2 cationic coordinates and 2 anionic coordinates. Again there is no separate solvent coordinate for H$_2$O due to the presence of both H$^+$ and OH$^-$ in the system. By lumping SO$_4^{2-}$ into PO$_4^{3-}$ and projecting the solvent edge (H$_3$PO$_4$·H$_2$O) onto Na$_3$PO$_4$-NaOH edge, the conceptual phase diagram shown in Figure 4-8 is obtained at a certain ratio of SO$_4^{2-}$/PO$_4^{3-}$. Projected components are labelled on the corresponding vertices of the phase diagram with a smaller font size. Similar to Figure 4-4, at different SO$_4^{2-}$/PO$_4^{3-}$ ratios, the compartment boundaries will be different, and there may also be saturation regions for Li$_2$SO$_4$, Na$_2$SO$_4$, and H$_3$PO$_4$, which would overlap with the depicted regions in this projection. The crystallization compartments in Figure 4-8 correspond to the precipitation of the component with bold and larger fonts in that vertex. As Li$_3$PO$_4$ is a lot less soluble than the other species, its compartment is much larger than that of those other species. The process path is
also plotted on the phase diagram, with stream numbers corresponding to the flowsheet in Figure 4-2. The mother liquor from Fe precipitation step (point 15) is concentrated by removing water to give point 17, which is located above the solubility surface of Li$_3$PO$_4$. Addition of Na$_3$PO$_4$ moves the mixture composition to point 19, which lies below the solubility surface of Li$_3$PO$_4$. Consequently, Li$_3$PO$_4$ precipitates out, giving a mother liquor shown as point 22.

![Conceptual phase diagram for the precipitation process of Li recovery in case study I.](image)

The same SLE experimental setup was used to determine the best operating condition for Li recovery. The mother liquor collected in the Fe recovery step after adding 7.5 mL of 2 M NaOH (optimal condition for Fe recovery) was used as the feed solution. This solution was concentrated
to 50 mL by evaporating water, then added to the jacketed glass vessel connected to a water bath to control the temperature at 60°C during the experiment. A higher temperature was used as Li$_3$PO$_4$ has a lower solubility when temperature increases, thus collecting more solids. Different volumes of 1M Na$_3$PO$_4$ were added to the solution mixture. After equilibration for 240 min, the solids and the mother liquor were separated by vacuum filtration. The concentration of Li$^+$ in the mother liquor was measured by ICP-OES, while the purity, identity, and crystallinity of the collected solids were analyzed by XRD instead of TGA because the crystallinity of recycled Li$_3$PO$_4$ is important for refabrication as LIB cathode material.

![XRD results for the solids collected from the precipitation process of Li recovery in case study I.](image)

Figure 4-9 XRD results for the solids collected from the precipitation process of Li recovery in case study I.
Experimental results of Li$^+$ concentration in the mother liquor after adding different volume of Na$_3$PO$_4$ are summarized in Table 4-4. Note that the initial concentration of Li$^+$ was 138.8 ppm. The results show that 90% of Li was precipitated by adding 3 mL of Na$_3$PO$_4$, and almost all Li was precipitated by increasing the volume of Na$_3$PO$_4$ to 5 mL. XRD analysis of the solids collected after adding 5 mL of Na$_3$PO$_4$ indicates that the recovered solids was pure Li$_3$PO$_4$ as its peaks matched exactly with that of pure Li$_3$PO$_4$ standard, as shown in Figure 4-9. The recovered solids also were of good crystallinity. Figure 4-10 shows a plot of the experimental data points on the phase diagram. The compositions of the mother liquor in these experiments are very close to the LiOH-NaOH edge, indicating that the Li$_3$PO$_4$ compartment extends nearly all the way to this edge. Note that the feed point, mother liquor, and Li$_3$PO$_4$ are collinear as the solids precipitated in these experiments are Li$_3$PO$_4$. 

Figure 4-10 Solubility data of the phase behavior for the Li precipitation process in case study I (Numbers refer to the corresponding sample in Table 4-4).
Table 4-4 Experimental results of adding different volumes of Na$_3$PO$_4$ to the precipitation process for Li recovery in case study I.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (Na$_3$PO$_4$) Volume (mL)</th>
<th>pH</th>
<th>Mother Liquor (ML)</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Concentration (ppm)</td>
<td>Li$^+$ % remained in ML</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>12.2</td>
<td>13.98</td>
<td>10.1%</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>12.2</td>
<td>3.08</td>
<td>2.2%</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>12.7</td>
<td>0.02</td>
<td>0.0%</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>12.7</td>
<td>0.01</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

4.3.3. Process validation

The selected process with the optimum conditions determined above was carried out to validate the recovery and purity of the solids recovered. After dismantling and separating the spent LIB into its components, the cathode with aluminum foil was immersed in N-Methyl-2-pyrrolidone (NMP) and heated at 60 °C with vigorous stirring for around 30 min. All cathode powders were then separated from the foil and around 27.1 g of LiFePO$_4$ cathode powder was collected for the recycling process. From this amount, 10 g were used to carry out the Fe and Li recovery experiments. For every 1 mmol (0.158 g) of LiFePO$_4$, 25 mL 0.32M H$_2$SO$_4$ with H$_2$O$_2$ was used to dissolve the cathode powder at 60°C, and 7.5 mL of 2M NaOH was added to precipitate Fe as FePO$_4$·2H$_2$O. The remaining mother liquor (32.5 mL) was evaporated to 10 mL. Finally, 5 mL of 1M Na$_3$PO$_4$ was added to precipitate Li$_3$PO$_4$ for every 1 mmol (0.158 g) of LiFePO$_4$ recycled. At the end, 9.33g FePO$_4$·2H$_2$O and 2.37g Li$_3$PO$_4$ were recovered, corresponding to Fe and Li recovery of 97.6% and 96.9%, respectively.

4.3.4. Flowsheet alternative with another precipitant

The addition of NaOH as precipitant to the Fe recovery process introduces an additional element Na$^+$ to the system, which at the end generates sodium salts as a waste. An interesting alternative is
to use NH$_3$·H$_2$O as precipitant instead, as NH$_4^+$ ion can be removed by calcination. Experiments were conducted using the same experimental setup. After adding the feed powders to the glass vessel, different volumes of 2M of NH$_3$·H$_2$O were added to precipitate Fe. The experimental results, which are summarized in Table 4-5, indicates that most of the Fe were precipitated, while Li stays in solution when different volumes of NH$_3$·H$_2$O was added. Mass balance calculations also indicate that the solids were essentially pure FePO$_4$·2H$_2$O. Since the addition of NH$_3$·H$_2$O created a buffer solution in the system, its pH remained stable in the acidic range, resulting in precipitation of only FePO$_4$·2H$_2$O in all samples, even when 10 mL of NH$_3$·H$_2$O was added. This is in contrast to the conversion of FePO$_4$·2H$_2$O to Fe(OH)$_3$ due to a sharp pH increase when NaOH is used as precipitant. In other words, applying NH$_3$·H$_2$O as precipitant allowed an easier control in solution pH for precipitating FePO$_4$·2H$_2$O. While the experimental data showed that NH$_3$·H$_2$O is a good substitute for NaOH, the possibility of using ammonium phosphate as precipitant for Li recovery has to be studied in order to completely remove Na$^+$ from the process.

Table 4-5: Experimental results of adding different volumes of another precipitant (NH$_3$·H$_2$O) to the precipitation process for Fe recovery in the process alternative of case study I.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (NH$_3$·H$_2$O)</th>
<th>Volume (mL)</th>
<th>pH</th>
<th>Li$^+$ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Fe$^{3+}$ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>PO$_4^{3-}$ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>7</td>
<td>2.39</td>
<td>60.8</td>
<td>95.7%</td>
<td>2.15</td>
<td>0.4%</td>
<td>333.8</td>
<td>28.2%</td>
<td>0.155</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>8</td>
<td>3.51</td>
<td>60.1</td>
<td>95.5%</td>
<td>0.65</td>
<td>0.1%</td>
<td>302.3</td>
<td>25.8%</td>
<td>0.160</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>9</td>
<td>4.23</td>
<td>59.8</td>
<td>95.9%</td>
<td>0.09</td>
<td>0.0%</td>
<td>309.3</td>
<td>26.6%</td>
<td>0.157</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>10</td>
<td>4.72</td>
<td>58.6</td>
<td>94.9%</td>
<td>0.00</td>
<td>0.0%</td>
<td>338.8</td>
<td>29.4%</td>
<td>0.152</td>
</tr>
</tbody>
</table>

4.4. Case Study II: Recycle of LiCo$_x$Mn$_{1-x}$O$_2$ cathode material

Many cathode materials, other than LiFePO$_4$, such as LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiCo$_{0.8}$Mn$_{0.2}$O$_2$ are commonly used. These cathode materials contain more than one transition metals and the process for separating Li and these transition metals becomes more complicated. This case study focuses the recycling of Li, Co, and Mn from LiCo$_x$Mn$_{1-x}$O$_2$ cathode material, which is commonly
used in mobile phones. Here, the ratio of Co and Mn is assumed to be 1:1. Again, the use of SLE phase behavior to optimize the operating conditions for enhancing the recovery yield and product purity is illustrated in this case study. A possible flowsheet alternative based on insights from phase behavior is also suggested for comparison with the conventional flowsheet. Based on similar recycling process reported in the literature and information on cathode materials chemistry [89, 90], the base case process flowsheet for metal recovery from LiCoO₂₋₀.₅MnO₂₋₀.₅ of spent LIB is shown in Figure 4-11. After dismantling and dissolution of the LIB, LiCoO₂₋₀.₅MnO₂₋₀.₅ cathode material is collected and dissolved in H₂SO₄ and H₂O₂. Na₂S was added in the first precipitation process to precipitate out a mixture of CoS and MnS. The mother liquor is then sent to another precipitation process where Na₃PO₄ is added to recover Li as Li₃PO₄. CoS and MnS are further separated by adding acetic acid where MnS is selectively dissolved while CoS remains in the solid phase. After filtering out the undissolved CoS, MnS or Mn(OH)₂ is precipitated by adding NaOH. In order to rationalize the design of the precipitation process, the SLE phase behavior of the relevant system is studied.

Figure 4-11 Base case process flowsheet for recycling spent LIB containing LiCoO₂₋₀.₅MnO₂₋₀.₅ cathode materials in case study II.

65
4.4.1. Precipitation process for Co and Mn recovery

Conceptual phase behavior

After dissolving cathode materials in H$_2$SO$_4$ and H$_2$O$_2$, Co and Mn are recovered by adding Na$_2$S as precipitant. The solution in the first precipitation process for Co and Mn recovery therefore contains simple ions Li$^+$, Co$^{2+}$, Mn$^{2+}$, Na$^+$, H$^+$, SO$_4^{2-}$, and S$^{2-}$, as well as H$_2$O as solvent. The presence of OH$^-$ from dissociation of water can be ignored since there is no other source of OH$^-$ in the system. According to Eqn. 4-1, a 6-dimensional phase diagram will be required to completely represent the isobaric-isothermal SLE phase behavior. In order to visualize the phase behavior, H$^+$ and Na$^+$ can be lumped into Li$^+$, as they would not take part in precipitation due to the high solubility of acids and Na salts. The resulting 4-dimensional cut can be further simplified by taking a Jänecke projection with respect to the solvent (H$_2$O) to come up with a 3-dimensional phase diagram, at a certain ratio of H$^+$/Li$^+$ and Na$^+$/Li$^+$, illustrated in Figure 4-12. Again, at different H$^+$/Li$^+$ and Na$^+$/Li$^+$ ratios, there may also be saturation regions for Na$_2$S and Na$_2$SO$_4$ overlapping with the depicted regions in this projection. The crystallization compartments correspond to the precipitation of component with bold and larger fonts.
Figure 4-12 Jänecke projection of the conceptual phase diagram for the precipitation process of Co and Mn recovery in case study II.

The diagram features the crystallization compartments of various species, namely Li$_2$S (S1), MnS (S2), CoS (S3), Li$_2$SO$_4$ (S4), MnSO$_4$ (S5), and CoSO$_4$ (S6), assuming that no solvate was formed at the given temperature. The boundaries between the compartments represent regions of double, triple, or quadruple saturation. Since Li$_2$S is much more soluble in water than MnS and CoS, the double saturation points S1S2 and S1S3, the triple saturation points S1S2S3, S1S2S4, and S1S3S4, and the quadruple saturation point S1S2S3S4 are located very close to the Li$_2$S-Li$_2$SO$_4$ axis. Therefore, the compartments of MnS and CoS are much larger than that of Li$_2$S. It is also expected that the compartment of CoS is larger than that of MnS because CoS has lower solubility than MnS in acidic condition.
Figure 4-13 Projection of LiS-Li$_2$SO$_4$ edge onto MnS-MnSO$_4$ edge in the Jänecke projection of the conceptual phase diagram for the precipitation process of Co and Mn recovery in case study II.

The process paths of CoS and MnS co-precipitation can also be represented on the phase diagram. In order to allow a better visualization of the process paths, the LiS-Li$_2$SO$_4$ edge is projected onto the MnS-MnSO$_4$ edge since the Li salts are not expected to precipitate out during the process. All compartment boundaries are projected to the front face of the prism, resulting in the two-dimensional diagram shown in Figure 4-13. The stream numbers correspond to the flowsheet in Figure 4-11. As the feed powder contained no sulfide, the feed composition (point 3) is located at the right surface of the prism (Li$_2$SO$_4$-MnSO$_4$-CoSO$_4$) in Figure 4-12, which is projected to be the right edge (MnSO$_4$-CoSO$_4$) in Figure 4-13. With the addition of Na$_2$S, the composition moved inside the prism and towards Na$_2$S vertex into the CoS compartment. Note that being a solvent-free projection, Figure 4-12 only shows the relative composition of the solutes in
a saturated solution, without displaying the amount of solvent corresponding to the saturated condition, which is different for each point inside the prism. At point M₀, the solvent content is equal to the saturation value at that particular location, so that CoS starts to precipitate out. As more Na₂S is added, the overall composition (M₁, M₂, and M₃) moves towards the Na₂S vertex, where the solubility of sulfide salts are lower (that is, higher solvent content in a saturated solution). Consequently, more CoS precipitates out and the mother liquor composition follows the path L₁-L₂-L₃. At L₂, the solution becomes saturated with both CoS and MnS as the mother liquor composition hits the S₂S₃-S₂S₃S₅-S₂S₃S₄S₅-S₁S₂S₃ plane, which is the boundary between CoS and MnS compartments. Further addition of Na₂S causes co-precipitation of both salts, and the mother liquor moves across the boundary plane.

**Experimental methods**

The same experimental setup was used in this case study. Instead of using actual cathode material recycled from spent LIB, a synthetic feed was prepared. To imitate the mole ratio of Li:Co:Mn = 1:0.5:0.5 as in the cathode material, feed powders containing 0.128g Li₂SO₄ (Li₂SO₄·H₂O, ACS reagent, ≥99.0% dry basis, Sigma-Aldrich), 0.281g CoSO₄ (CoSO₄·7H₂O, purum, ≥95%, Sigma-Aldrich), and 0.169g MnSO₄ (MnSO₄·H₂O, ReagentPlus, ≥99%, Sigma-Aldrich) were mixed and dissolved in a jacketed glass vessel containing 100 mL 0.04M H₂SO₄. Temperature was kept at 25 °C by connecting the outer jacket to a water bath. A specific volume of 1 M Na₂S solution (Na₂S·9H₂O, ≥98.0%, Sigma-Aldrich) was added to the mixture to precipitate Co and Mn salts. After equilibration for 240 min, the solids and the mother liquor were separated by vacuum filtration. The concentrations of Li⁺, Co²⁺, and Mn²⁺ in the mother liquor were measured by ICP-OES, while the solids were washed with DDI water and dried, and their weight was measured.

**Results**

Table 4-6 shows a summary of the experimental results for the first precipitation process where Mn and Co were co-precipitated. The initial concentration of Li⁺, Mn²⁺, and Co²⁺ are 138.8, 549.4,
and 589.3 ppm, respectively. The results indicate that almost all Li remained in the solution, while essentially all Co and Mn ended up being precipitated by adding Na₂S. However, addition of 4.75 mL of Na₂S solution significantly decreased the concentration of Co²⁺ in the mother liquor from 589.3 to 1.6 ppm, while the concentration of Mn²⁺ in the mother liquor stayed almost the same as the initial concentration. This is consistent with the process path shown in Figures 4-12 and 4-13, which CoS precipitated first, followed by co-precipitation of MnS as more Na₂S was added. The results also show that practically all CoS and MnS were precipitated after addition of 8 mL of Na₂S solution. This provides the optimal condition for the first precipitation process in recovering both CoS and MnS.

Table 4-6 Experimental results of adding different volumes of Na₂S to the precipitation process for Co and Mn recovery in case study II.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (Na₂S) Vol. (mL)</th>
<th>pH</th>
<th>Li⁺ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Mn²⁺ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Co²⁺ Concentration (ppm)</th>
<th>% remained in ML</th>
<th>Solid Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.94</td>
<td>137.3</td>
<td>100.0%</td>
<td>568.8</td>
<td>104.6%</td>
<td>579.0</td>
<td>99.2%</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.09</td>
<td>135.8</td>
<td>99.8%</td>
<td>564.5</td>
<td>104.8%</td>
<td>474.2</td>
<td>82.1%</td>
<td>0.029</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>2.39</td>
<td>134.5</td>
<td>99.8%</td>
<td>553.7</td>
<td>103.8%</td>
<td>365.3</td>
<td>63.8%</td>
<td>0.062</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>2.78</td>
<td>133.7</td>
<td>100.2%</td>
<td>547.8</td>
<td>103.7%</td>
<td>221.4</td>
<td>39.1%</td>
<td>0.099</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
<td>3.67</td>
<td>132.7</td>
<td>100.0%</td>
<td>542.1</td>
<td>103.1%</td>
<td>59.0</td>
<td>10.5%</td>
<td>0.147</td>
</tr>
<tr>
<td>6</td>
<td>4.75</td>
<td>4.24</td>
<td>132.4</td>
<td>100.0%</td>
<td>538.9</td>
<td>102.7%</td>
<td>1.62</td>
<td>0.3%</td>
<td>0.160</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>6.39</td>
<td>131.6</td>
<td>99.6%</td>
<td>529.2</td>
<td>101.2%</td>
<td>0.95</td>
<td>0.2%</td>
<td>0.165</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>8.98</td>
<td>130.7</td>
<td>99.8%</td>
<td>332.4</td>
<td>64.1%</td>
<td>0.66</td>
<td>0.1%</td>
<td>0.211</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>10.8</td>
<td>128.1</td>
<td>98.8%</td>
<td>3.74</td>
<td>0.7%</td>
<td>0.00</td>
<td>0.0%</td>
<td>0.288</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>12.2</td>
<td>128.5</td>
<td>100.0%</td>
<td>0.00</td>
<td>0.0%</td>
<td>0.00</td>
<td>0.0%</td>
<td>0.294</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
<td>12.2</td>
<td>127.3</td>
<td>99.9%</td>
<td>0.00</td>
<td>0.0%</td>
<td>0.00</td>
<td>0.0%</td>
<td>0.294</td>
</tr>
</tbody>
</table>

4.4.2. Selective dissolution of MnS

CoS and MnS recovered in the first precipitation process are further separated by selectively dissolving MnS in acetic acid (HOAc), which does not dissolve CoS. Assuming that Co(OAc)₂ and Mn(OAc)₂ would not precipitate in the dissolution process, the conceptual phase diagram for the selective dissolution process at a specific acetic acid concentration can be represented by Figure
4-14. The compartment of CoS is much larger than that of MnS due to its much lower solubility in acetic acid. Assuming that the cathode material contains Co:Mn at a ratio of 1:1, the feed point will be located at point a in Figure 4-14. After acetic acid addition, the feed point moves upward towards the solvent vertex. If it falls in the CoS region (point b), only CoS will be collected in the solids while all MnS are dissolved. However, both CoS and MnS will be collected in the solids if the mixture falls in the solid mixture region (point c), resulting in no separation between CoS and MnS. Thus, the minimum amount of acetic acid to be added corresponds to an overall mixture indicated by point d, which is at the boundary between the pure CoS and solid mixture regions. At a different acetic acid concentration, the phase behavior would be similar, but the exact location of the saturation regions would be different. Therefore, both the acid concentration and its amount are important in achieving the optimal operating condition for isolating pure CoS.

It should be noted that although a cathode material with a ratio of Co:Mn = 1:1 was used for this example, other cathodes that contain more Mn, such as LiCo$_{0.1}$Mn$_{0.9}$O$_2$, are also commonly found in LIB. If the relative amount of Mn to Co in the cathode material is higher than that in the double saturation point (point 2 in Figure 4-14), the feed point to the dissolution process will be located at point e, such that addition of acetic acid results in selective dissolution of CoS while MnS remained undissolved. In that case, the mixture composition represented by point f corresponds to the minimum amount of acetic acid for completely dissolving CoS and at the same time keeping as much MnS as possible in the solid phase.
The same experimental setup was used to determine the optimal acetic acid concentration. The solids collected in the first precipitation process by adding 8 mL of Na₂S were used as the feed for the dissolution process, and 50 mL of acetic acid (analytical reagent, 100%, AnalaR NORMAPUR) of different concentrations (0.01 M – 1 M) were added to dissolve the crystals. After equilibration for 240 min, the solids and the mother liquor were separated by vacuum filtration. The concentrations of Co²⁺ and Mn²⁺ in the mother liquor were measured by ICP-OES. As previous results already indicate that there should be no Li in the solids from the first precipitation process, Li⁺ concentration is not measured in these experiments.

Figure 4-14 Conceptual phase diagram for the selective dissolution process at a specific acetic acid concentration in case study II.
Table 4-7 Experimental results of adding acetic acid of different concentration to the selective dissolution process in case study II.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Acetic acid Concentration (mol/L)</th>
<th>pH</th>
<th>Mother Liquor (ML)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn$^{2+}$</td>
<td></td>
<td>Co$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentration (ppm)</td>
<td>% dissolved in ML</td>
<td>Concentration (ppm)</td>
<td>% dissolved in ML</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
<td>5.4</td>
<td>100.1</td>
<td>9.1%</td>
<td>0.3</td>
<td>0.0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.025</td>
<td>5.0</td>
<td>591.7</td>
<td>53.9%</td>
<td>1.0</td>
<td>0.1%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>4.7</td>
<td>1086</td>
<td>98.8%</td>
<td>6.3</td>
<td>0.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>4.4</td>
<td>1094</td>
<td>99.5%</td>
<td>208.0</td>
<td>17.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>4.0</td>
<td>1086</td>
<td>98.8%</td>
<td>510.3</td>
<td>43.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>6</td>
<td>0.5</td>
<td>2.4</td>
<td>1094</td>
<td>99.6%</td>
<td>739.5</td>
<td>62.7%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>2.0</td>
<td>1101</td>
<td>100.2%</td>
<td>1078</td>
<td>91.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental results showing the mother liquor concentration at the end of the experiments are summarized in Table 4-7. Note that if MnS and CoS solids were completely dissolved, the concentration of Mn$^{2+}$ and Co$^{2+}$ in the solution would be 1098.8 ppm and 1178.6 ppm, respectively. The percentages in Table 4-7 are calculated with respect to these concentrations. The results show that adding acetic acid with a concentration of up to 0.05 M, the amount of CoS dissolved was negligible, while up to about 99% of MnS was dissolved. With higher acetic acid concentrations, significant amount of CoS was dissolved together with MnS. Therefore, 0.05 M acetic acid was selected as the optimal concentration for selective dissolution of MnS.

Experiments were also conducted by dissolving the same amount of CoS and MnS in different volumes of 0.05 M acetic acid in order to determine the amount of acid needed for the selective dissolution process. The results, summarized in Table 4-8, suggest that by decreasing the volume of acetic acid solution to 25 mL, 99.8% of CoS and 41.3% of MnS remained undissolved, indicating that the composition is located in the double saturation region. Increasing the volume to 75 mL, on the other hand, caused complete dissolution of MnS but also with 11.4% of CoS remained in the mother liquor, meaning that the recovery of CoS was smaller.
Table 4-8 Experimental results of adding different volumes of 0.05M acetic acid to the selective dissolution process in case study II.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Acetic acid Volume (mL)</th>
<th>Concentration if solids completely dissolved</th>
<th>pH</th>
<th>Mother Liquor (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn(^{2+})</td>
<td>Co(^{2+})</td>
<td>Mn(^{2+}) Concentration (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>2198</td>
<td>2357</td>
<td>4.69</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1099</td>
<td>1179</td>
<td>4.74</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>732.5</td>
<td>785.7</td>
<td>4.83</td>
</tr>
</tbody>
</table>

4.4.3. Precipitation process for Mn recovery

After filtering CoS solids, 2M NaOH solution was added to the remaining mother liquor to precipitate Mn. Assuming all CoS remained undissolved in the previous dissolution process, the system in hand contains Na\(^+\), Mn\(^{2+}\), H\(^+\), S\(^2-\), OAc\(^-\), and OH\(^-\), leading to a dimensionality of 4 in the SLE phase diagram. As Mn(OAc)\(_2\) and NaOAc are not expected to precipitate due to their relatively high solubility, the dimensionality can be reduced by lumping OAc\(^-\) into OH\(^-\). By projecting the solvent edge (H\(_2\)S-H\(_2\)O) onto the Na\(_2\)S-NaOH edge, the conceptual phase behavior in 2-dimension, at a certain ratio of OAc\(^-\)/OH\(^-\), is shown in Figure 4-15. Again, there may also be saturation regions for Mn(OAc)\(_2\), NaOAc, and HOAc at different ratios of OAc\(^-\)/OH\(^-\), and the crystallization compartments in Figure 4-15 correspond to the precipitation of the component with bold and larger fonts in that vertex. As the solubility of MnS and Mn(OH)\(_2\) are much smaller than their Na counterparts, the solubility surfaces of MnS and Mn(OH)\(_2\) are much larger in the diagram. The process path of the Mn recovery process is also shown in Figure 4-15. The numbers on the process paths correspond to stream numbers in Figure 4-11. The feed to the Mn recovery process (point 13) is located at the interior of the phase diagram as it contains H\(^+\) and OH\(^-\) from water (which is assumed to be completely dissociate into H\(^+\) and OH\(^-\) for plotting purposes). Note that being a solvent-free projection in Figure 4-15, the feed point is actually located above the saturation surface. With the addition of NaOH, the process point moves towards the NaOH vertex to point 15 and MnS precipitates out, producing a mother liquor with a composition indicated by point 18.
Alternatively, a larger amount of NaOH can be added to the feed to move point 15’ inside the precipitation region for Mn(OH)$_2$, leading to a mother liquor with a composition given by point 18’ after Mn(OH)$_2$ precipitates.

Experiments were conducted with the same setup to determine the best condition for recovering Mn after Co removal. In all experiments, the filtrate after filtering undissolved CoS in the previous dissolution process, in which 50mL of 0.05M acetic acid was added to selectively dissolve MnS, was used as the feed. Different volumes of 2M NaOH were added as precipitant and samples were collected from the mother liquor to determine its concentration of Mn$^{2+}$.

![Conceptual phase diagram for the precipitation process of Mn recovery in case study II.](image)

Figure 4-15 Conceptual phase diagram for the precipitation process of Mn recovery in case study II.
The experimental results of the Mn recovery process are summarized in Table 4-9. The initial concentration of Mn in the feed was 549.4 ppm. With more NaOH added, the amount of Mn remaining in the mother liquor decreased. Practically all Mn in the solution was precipitated when 6 mL NaOH solution was added. Similar to Fe precipitation in case study I, the precipitated solids could actually be either MnS or Mn(OH)$_2$, depending on the amount of NaOH added. Although it is possible to confirm the identity of the collected solids by analytical measurement, no further analysis was carried out because the recovered solids always have to undergo calcination before cathode refabrication, and both MnS and Mn(OH)$_2$ will be converted to MnO after calcination.

Table 4-9 Experimental results of adding different volumes of NaOH to the precipitation process for Mn recovery in case study II.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (NaOH)</th>
<th>Mother Liquor (ML)</th>
<th>Mn$^{2+}$ Concentration (ppm)</th>
<th>% remained in ML</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume (mL)</td>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>9.2</td>
<td>343.0</td>
<td>64.3%</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>10.1</td>
<td>219.7</td>
<td>41.6%</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>11.4</td>
<td>122.2</td>
<td>23.3%</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>12.3</td>
<td>0.75</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

4.4.4. Precipitation process for Li recovery

The Li precipitation step is very similar to the one described in case study I. As S$^{2-}$ is present at a small concentration, and sodium and lithium sulfides are very soluble, it is assumed that its presence would not affect the precipitation process. Therefore, the same amount of precipitant used in case study I (5 mL of 1M Na$_3$PO$_4$) is expected to be sufficient for complete recovery of Li as Li$_3$PO$_4$, and no further experiments were performed.
4.4.5. Process alternative for Co and Mn recovery

The SLE phase behavior shown in Figures 4-12 and 4-13, which is supported by the experimental results in Table 4-6, suggests that it is possible to selectively precipitate CoS, but not MnS, by controlling the amount of Na$_2$S added. This insight opens up a possibility for a process alternative in which Co and Mn are separately recovered in two separate steps instead of co-precipitating them in the first precipitating process. The flowsheet of this process alternative is shown in Figure 4-16. According to Table 4-6, with an addition of 4.75 mL of Na$_2$S, almost all Co was precipitated while Mn stayed in the mother liquor. Therefore, pure CoS can be recovered in the first precipitation process, and the remaining mother liquor can be sent to a second precipitation process to recover MnS or Mn(OH)$_2$. This leads to a simpler process, as selective dissolution and the subsequent solids filtration and washing steps will not be needed. The process for recovering Li from the remaining solution is similar to the base case process.

![Flowsheet of process alternative](image)

Figure 4-16 Process alternative for recycling spent LIB containing LiCo$_{0.5}$Mn$_{0.5}$O$_2$ cathode materials in case study II.

Since the feed to the second precipitation process contains Li$^+$, Mn$^{2+}$, Na$^+$, H$^+$, SO$_4^{2-}$, S$^2$-, and OH$^-$ (with negligible amount of Co$^{2+}$ as it can be considered completely removed in the first precipitation process), leading to a 5-dimensional SLE phase diagram. By lumping Li$^+$ into Na$^+$ and SO$_4^{2-}$ into S$^2$-, and projecting the solvent edge (H$_2$S-H$_2$O) onto Na$_2$S-NaOH edge, the
conceptual phase diagram (Figure 4-16), at a certain ratio of \( \text{Li}^+/\text{Na}^+ \) and \( \text{SO}_4^{2-}/\text{S}^{2-} \), is analogous to the one illustrated in Figure 4-4. Note that there may also have saturation regions for \( \text{LiOH}, \text{MnSO}_4, \text{Li}_2\text{S}, \text{Na}_2\text{SO}_4, \) and \( \text{Li}_2\text{SO}_4 \) at different \( \text{Li}^+/\text{Na}^+ \) and \( \text{SO}_4^{2-}/\text{S}^{2-} \) ratios, and the crystallization compartments correspond to the precipitation of the component with bold and larger fonts in that vertex. The process paths for this precipitation process is also illustrated in Figure 4-17, and the numbers on process paths correspond to stream numbers in Figure 4-16. The feed to the precipitation process (point 8) is located in the interior of the diagram as it contains \( \text{OH}^- \) from water. By adding \( \text{NaOH} \), the composition moves into the precipitation region of \( \text{MnS} \) (or \( \text{Mn(OH)}_2 \), depending on the amount of \( \text{NaOH} \) added), leading to precipitation of the corresponding solids.

![Diagram](image)

Figure 4-17 Conceptual phase diagram for the precipitation process of Mn recovery in the process alternative of case study II.
Table 4-10 Experimental results of adding different volumes of NaOH to the precipitation process for Mn recovery in the process alternative of case study II.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Precipitant (NaOH)</th>
<th>Mother Liquor (ML)</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Precipitant Volume (mL)</td>
<td>pH</td>
<td>Mn²⁺</td>
</tr>
<tr>
<td></td>
<td>Concentration (ppm)</td>
<td>% remained in ML</td>
<td>Concentration (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>10.1</td>
<td>298.7</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>10.8</td>
<td>185.9</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>11.9</td>
<td>112.3</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>12.7</td>
<td>0.10</td>
</tr>
</tbody>
</table>

To determine the optimum amount of NaOH to be added, experiments were conducted with the same setup. The mother liquor collected in the first precipitation process after adding 4.75 mL of 1M Na₂S (the optimal condition for selective Co recovery from Table 4-6), was used as the feed solution and was added to the jacketed glass vessel. Different volumes of 2M NaOH solution were added as precipitant, and the concentration of Mn²⁺ and Li⁺ remaining in the mother liquor was determined. The initial concentration of Mn²⁺ and Li⁺ in the solution was 549.4 and 138.8 ppm, respectively. Experimental results in Table 4-10 indicate that the concentration of Mn²⁺ remaining in the mother liquor decreased and the amount of solids collected increased with increasing volume of NaOH added. All Mn was precipitated by adding 5mL of NaOH to the system. The concentration of Li⁺ in the mother liquor remained nearly the same as the feed concentration, suggesting that Mn was selectively precipitated, either as MnS or Mn(OH)₂. Because MnS and Mn(OH)₂ have similar molecular weights, no clear indication can be obtained by observing the weight of the collected solids in the experiments. But as previously mentioned, it is immaterial whether Mn is recovered as MnS or Mn(OH)₂, since both would end up producing MnO upon calcination.
4.5. Conclusions

With the rapid development of electronic products, recycling of spent LIB becomes an important issue as they are not suitable to be disposed to the landfills. The recycling process of spent LIB by selectively precipitating metal salts in a series of chemical precipitation process has been studied in this chapter, with LiFePO$_4$ and LiCo$_x$Mn$_{1-x}$O$_2$ as examples in two case studies. In both case studies, pure metal salts with high yield can be recovered from the system. The SLE phase behavior governs the product to be recovered in these precipitation processes. By conducting experiments to determine regions of phase diagram that are of interest to the precipitation process, the optimal operating conditions can be identified. The SLE phase behavior also rationalizes the process and operating conditions that previous researchers developed based on trial and error. For example, the case study of recycling LiFePO$_4$ demonstrates that there was an optimal amount of NaOH to be added such that pure FePO$_4$ with high yield can be recovered in the precipitation process. Too less NaOH lowers the recovery, while too much NaOH leads to the precipitation of Fe(OH)$_3$. 
5. Process Development for the Recycle of Spent Lithium Ion Batteries by Solvent Extraction and Crystallization

5.1. Introduction

Li-ion batteries (LIBs) have attracted increasing attention than other battery technology and become the major power supply for electric vehicles and portable electronics such as mobile phones and laptops due to their high energy density, high capacity, high rate capability, long cycle life and lightweight [65]. In today’s industry, LIBs remain the most widely used and account for more than 60% of the worldwide sales of portable batteries [91-93]. This results in an increased LIB consumption in recent years. A global production of 4.5 billion cells of LIB that worth 9.3 billion USD was reported in 2011 [66]. The annual production of LIB is expected to reach 6 billion cells in 2015 [3]. From an economic point of view, the incentive of recycling LIBs depends on the metal market price as well as the electrode technologies used in LIBs.

The increased reliance of LIBs in electronic equipment also increases the number of spent batteries being disposed to the landfills. The number is expected to grow in the near future due to the faster replacement and development of the electronic products. LIBs along with the electrode scraps generated during manufacturing process are discarded as solid wastes at the end-of-life stage. However, disposing spent LIB that contains organic electrolyte and metals such as Ni, Co, Cu, and Li leads to serious environmental problems such as soil and underground water contamination[32]. A typical LIB includes anode, cathode, current collector, separator, liquid electrolyte, container, and outer shell. The anode is made of graphite, conductive carbon and a polyvinylidene fluoride (PVDF) binder. The anode current collector is made of Cu foil. The cathode consists of conductive carbon, a PVDF binder, and a Li compound. LiCoO₂, LiMnO₂, LiNiO₂ and LiFePO₄ are the most commonly used compounds for cathode. A cathode current collector is made of Al foil. The separator is made of polypropylene (PP) or polyethylene (PE). The common electrolyte is lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) or a mixture of these. The outer shell of the battery is made of metal or plastics and sealing parts are made of plastics.

Several methods have been proposed to recover valuable metals (like Co and Li) from the
cathodes of spent LIBs. These methods include pyrometallurgical, hydrometallurgical, electroplating and biometallurgical processes [94-99]. Most of these processes are based on hydrometallurgical chemistry and are developed in a laboratory scale. Selective precipitation of individual metals is not efficient probably due to co-precipitation of other metals that may result in the loss of valuable metals, and the process needs to be controlled carefully. Solvent extraction is an appropriate method for efficient separation of similar metals as extractant is highly selective for a particular metal ion. [96]. The solvent extraction process is usually coupled with chemical precipitation to produce high purity metal salts, and is a good way for the recycle of valuable metals in an industrial scale. Before solvent extraction or precipitation, processes such as dismantling of the batteries shell, detaching of the electrode plate, and acid leaching are required to obtain the solution rich of cathode metals. All these processes are same as those discussed in Chapter 4. From the leach liquor, metals are separated either by precipitation or solvent extraction. Suzuki et al. [100] reported a multistage hydrometallurgical process for the separation of aluminum, cobalt, copper and lithium in acidic sulfate media, which is difficult for selective precipitation.

In order to use solvent extraction to separate metal ions from other ions, an appropriate extractant and operating condition should be chosen. The commercial extractant P507, also called PC88A, was used to extract selectively Co from Ni and Li. [101] Zhang et al. [102] reported a hydrometallurgical study on the separation and recovery of lithium and cobalt from waste LIBs using HCl as leachant and PC-88A as extractant. The P204 extractant, also called D2EHPA, can be used to extract selectively Mn (II) from Co and Li. Devi et al.59 studied the extraction and separation of Mn (II) and Co (II) from sulfate solutions using sodium salts of D2EHPA in kerosene, and 81.6% manganese and 5.3% cobalt were extracted at pH 4.45 with $D_{	ext{Mn}}/D_{	ext{Co}} = 80$. Additionally, the extractant Cyanex 272 can separate Co from Ni and Li in an ionic solution. Kang et al. [103] reported that Co was separated from Li and Ni using 0.4 mol L$^{-1}$ 50% saponified Cyanex 272 in kerosene. The Co/Li and Co/Ni separation factors at pH 6.0 were close to 750.

For comparing the solvent extraction and selective precipitation, the same case study of recycling LiMnxCo$_{1-x}$O$_2$ cathode material was conducted in this Chapter. The aim of the present work was to recover the valuable metal from a spent LiMnxCo$_{1-x}$O$_2$ cathode material LIBs by solvent extraction and crystallization. The integrated process has the advantages of high product purity, high recovery yield, less chemical consumption and simplified recycling process, and can
be used in large scale. To achieve this objective, selective precipitation and solvent extraction experiments were performed using artificially prepared metal solutions to simulate H$_2$SO$_4$ leach liquors, and the performance of the processes based on these two separation technologies was evaluated in terms of metal recovery and metal selectivity. The proposed process alternatives in this chapter was then compared with process from chapter 4 to determine a better proposed process.

5.2. Solvent extraction process

In a solvent extraction, the process includes three steps, and the schematic figure of the whole process is shown in Figure 5-1. (1) Extraction: solvent extraction is a method to separate compounds based on their relative solubility into two different immiscible liquids, usually water and organic solvent. (2) Scrubbing: removal of the impurity substance from organic phase to aqueous phase. (3) Stripping: removal of metal from organic phase to aqueous phase, by inorganic acid (i.e., H$_2$SO$_4$). As extraction is critical to the whole process, this Chapter mainly focus on studying the extraction process.

![Figure 5-1 Schematic diagram of the whole process of solvent extraction.](image)

5.2.1. Process Parameters of Extraction

Extraction

In order to extract different metal ion in a solvent extraction process, the appropriate extractant should be chosen. Also, the optimal concentration of the extractant in organic phase needs to be determined, in order to have a better extraction result. Since extractants and the cathode leach liquor are acidic, saponification still needs to be considered. Kerosene is chosen as the only diluent in the
organic phase, yet the organic/aqueous (O/A) volumetric ratio is studied for optimizing the extraction result. The acidity of the aqueous phase (pH value) is also studied for determining the best extraction effect, yet the temperature in the extraction is fixed at room temperature (25 °C).

**Scrubbing and stripping**

In the scrubbing and stripping steps, the inorganic acid in the aqueous phase, pH value in the aqueous solution, and the organic/scrubbing solution volumetric ratio should be determined for a better scrubbing and stripping results; because these process parameters will highly affect the result.

### 5.2.2. Introduction of extraction

**Cyanex272**

Cyanex272 (C272) is a new type of synthetic organic phosphonic extractant made in 1980s by American Cyanamid Company, which has proven to be the reagent of choice for the separation of cobalt from nickel in both sulfate and chloride media. Since the active component of the C272 extractant is a phosphinic acid, the structure of C272 is shown in Figure 5-2, the active component of C272 extractant is bis (2,4,4-trimethylpentyl) phosphinic acid, and metals are extracted through a cation exchange mechanism. Although C272 has a high separation factor for cobalt in the presence of nickel, a variety of other cations can also be extracted depending upon the pH of the aqueous feed. Also, it is totally miscible with common aromatic and aliphatic diluents, and is extremely stable to both heat and hydrolysis. Note that the loading capacity of C272 depends on various parameters such as pH, temperature, extractant concentration, and organic and aqueous (O/A) ratio.

**P204**

P204 Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is an acid type extractant made by Chinese Academy of Science in China. P204 extractant is an organophosphorus compound with the formula
of \((C_8H_{17}O)_2PO_2H\), which is shown in Figure 5-3. P204 is a highly effective extractant used to recover uranium, yttrium, manganese, rare earth, and other valuable metals. Particularly, P204 has better choice for the separation of manganese from cobalt in both sulfate and chloride media when the pH value is \(~7\). The extraction yield of P204 is affected by pH, temperature, extractant concentration, and O/A ratio.

![Chemical structure of Cyanex 272](image1)

**Figure 5-2 Chemical structure of Cyanex 272.**

![Chemical structure of P204](image2)

**Figure 5-3 Chemical structure of P204.**

**P507**

P507 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC88A) is a weak acidic type extractant made by Chinese Academy of Science in China. P504 extractant is an organophosphorus
compound with the formula of \((C_8H_{17})_2HPO_3\), and shown in Figure 5-4. P507 is an excellent reagent for the solvent extraction of various metals. Particularly, in the separation of cobalt from nickel, P507 is superior to P204. Generally, P507 is very suitable for the process of separating and refining of rare earth metals.

![Chemical structure of P507](image)

**Figure 5-4 Chemical structure of P507.**

### 5.3. Experiments

#### 5.3.1. Material

Bench scale solvent extraction studies were carried out by mixing the aqueous solution and organic phase at a specific ratio with the help of a mechanical stirrer for a specific time. All solutions were prepared with distilled deionized (DDI) water with a resistivity at 18.2 M\(\Omega\) cm\(^{-1}\). The required pH for the aqueous feed was adjusted with NaOH or H\(_2\)SO\(_4\) solution. Instead of using actual cathode material recycled from spent LIB, a synthetic feed was prepared. The feed powders containing Li\(_2\)SO\(_4\) (Li\(_2\)SO\(_4\)_H\(_2\)O, ACS reagent, \(\geq\)99.0% dry basis, Sigma-Aldrich), CoSO\(_4\) (CoSO\(_4\)_7H\(_2\)O, purum, \(\geq\)95%, Sigma-Aldrich), and MnSO\(_4\) (MnSO\(_4\)_H\(_2\)O, ReagentPlus, \(\geq\)99%, Sigma-Aldrich). The commercial extractants, P204 Di-(2-ethylhexyl) phosphoric acid and P507 2-ethylexyl hydrogen 2-ethylhexyl phosphonate were supplied by China Luoyang Aoda Chemical Company with purity higher than 97%. Cyanex 272 (C272) was supplied by US Cytec Chemical Company, with purity higher than 98%. Kerosene, used as a diluent for organic phases in solvent extraction experiments, was purchased from Fisher.
5.3.2. Solvent extraction experiment

To imitate the mole ratio of Li:Co:Mn = 1:0.5:0.5 in the cathode material of LiMn$_{0.5}$Co$_{0.5}$O$_2$, feed powders containing 51.2 mg Li$_2$SO$_4$, 112.4 mg CoSO$_4$, and 67.6 mg MnSO$_4$ were mixed and dissolved in a jacketed glass vessel containing 10 mL DDI water. 10 mL of the aqueous solution was transferred into a 50 mL glass conical flask, and the pH of the solution was adjusted to the predetermined pH by slowly adding concentrated H$_2$SO$_4$ or NaOH solutions as required. The change in volume during pH adjustment was negligible. A specific concentration of the extractants (Cyanex 272, P204, P507) mixed in kerosene with a specific volume were added to the mixture to extract the metal ions from the aqueous solution. The conical flasks were immersed in a water bath for controlling the temperature, and the two phases were mixed by magnetic stir bar. After equilibration, both phases were allowed to settle and separated in separating funnel. The pH value of the synthetic feed was measure by pH probe. The concentrations of Li$^+$, Co$^{2+}$, and Mn$^{2+}$ in the mother liquor were measured by ICP-OES, and the metal concentration in the organic phase was calculated from the difference between the metal concentration in the aqueous phase before and after extraction.

5.3.3. Scrubbing and stripping experiment

After the extraction, the scrubbing step was using H$_2$SO$_4$ to remove the impurities in the loaded organic solvent. The scrubbing tests were performed at an A/O ratio of 1:1 and 25 °C, 10 mL of loaded organic solution and 10 mL 0.05M H$_2$SO$_4$ (O:A ratio is 1:1) was mixed and shaken in an air bath shaker, with a shaking speed of 300 rpm and at temperature 25 °C for a period of 3 h. The pH control during scrubbing process is not required because scrub liquor is pre-adjusted to the desired pH value.

After the scrubbing, a batch experiment of stripping, 10 mL of loaded organic and 10 mL H$_2$SO$_4$ (O:A ratio is 1:1) with concentration of 0.2, 0.1, 0.05, 0.01 mol/L were mixed and shaken in an air bath shaker, with a shaking speed of 300 rpm and at temperature 25 °C for a period of 3 h. The pH during stripping process is controlled the addition of the specific concentration H$_2$SO$_4$. The striping results with different concentration H$_2$SO$_4$ were confirmed by ICP-OES.
5.3.4. **Chemical precipitation experiment**

The same experimental setup of last chapter was used in this case study, the temperature was kept at 25 °C by connecting the outer jacket to a water bath. The raffinates after solvent extraction or stripped metal loaded solution were transferred to this setup, and the pH of the solution was adjusted to the predetermined pH by slowly adding concentrated H\textsubscript{2}SO\textsubscript{4} or NaOH solutions as required. The precipitants were added to the solution, and the metal precipitation and mother liquor were obtained by vacuum filtration. The target metals were recovered by precipitation.

5.3.5. **Analytical methods**

The pH of the mother liquor was measured with a pH/mV meter (Model Mettler-Toledo AG SevenGo2, Switzerland) and the concentration of metals in the aqueous solution were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES) (Model Varian 725-ES, Australia).

5.4. **Results and Discussion**

5.4.1. **Process alternatives**

As the solvent extraction is used in the case study of recycling LiMn\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} cathode material, several possible process alternatives can be synthesized from the solvent extraction separation factors and solubility data. Five possible process alternatives are shown in Figure 5-5, and all processes were started with LiMn\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} leach liquor, “Ext” and “Cry” mean solvent extraction and crystallization processes, respectively. For the sake of recovering the valuable metals with high purity and high yield, the processes seem more effective were elaborated to be studied. For example, the process (a) used solvent extraction to separate Mn from Li and Co, then Li and Co were separated by selective precipitation, and finally Li was recovered by crystallization. In process (b), solvent extraction was first used to extract Co from Mn and Li, then Mn and Li were separated by selective precipitation, and finally Li was recovered by crystallization. Process (d) and (e) started
with Mn and Co co-extraction, and process (f) only contains crystallization by selective precipitation, which was introduced in chapter 4.

![Diagram](image)

Figure 5-5 Process alternatives with solvent extraction for recycling of LiMn$_x$Co$_{1-x}$O$_2$ cathode material.

5.4.2. Extraction condition optimization in Li Mn and Co sulfate solution

Since the process parameters of solvent extraction may vary in recycling of different cathode material, the optimal condition of extraction should be confirmed first. The effect of extractants, pH value in aqueous phase, concentration of extractants in organic solvent, and O/A ratio will be studied in the following section. In the solvent extraction study, the LiMn$_{0.5}$Co$_{0.5}$O$_2$ cathode was used as case study for comparing with the selective precipitation in Chapter 4.

pH-extraction isotherms

Extraction of metal ions with different extractants are greatly affected by the equilibrium pH of the aqueous solution. Therefore, the effect of pH on the extraction of Mn, Co and Li from an aqueous solution containing 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L of Li with 0.4mol/L C272, P204 and P507 in kerosene solution was studied. The results of pH-extraction isotherms for
Li, Mn and Co by C272, P204 and P507 are listed in Table 5-1. Since the synthetic cathode leach liquor was acidic, and when the equilibrium pH was above 7.5, the extraction behavior could not be determined correctly as Mn and Co were started to be precipitated. Therefore, the pH-extraction isotherms were measured from pH 2.5 to 7.5.

Table 5-1 Experimental results of Li Mn and Co extraction by different 0.4mol/L extractants at different pH.

<table>
<thead>
<tr>
<th>Extractants</th>
<th>pH</th>
<th>Extraction (%)</th>
<th>Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li</td>
<td>Mn</td>
</tr>
<tr>
<td>C272</td>
<td>2.5</td>
<td>3.6</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.9</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.0</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.2</td>
<td>7.9</td>
</tr>
<tr>
<td>P204</td>
<td>2.5</td>
<td>4.3</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.2</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.9</td>
<td>42.8</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>3.9</td>
<td>42.9</td>
</tr>
<tr>
<td>P507</td>
<td>2.5</td>
<td>3.7</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.0</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.9</td>
<td>22.6</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.2</td>
<td>23.2</td>
</tr>
</tbody>
</table>

Distribution coefficient ($D$) is equal to the concentration of a solute in the organic phase divided by its concentration in the aqueous phase, as defined in equation (5) for Mn. The selectivity of Mn over Li was determined in terms of separation factor ($\beta$) which is defined in equation (6).

$$D_{Mn} = \frac{[Mn]_{org}}{[Mn]_{aq}}$$ (5)

$$\beta_{Co/Li} = \frac{\text{Distribution coefficient of Mn}}{\text{Distribution coefficient of Li}}$$ (6)

In pH-extraction isotherms of C272 (Figure 5-6), the extraction of Co from synthetic leach liquor by 0.4mol/L C272 increased from 24.1% to 32.1%, while that of Mn was increased from 4.3% to 7.9% and Li remained at around 4%. It was observed that the extraction of Li was very low in comparison to Mn and Co extraction, and the extraction of Co was much higher than that of
the Mn. This means C272 had a higher selectivity for Co. From the result of pH-extraction isotherms of C272 in Figure 5-6, the extractions of Co and Mn ions increased when pH increased from 2.5 to 7.5. Therefore, the extraction of Co and Mn by C272 had a higher efficiency with higher pH aqueous solution. Comparing with other solvent extraction studies [37, 103, 104], the Co extraction is highly disturbed by Mn in this case study, as C272 will also react with Mn ion.

![Image](image.png)

Figure 5-6 Extraction of Li Mn and Co at different equilibrium pH. [Aqueous –10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L of Li in sulfate medium, organic – 0.4mol/L C272 in kerosene, O:A ratio –1:1.]

The extraction efficiency of 0.4mol/L P204 at different pH for Li, Mn and Co are shown in Figure 5-7. From the observation of pH-extraction isotherms, the extraction of Mn increased from 41.0% to 42.9%, while that of Co remained at around 10% and Li remained at around 4%. The results indicated that the extraction of Li was very little in comparison to Mn and Co, and the extraction of Co was affected by Mn. From the result of pH-extraction plot in Figure 5-7, the extractions of metal ions were not significantly increased as equilibrium pH increased from 2.5 to 7.5. Since the extraction of Mn was higher than 40%, and only around 10% of Co was extracted simultaneously, P204 extractant is fit for separating of Mn from Co and Li in recycle of LiMn₀.₅Co₀.₅O₂ cathode.
Figure 5-7 Extraction of Li Mn and Co at different equilibrium pH. [Aqueous – 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L of Li in sulfate medium, organic – 0.4mol/L P204 in kerosene, O:A ratio – 1:1.]

From the pH-extraction isotherms of P507 in Figure 5-8, as the pH increased from 2.5 to 7.5, the extraction of Mn and Co with 0.4mol/L P204 increased from 14.3% and 9.4% to 23.2% and 21.3%, respectively, while that of Li remained around 4%. The extractions of Mn and Co were significant increased as equilibrium pH was increased from 2.5 to 7.5. However, Mn and Co could not effectively separated by P507 and required an extra step for separating Mn and Co. In solvent extraction of LiMn$_{0.5}$Co$_{0.5}$O$_2$ cathode, P507 can be used for co-extracting of Mn and Co, and then Mn and Co mixed solution can be used for further separation or re-synthesis of LiMn$_x$Co$_{1-x}$O$_2$ or LiMn$_x$Co$_y$Ni$_z$O$_2$ cathode materials. In the recycle of LiMn$_{0.5}$Co$_{0.5}$O$_2$ by solvent extraction, a higher pH had a better effect on extraction by C272, P204, and P507, the optimal condition of equilibrium pH for extraction is fixed at 7.5.
Concentration-extraction isotherms

Since the P204 had good selectivity for Mn extraction (higher than 40% at 0.4mol/L), the effect of concentration on extraction is studied with the case of P204. The effect of P204 concentration on the extraction of Mn, Co and Li from the synthetic leach solution was studied at pH 7.5 and O:A ratio 1:1. The concentration-extraction isotherms are presented in Figure 5-9. As P204 concentration increased from 0.2 to 1.2mol/L, the extraction of Mn increased from 28.8% to 72.6%, while the extraction of Co and Li are 6.3–12.7% and 2.6–7.6%, respectively. From the trend of the concentration-extraction isotherms, the extraction of Mn increased significantly when the concentration was increased from 0.2 to 1 mol/L. However, when the concentration was increased from 1 to 1.2 mol/L, the increase in Mn extraction was indistinctive. In the extraction of Mn by P204 for recycle of LiMn$_{0.5}$Co$_{0.5}$O$_2$, 1mol/L of P204 extractant is chosen as the optimal condition. Also, for P507 and C272 extractants, the concentration were fixed at 1mol/L because of its higher extraction efficiency.
Phase ratio-extraction isotherms

The effect of O:A ratio was studied by aqueous feed containing 2.747 g/L Mn, 2.947 g/L Co, and 0.694 g/L Li with 1mol/L P204 in kerosene. The experiment results presented in Figure 5-10 indicate that the extraction of Mn increased from 48.8% to 92.9% with the O:A ratio increased from 0.5 to 3.0, which was resulted from the increase of reagent availability at high O:A ratio. The extraction of Co and Li was also found to increase from 9.6% to 12.6% and 4.5% to 8.5% with increase in O:A ratio. From the phase-extraction plot in Figure 5-10, the increase of the extraction of Mn was quite significant when the O:A ratio was increased from 0.5 to 2; but the increase of Mn extraction was smaller when the O:A ratio was increased from 2 to 3. Since the counter-current solvent extraction was used in the recycle of LiMn$_{0.5}$Co$_{0.5}$O, in order to reduce the usage of organic extractant but still have a good recovery yield, the O:A ratio for Mn extraction by P204 was fixed at 1 in the process design section.
Figure 5-10 Extraction of Li Mn and Co at different O:A ratio. [Aqueous – 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L Li in sulfate medium, aqueous solution pH – 7.5, organic – 1mol/L P204 in kerosene.]

5.4.3. Extraction condition optimization in Li and Co sulfate solution

In order to recover Co by solvent extraction, C272 is chosen as the extractant in this step, because the selectivity of C272 in extraction of Co is the best among three extractants. However, the extraction of Co should be proceeded after the separation of Mn in recycle of LiMn$_{0.5}$Co$_{0.5}$O$_2$, as the result in pH-extraction (Table 5-1) indicated that the existing of Mn will largely disturb the Co from extraction. After the separation of Mn by P204, the condition for extraction of Li and Co in LiMn$_{0.5}$Co$_{0.5}$O$_2$ recycle process should be optimized. As the extraction of Co are also greatly affected by the equilibrium pH of the aqueous solution, concent-ration of extractants, and O/A ratio. The effects of pH, extractant concentration, and O/A ratio on the extraction of Co and Li from an aqueous solution containing 11.79 g/L of Co and 2.78g/L of Li with C272 were studied in the following. Since the effect of concentration has been studied in extraction of Li, Mn and Co sulfate solution, the optimal extractant concentration for C272 was also fixed at 1mol/L in this optimization.
pH-extraction isotherms

The results of pH-extraction for Li and Co by 1mol/L C272 are shown in Figure 5-11. The extraction behavior could not be determined when pH was above 7.5 because of Co precipitation. When the equilibrium pH was varied from 3 to 7.5, the extraction of Co from synthetic leach liquor increased from 59.3% to 67.1%, while that of Li was increased from 1.9% to 3.3%. The extraction of Li was very low when comparing with Co extraction. From the observation of the pH-extraction plots, Co ion was preferred to be extracted by C272 at a higher pH; as a result, in recovery of Co by C272, the pH of the aqueous phase is adjusted to 7.5.

![Figure 5-11 Extraction of Li and Co at different equilibrium pH. [Aqueous – 11.79 g/L of Co and 2.78g/L Li in sulfate medium, organic – 1mol/L C272 in kerosene, O:A ratio – 1:1.]](image)

Phase ratio-extraction isotherms

The effect of O:A ratio in Li and Co extraction by 1mol/L C272 was studied using aqueous feed containing 11.79 g/L of Co and 2.78g/L of Li at pH 7.5. The results of phase ratio-extraction for Li and Co by 1mol/L C272 are shown in Figure 5-12, the extraction of Co increased from 47.7% to 81.7% when the O:A ratio increased from 0.5 to 3.0, which also due to the increase of reagent
availability. The extraction of Li was also found to increased merely from 1.7% to 4.8% with increasing O:A ratio. The optimal condition for Co extraction (76.9%) after Mn removal should be equilibrium pH at 7.5, C272 extractant concentration at 1 mol/L, and O:A ratio at 2:1. However, the counter-current solvent extraction was chosen in the process; thus, the O:A ratio for Co extraction by C272 was fixed at 1 in the recycle of LiMn_{0.5}Co_{0.5}O_{2}.

![Graph showing extraction of Li and Co at different O:A ratio.](image)

Figure 5-12 Extractions of Li and Co at different O:A ratio. [Aqueous –11.79 g/L of Co and 2.78g/L Li in sulfate medium, aqueous solution pH – 7.5, organic – 1mol/L C272 in kerosene.]

### 5.4.4. Extraction condition optimization for Mn and Co co-extraction

Since the Mn and Co can be extracted by P507 simultaneously in one extraction, P507 can be used for separation of Mn and Co from Li at first. As co-extraction of Mn and Co are highly affected by the equilibrium pH of the aqueous solution, concentration of extractants, and O/A ratio, the condition for extraction of Li and Co in LiMn_{0.5}Co_{0.5}O_{2} recycle process should be optimized. The effects of pH and O/A ratio on the extraction of Co and Li from an aqueous solution containing 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L of Li with 1mol/L P507 were studied in the following.
**pH-extraction isotherms**

The results of pH-extraction for Mn, Co and Li by 1 mol/L P507 are shown in Figure 5-13. When the equilibrium pH was varied from 2.5 to 7.5, the extraction of Mn and Co increased from 34.2% and 29.6% to 45.1% to 43.4%, respectively, while that of Li remained around 4%. The extractions of Mn and Co were significant increased as equilibrium pH was increased from 2.5 to 7.5. From the observation of the pH-extraction plots, Mn and Co ions were preferred to be extracted at a higher pH; as a result, in co-extraction of Mn and Co by P507, the pH of the aqueous phase is adjusted to 7.5.

![Figure 5-13 Extraction of Li Mn and Co at different equilibrium pH. [Aqueous – 10.99 g/L of Mn, 11.79 g/L of Co and 2.78 g/L Li in sulfate medium, organic – 1 mol/L P507 in kerosene, O:A ratio –1:1.]](image)

**Phase ratio-extraction isotherms**

The results of phase ratio-extraction for Mn, Co and Li by 1 mol/L P507 are shown in Figure 5-14, the extraction of Mn and Co increased from 30.2% and 26.4% to 63.1% and 60.0% when the
O:A ratio increased from 0.5 to 3.0. The extraction of Li was also found to increased merely from 5.1% to 6.2% with increasing O:A ratio.

Figure 5-14 Extraction of Li Mn and Co at different O:A ratio. [Aqueous – 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L Li in sulfate medium, aqueous solution pH – 7.5, organic – 1mol/L P204 in kerosene.]

5.4.5. Scrubbing and stripping results in solvent extraction

After the extraction step, the organic phase and aqueous phase were separated by separating funnel. Since some impurity may co-extracted with the target metal loaded organic solution, the organic phase should be scrubbed by some strong acid (e.g. HCl, H₂SO₄). After the enough stages of scrubbing, majority of the impurity were back-streamed to the aqueous feed, and the purity target metal should be higher than 99%. Since some literature stated that the metal loaded organic solution can be fully scrubbed by several stages of scrubbing [93, 105], the scrubbing efficiency of the recycle process is assumed to be 100% percent. Note that this assumption means all the impurity of the target metal loaded organic solution will be back-streamed to the aqueous phase, and the purity of the target metal in the extractant were 100%.
H$_2$SO$_4$ were used as the stripping agent to strip the extracted metal ions (Mn, Co, and Li) from the loaded extractants. Different authors also used H$_2$SO$_4$ to separate metals from the loaded organic. Various concentrations of sulfuric acid (0.01M, 0.05M, 0.1M and 0.2M) were used for cobalt stripping from the scrubbed organic at an equal phase ratio. The results of the stripping efficiency of Mn, Co and Li are shown in Table 5-2. The stripping of Mn and Co increased from 38.8% and 42.1% to 99.0% and 99.1% with a rise in acid concentration from 0.01M to 0.2M. It was found that 98.9% Mn, 99.0% Co and 99.1% Li can be stripped using a 0.1M concentration of H$_2$SO$_4$, and the stripping efficiency of 0.1M H$_2$SO$_4$ is high enough for recovery of the metal ions by crystallization. Since H$_2$SO$_4$ may also strip Co and Li from the extractant, it is recommended that the stripping be carried out when organic is fully loaded with Mn and other impurities have been scrubbed back to the aqueous feed.

Table 5-2 Stripping results by different concentration of H$_2$SO$_4$ with equal phase ratio of scrubbed organic.

<table>
<thead>
<tr>
<th>Concentration of H$_2$SO$_4$ (mol/L)</th>
<th>Stripping Efficiency (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Co</td>
</tr>
<tr>
<td>0.01</td>
<td>38.8</td>
<td>42.1</td>
</tr>
<tr>
<td>0.05</td>
<td>80.1</td>
<td>84.1</td>
</tr>
<tr>
<td>0.1</td>
<td>98.9</td>
<td>99.0</td>
</tr>
<tr>
<td>0.2</td>
<td>99.0</td>
<td>99.1</td>
</tr>
</tbody>
</table>

5.4.6. Process synthesis

After the optimization of the extraction process, the feasible processes for recycle of LiMn$_{0.5}$Co$_{0.5}$O$_2$ cathode can be synthesized, all the flow sheets of these feasible processes (a, c, d, and e in Figure 5-5) are presented in Figure 5-15. The process (a) was synthesized with one solvent extraction process for the separation of Mn from Co and Li, and two chemical precipitation for precipitating Co and Li, separately. The solvent extraction for Mn can be conducted with 1mol/L P204 at pH 7.5 in counter-current liquid-liquid extraction. After the scrubbing and stripping, the Mn loaded solution was crystallization by evaporation of the water. Co was recovered by adding of enough NaOH, and Li can be recovered by addition of Na$_3$PO$_4$ in hot water after the removal of Mn and Co.
In process (b), the process starts with a Co separation by solvent extraction, and followed by Mn and Li separation. From the discussion above, Co cannot be separated respectively, as the existing of Mn will largely disturb the Co from extraction. As a result, the process (b) cannot be conducted only with C272, P204 and P507 extractants. The process (c) was synthesized with two solvent extractions for separation of Mn and Co, respectively, and followed by a chemical precipitation for Li recovery. The solvent extraction for Co can be conducted with 1mol/L C272 at pH 7.5 in counter-current liquid-liquid extraction.

The recycle process (d) can be synthesized with one solvent extraction for co-extraction of Mn and Co, selective precipitations for Mn and Co recovery (studied in chapter 4), and a crystallization for Li recovery by solvent evaporation. The solvent extraction of process (d) can be proceeded with 1mol/L P507 at pH 7.5, and the flow sheet is shown in Figure 5-15 (d). The recycle process (e) starts with a co-extraction of Mn and Co, and then use solvent extraction by P204 to separate Mn from Co, and the flow sheet is shown in Figure 5-15 (e). The process (f) for recycle of LiMn$_x$Co$_{1-x}$O$_2$ by selective precipitation has been introduced in chapter 4, and it can recover the target metal ion with high purity and high recover yield.
5.4.7. McCabe Thiele method

Introduction of McCabe Thiele diagram

The McCabe Thiele method is considered to be the simplest and perhaps most instructive method for the analysis of binary distillation or separation [40, 106]. It uses the fact that the composition at each theoretical tray (or equilibrium stage) is completely determined by the mole fraction of one of the two components and is based on the assumption of constant molar overflow. Before starting the construction and use of a McCabe Thiele diagram for the extraction of a binary feed, the liquid–liquid equilibrium data must be obtained for the concentration of the component of the feed. The first step is to draw equal sized vertical and horizontal axes of a graph. The horizontal axis will be for the concentration (denoted by $x$) of the desired metal ion in the aqueous phase. The vertical axis will be for the concentration (denoted by $y$) of the desired metal ion in the organic phase. The next step is to draw a straight line from the origin of the graph to the point...
where x and y both equal 1.0, which is the x = y line. Then draw the equilibrium line using the liquid–liquid equilibrium data points of the desired metal concentration, representing the equilibrium ion concentration for each value of liquid phase composition.

**Construction and use of the McCabe Thiele diagram**

Since the solvent extraction of Mn by P204 in process (a) and (c) is counter-current, the number of stages for fully extracting Mn needs to be decide. To determine the theoretical number of stages required for complete extraction of Mn at a chosen phase ratio, the extraction isotherm was drawn from the results which were obtained by contacting the aqueous phase containing Mn, Co and Li with 1mol/L P204 at different A/O phase ratios from 10 to 1 and O/A phase ratios from 5 to 1 in kerosene diluent. The McCabe Thiele plot is confirmed by solvent extraction experiment data, and shown in Figure 5-16. The McCabe Thiele plot of Mn extraction by 1mol/L P204 extractant suggests that three counter current extraction stages are required for complete extraction of Mn (99.2%) from the feed solution of 10.99g/L of Mn, 11.79 g/L of Co and 2.78g/L of Li at equilibrium pH 7.5 and O:A ratio 1:1.

In McCabe Thiele diagram, it uses the fact that the composition at each theoretical tray (or equilibrium stage) is completely determined by the mole fraction of one of the two components and is based on the assumption of constant molar overflow and the assumption that all extraction stages are completely equilibrium. In the diagram, the straight line is the working line, when the O:A ratio of the extraction is 1:1, and slope of this line is 1. The curve in the diagram is the equilibrium line, which is made of experimental data.
Figure 5-16 McCabe Thiele diagram of Mn extraction at different A:O ratio. [Aqueous –10.99 g/L Mn, 11.79 g/L Co, and 2.78 g/L Li in sulfate medium, aqueous solution pH – 7.5, organic – 1mol/L P204.]

After the separation of Mn in recycle of LiMn_{0.5}Co_{0.5}O_2, the number of stages for fully extracting Co by C272 with counter-current needs to be determined. In order to confirm the theoretical number of stages required for totally recover Co at a chosen phase ratio, the extraction isotherm was drawn from the results which were obtained by contacting the aqueous phase containing Co and Li with 1mol/L C272 at different A/O phase ratios from 10 to 1 and O/A phase ratios from 5 to 1 in kerosene diluent. The McCabe Thiele plot, shown in Figure 5-17, is also confirmed by experimental results. The McCabe Thiele plot suggests that four counter-current extraction stages can recover 91.5% of Co from the feed solution of 11.79 g/L of Co and 2.78g/L of Li at an equilibrium pH 7.5 and O/A ratio 1:1. Since the McCabe Thiele plot in Figure 5-17 was drawn from extraction experimental results, the results of O:A ratio above 6 may be not accurate, it is
assume that five counter-current extraction stages are required for complete extraction of Co (higher than 98%).

![McCabe Thiele diagram of Co extraction at different A:O ratio.](image)

Figure 5-17 McCabe Thiele diagram of Co extraction at different A:O ratio. [Aqueous –11.79 g/L Co and 2.78 g/L Li in sulfate medium, aqueous solution pH – 7.5, organic – 1mol/L C272.]

In order to compare the recycle processes with the same consistency, all the solvent extraction were maintain the O/A ratio at 1:1. Since the efficiency of co-extraction of Mn and Co by P507 is relative low, it is not possible use 1:1 O/A ratio working line in the McCabe Thiele diagram of Mn and Co extraction by P507. The counter-current extraction experiment by 1mol/L P507 at pH 7.5 in 10.99 g/L Mn, 11.79 g/L Co, and 2.78 g/L Li sulfate solution with 1:1 O/A ratio was conducted. The extraction results showed that four stages of counter-current extraction can extract 90.3% and 89.1% of Mn and Co, respectively.
5.4.8. Process comparison

After the introduction of the feasible recycle processes, the steps of solvent extraction and metal ion crystallization were summarized in Table 5-3. In order to compare all the feasible process alternatives (including solvent extraction and selective precipitation), five processes were compared with the material consumption, process complexity, product quality and recover yield. All the processes were simulated with 1 L cathode leached liquor, which contains 0.4mol/L Li, Mn and 0.2mol/L of Co in sulfate solution, respectively. By mass balance calculation, the reagent consumption, product purity, and recycle yield are listed in Table 5-4.

Table 5-3 Summary of process alternatives.

<table>
<thead>
<tr>
<th>Process</th>
<th>Extraction(^1)</th>
<th>Stripping</th>
<th>Crystallization(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Extraction 1: P204 (3 stages 99.2% of Mn)</td>
<td>Mn stripping (98.9%)</td>
<td>Crystallization 1 for Mn by SE Crystallization 2 for Co by NaOH Crystallization 3 for Li by Na(_3)PO(_4)</td>
</tr>
<tr>
<td>c</td>
<td>Extraction 1: P204 (99.2% of Mn) Extraction 2: C272 (4 stages 91.5% of Co)</td>
<td>Mn (98.9%), Co (99.0%)</td>
<td>Crystallization 1 for Mn by SE Crystallization 2 for Co by SE Crystallization 3 for Li by SE</td>
</tr>
<tr>
<td>d</td>
<td>Extraction 1: Mn and Co co-extracted by P507 (4 stages, Mn=90.3%, Co=89.1%)</td>
<td>Mn (98.9%), Co (99.0%)</td>
<td>Crystallization 1 for Co by SP (Na(_2)S) Crystallization 2 for Mn by NaOH Crystallization 3 for Li by Na(_3)PO(_4)</td>
</tr>
<tr>
<td>e</td>
<td>Extraction 1: Same as process d Extraction 2: Same as process a</td>
<td>Mn (98.9%), Co (99.0%)</td>
<td>Crystallization 1 for Mn by NaOH Crystallization 2 for Co by Na(_2)S Crystallization 3 for Li by Na(_3)PO(_4)</td>
</tr>
</tbody>
</table>

Note:
(1) In solvent extraction, all the concentration of the extractants are 1mol/L, the O/A ratio are 1:1, and the aqueous solution are adjusted to pH 7.5 before extraction.
(2) In crystallization, SE means solvent extraction, SP means selective precipitation (need to adjust pH first).
Table 5-4 Details of process comparison.

<table>
<thead>
<tr>
<th>Process</th>
<th>Extraction(^{1,2})</th>
<th>Crystallization(^3)</th>
<th>Purity (%)(^{4,5})</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Li</td>
<td>Mn</td>
</tr>
<tr>
<td>a</td>
<td>1mol P204 (Mn), 0.1mol H(_2)SO(_4) (stripping)</td>
<td>0.8 mol NaOH (Co), 0.6 mol Na(_3)PO(_4) (Li)</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>c</td>
<td>1mol P204 (Mn), 1mol C272 (Co), 0.2mol H(_2)SO(_4) (Mn, Co stripping)</td>
<td>Solvent evaporation only</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>d</td>
<td>1 mol P507 (Mn and Co), 0.1mol H(_2)SO(_4) (Mn and Co stripping)</td>
<td>0.9 mol Na(_2)S (Co), 0.8 mol NaOH (Mn), 0.6 mol Na(_3)PO(_4) (Li)</td>
<td>99 M(^6)</td>
<td>99</td>
</tr>
<tr>
<td>e</td>
<td>No consumption</td>
<td>Same as process d</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
</table>

Note:

1. In solvent extraction, the consumption of H\(_2\)SO\(_4\) for pH adjust to 7.5 before extraction is not listed, and the consumption of kerosene for extractants is not listed.
2. The reagent consumption for scrubbing has not been mention, and the scrubbing efficiency is assumed to be 100%.
3. In crystallization, the consumption of H\(_2\)SO\(_4\) for pH adjustment is not listed.
4. As all the Li is recovered by solvent evaporation or precipitation by adding Na\(_3\)PO\(_4\), the purity of its recover product is higher than 99%.
5. From the experimental data in chapter 4, the purity of the Mn and Co recover product by precipitation are higher than 99%.
6. M stands for mixture, as the Mn is precipitated after selective precipitation of Co by ading Na\(_2\)S, and Mn will be precipitated as Mn(OH)$_2$ and MnS mixture.

From the process comparison in Table 5-4, the selective precipitation recycle process (f) can recover all the metal ion with high purity and high recover yield, and no organic solvent is need;
however, it is not easy to be used in continual production with large scale, because the pH adjustment should be accurate for separating the metal ion by adding different precipitants. Also, the reagent of Na2S and is not good for the environment. The process (a) can also recover the metal ion with high purity and yield, and the process is more simplified than other process. Comparing with process (f), process (a) does not need to adjust the pH of the solution accurately, and all the extractants and precipitants are inexpensive. As a result, the process (a) may be more suitable for large scale industrial production.

5.5. Conclusions

The recycling process of spent LIB by integrated solvent extraction and chemical precipitation has been studied in this chapter, and LiCo$_x$Mn$_{1-x}$O$_2$ as case studies. With the combination of solvent extraction and chemical precipitation, possible process alternatives can be designed for recycle of LiCo$_x$Mn$_{1-x}$O$_2$. In the case studies of recycle LiCo$_{0.5}$Mn$_{0.5}$O$_2$, the operating conditions for solvent extraction process were optimized. By conducting extraction experiments with optimized conditions, 90.8% Mn can be extracted by 1mol/L P204 at pH 7.5 with 2:1 O:A ratio in one stage, and 76.9% Co was extracted by 1mol/L C272 with the same condition. Also, ~50% of Mn and Co can be co-extracted by 1mol/L P507 at pH 7.5 with 2:1 O:A ratio. After the extraction, ~99% of the extracted metal ion can be stripped out by 0.1mol/L H$_2$SO$_4$ in 1:1 O:A ratio. After studying the effects of operating conditions, four feasible processes were synthesized in the recycle of LiCo$_{0.5}$Mn$_{0.5}$O$_2$. In order to determine the theoretical number of stages required for total recovery of Mn and Co at a chosen phase ratio by P204 and C272, the corresponded McCabe–Thiele diagrams were constructed and used. The McCabe Thiele plots suggest that three counter-current extraction stages can recover 99.5% of Mn, and four counter-current extraction stages can recover 91.5% from the feed solution of 11.79 g/L of Co and 2.78g/L of Li at equilibrium pH 7.5 and O:A ratio 1:1. With the combination of solvent extraction and chemical precipitation, valuable metals in the cathode of the spent LIBs can be recovered with high purity and yield. Comparing with selective precipitation process in chapter 4, the process (a) with solvent extraction for Mn recovery may be more suitable for large scale industrial production.
6. Conclusions and Future work

6.1. Conclusions

LIBs are attractive in many applications due to the high capacity, lightweight and larger power density. LIBs used for different products usually have different requirements on the electrochemical performance, which is affected by the LFP particle quality. A causal table is summarized in this study to illustrate the effect of various particle qualities on the electrochemical performance. The causal table is validated with some reported studies in the literature and also experiments conducted in this thesis. Among the commercial LFP cathode materials tested, the sample II with 0.15*0.4*0.6 μm particle size (0.15 μm as the diffusion path of Li ion), 2.4% carbon coating, and plate-like morphology exhibited the best specific capacity (164.9 mAh g\(^{-1}\) at 0.1C) and rate capability (88.5% at 1.5 C). Also, the charge transfer resistance measured from the EIS was the smallest. On the other hand, samples VI with larger particle size and spherical shape had lower specific capacity and rate capability. With the causal table, desired particle attributes can be identified for producing LFP particles targeted for specific applications. This in turn determines the synthesis conditions to produce particles with the desired qualities.

In order to fulfill the requirements on the electrochemical performance in many areas, high quality cathode materials can be synthesized by poly refluxing process. This process is used to synthesis the morphologically-tailored LFP cathodes in this thesis. The single-phase spherical LFP nano-particles were synthesized with the optimized conditions. With the carbon coating process, a uniform ~4 nm thick carbon layer was coated on the surface of the LFP nano-particles. By adding surfactants in the polyol refluxing step, four different morphology LFP nano-particles were produced. Among the four LFP cathode materials tested, the LFP sample with around 140*40 nm particle size, 2.9% carbon coating, and rod-like morphology exhibited the best specific capacity (160.5 mAh g\(^{-1}\) at 0.1C) and rate capability (77.1% at 1.5 C). Also, the charge transfer resistance measured from the EIS was the smallest. With this study, desired high quality LFP particles targeted for specific applications can be produced by determining the synthesis conditions.

With the rapid development of electronic products, recycling of spent LIB becomes an important issue as they are not suitable to be disposed to the landfills. The recycling process of spent LIB by
selectively precipitating metal salts in a series of chemical precipitation process has been studied in this thesis, with LiFePO$_4$ and LiCo$_x$Mn$_{1-x}$O$_2$ as examples in two case studies. In both case studies, pure metal salts with high yield can be recovered from the system. The SLE phase behavior governs the product to be recovered in these precipitation processes. By conducting experiments to determine regions of phase diagram that are of interest to the precipitation process, the optimal operating conditions can be identified. The SLE phase behavior also rationalizes the process and operating conditions that previous researchers developed based on trial and error.

The SLE phase behavior also provides insights to the development of process alternatives which can be compared with the conventional process in order to come up with a process that is better for recycling spent LIB. Based on the insights obtained from the SLE phase behavior, a simpler process has been developed for the recycling of LiCo$_x$Mn$_{1-x}$O$_2$. Instead of co-precipitating CoS and MnS, and separating them by selective dissolution in acetic acid, phase behavior suggests that CoS can be selectively precipitated in the first precipitation process by controlling the amount of Na$_2$S added, and MnS can be recovered in the subsequent precipitation process. All of these show that SLE phase behavior is crucial in designing the chemical precipitation processes for the recycle of spent LIB. With the SLE phase behavior available for other systems, the same idea can be applied to the design and optimization of the recycling process for other battery materials.

The recycling process of spent LIB by solvent extraction and chemical precipitation combined also has been studied in this thesis. With the combination of solvent extraction and chemical precipitation, possible process alternatives can be designed for recycle of LiCo$_x$Mn$_{1-x}$O$_2$. In the case studies of recycle LiCo$_{0.5}$Mn$_{0.5}$O$_2$, the operating conditions for solvent extraction process were optimized. By conducting extraction experiments with optimized conditions, 90.8% Mn can be extracted by 1mol/L P204 at pH 7.5 with 2:1 O:A ratio, and 76.9% Co was extracted by 1mol/L C272 at pH 7.5 with 2:1 O:A ratio. After study the condition effects on extractions, three feasible processes were synthesized in recycle of LiCo$_{0.5}$Mn$_{0.5}$O$_2$, which combines the solvent extraction and chemical precipitation. The McCabe Thiele plots suggest that three counter-current extraction stages can recover 99.2% of Mn, and four counter-current extraction stages can recover 91.5% from the feed solution of 11.79 g/L of Co and 2.78g/L of Li at equilibrium pH 7.5 and O:A ratio 1:1. With the combination of solvent extraction and chemical precipitation, the valuable metal in cathode of the spent LIBs can be recovered with high purity and yield. Comparing with selective
precipitation process, the process with solvent extraction and chemical precipitation may be more suitable for large scale industrial production because it does not need to adjust the process parameters accurately.

6.2. Future work

With the insights from chapter 2, other particles of LIBs cathode material (e.g., LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\), LiMnPO\(_4\), and LiMn\(_2\)O\(_4\)) can be studied to understand their particle characteristics effects on the battery performance, and provide more information and understanding on production of that kind of cathode particles. Also, other high quality LIBs cathode materials can be synthesized by different methods. After understanding the particle characteristics effects on the battery performance of LFP, the high performance LFP nano-particles can also be synthesized with the other lower cost synthesis method, and then compared with the polyol refluxing process.

With the insights from the SLE phase behavior, the recycle process for different kind of LIB cathode material can be synthesized. Also, the existing process for spent batteries recycle can be optimized by studying the phase behavior in some steps of the process.

In the solvent extraction process, the steps of scrubbing and stripping should be further studied in order to have a higher recovery purity and yield. The whole solvent extraction and crystallization combined process should be studied with other alternatives to evaluate its simplicity, cost, and yield. The comparison of the recycle processes should be studied with more experimental data and details.
Reference


M. Gaberscek, R. Dominko, and J. Jamnik, "Is small particle size more important than carbon coating? An example study on LiFePO$_4$ cathodes," *Electrochemistry Communications*, vol. 9, pp. 2778-2783, 12/2007.


B. Pei, H. Yao, W. Zhang, and Z. Yang, "Hydrothermal synthesis of morphology-controlled LiFePO$_4$ cathode material for lithium-ion batteries," *Journal of Power Sources*, vol. 220, pp. 317-323, 12/15/2012.


