Development of a Recycling Process for Li-Ion Batteries

Haiyang Zou
Worcester Polytechnic Institute

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Development of a Recycling Process
for Li-Ion Batteries
by
Haiyang Zou

A Thesis
Submitted to the Faculty
of the
WORCESTER POLYTECHNIC INSTITUTE
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Abstract

The rechargeable secondary Lithium ion (Li-ion) battery is expected to grow to more than $6.3 billion by 2012 from ~$4.6 billion in 2006. With the development of personnel electronics, hybrid and electric vehicles, Li-ion batteries will be more in demand. However, Li-ion batteries are not widely recycled because it is not economically justifiable (in contrast, at present more than 97% Lead-acid batteries are recycled). So far, no commercial methods are available to recycle different chemical Li-ion batteries economically and efficiently. Considering our limited resources, environmental impact, and national security, Li-ion batteries must be recycled. A new methodology with low temperature and high efficiency is proposed in order to recycle Li-ion batteries economically and with industrial viability. The separation and synthesis of cathode materials (most valuable in Li-ion batteries) from recycled components are the main focus of the proposed research. The analytical results showed that the recycling process is practical and has high recovery efficiency, create great commercial value as well.
Acknowledgements

First and foremost I owe my deepest gratitude to my family. They give me love and encouragement, making me feel quite warm. Especially my parents, they tried their best to support me in all my pursuits.

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My sincere thanks go to our department professors Professor Richard D. Sisson Jr., Professor Makhlof M. Makhlof, Professor Satya S. Shivkumar, Dr. Boquan Li. They shared their valuable knowledge, experience and advice with me in classes. They have been a great help in my academic performance. I want to thank our department secretary Rita Shilansky. I thank all of those who supported me in any respect during the completion of my thesis. It is my pleasure to pay tribute to all the WPI faculty and staff.

I would like to express my gratitude to my friends here. I am so happy to have a pleasant and comfortable life here with all my friends. I express my apology to anyone who I did not mention personally.

The life in WPI has been a wonderful journey in my whole life. With the great joy and pride, sheer determination and perseverance, I have courage and conviction in pursuing my goals and ideals.
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1 Introduction

1.1 Energy, electricity & batteries

Energy is one of the most basic needs for human beings. Divided by power sources, energy supply contains oil, coal, gas, renewable energy (hydro, solar, wind, geothermal power and biofuels), nuclear and other, while oil and coal combined represented over 60% of the world energy supply in 2008 (Figure 1) [1]. However, the trouble with fossil fuels is that we cannot use fossil fuels forever as they are non-renewable and finite resource. Also, burning fossil fuels brought negative effects on air pollution, acid precipitation and global warming (climate change). Oil exists in limited supplies, and growing demand even causes world tensions and wars; though gas moves from place to place easily, can be dangerous when leaking or escaping [2]. The energy consumption has maintained rapid growth (Figure 2) and the price of fuel is increasing steadily (Figure 3) [1, 3, 4].

Figure 1: World energy consumption by power sources, 1990-2035 (quadrillion Btu) [1].

Figure 2: World energy consumption, 1990-2035 (quadrillion Btu) [1].
Fortunately, electricity provides a method to fix the energy crisis. As it is so versatile that it can be made not only in power plants by burning fuels but also from renewable or green energy (biomass energy, hydro power, nuclear energy, ocean energy, solar energy, wind energy, hydrogen); electricity can be easily transmitted from one place to another along cables, then turned back into other kinds of energy by a wide range of appliances. Electrochemical battery converts stored chemical energy into electrical energy, and can store energy for a long time and still work to provide power. Since the first battery (or “voltaic pile”) was invented in 1800 by Alessandro Volta and improved (Daniell cell) by John Frederic Daniell, batteries have become a common power source for personal, household and industrial applications. Batteries are classified into two broad categories: primary batteries and secondary batteries. Primary batteries irreversibly transform chemical energy to electrical energy, and energy cannot be restored to the battery by electrical means. Secondary batteries can be recharged, and can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition. With the steady population increase, resource depletion, people bring forward higher requirement on chemical energy: higher performance, longer working life and lower
pollution [4]. This has resulted in developing batteries which have lighter weight, higher energy density, and a longer life cycle.

1.2 Lithium-ion batteries

In 1979, John Goodenough invented a rechargeable cell using lithium cobalt oxide (LiCoO$_2$) as the positive electrode and lithium metal as the negative electrode. This innovation provided the positive electrode material containing lithium ions, which made Lithium-ion batteries (LIBs) possible. LiCoO$_2$, acting as a donor of lithium, enables the use of stable and easy-to-handle negative electrode materials. In 1991, Sony and Asahi Kasei released the first commercial lithium-ion battery.

In the past decades, advances in lithium-ion batteries have been so spectacular that they become the most popular power source for portable electronics equipment, and also growing in popularity for military, electric vehicle, and aerospace applications [6, 7]. No other systems threaten to interfere with its dominance at this time (Figure 4).

![Figure 4: Revenue contribution by different battery chemistries in 2009](image)

(The applications in lead acid market are divided into starter battery for automotive, stationary for power backup, and deep-cycle for wheeled mobility.)
Table 1: Comparisons among three battery technologies [8, 9].

<table>
<thead>
<tr>
<th>Items</th>
<th>Li-ion</th>
<th>Ni-MH</th>
<th>Lead-acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working voltage (V)</td>
<td>3.7</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>Gravimetric energy density (Wh/kg)</td>
<td>130-200</td>
<td>60-90</td>
<td>30-40</td>
</tr>
<tr>
<td>Volumetric energy density (Wh/L)</td>
<td>340-400</td>
<td>200-250</td>
<td>130-180</td>
</tr>
<tr>
<td>Cycle life (cycles)</td>
<td>500</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>Capacity self discharge rate (% per month)</td>
<td>5%</td>
<td>30%</td>
<td>10%</td>
</tr>
<tr>
<td>Memory effect</td>
<td>None</td>
<td>40%</td>
<td>None</td>
</tr>
<tr>
<td>Coulombic efficiency ($C_{discharge}/C_{charge}$)</td>
<td>99%</td>
<td>70%</td>
<td>75%</td>
</tr>
<tr>
<td>Weight comparison for the same capacity</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Size comparison for the same capacity</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Reliability</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

Figure 5: Comparison of Energy Densities: Lithium Chemistry is still king [11].

Comparing with other conventional batteries (Table 1), lithium ion batteries have following advantages [10]:

a) High specific energy (Figure 5);

Lithium has the lightest weight, and greatest electronegativity of all metals. Consuming the same amount of battery materials, lithium ion batteries can provide more energy than other traditional rechargeable batteries [12]. From Figure 5, comparing with other batteries, lithium ion batteries have higher energy density ranging from ~100-180 Wh/kg.
b) High open circuit voltage;
Comparing with aqueous batteries like lead acid, nickel-metal hydride and nickel-cadmium batteries, lithium ion batteries have high open circuit voltage, which can increase the amount of power that can be transferred at a lower current [13].

c) No memory effect;
After repeatedly recharged and partially discharged, nickel-cadmium or nickel-metal hydride batteries gradually lose their maximum energy capacity. They appear to “remember” the smaller capacity. However, lithium ion batteries can supplementarily charge anytime, which make them more convenient and maximize the performance of batteries [14].

d) Wide working temperature range (Figure 6);
Most chemical power source use aqueous solution as electrolyte solution and their performance at low temperature will be affected by freezing point.

![Figure 6: Specific energy of batteries in different working temperature [14].](image)

---

e) Environmentally safe;
No poison elements such as Hg, Cd, Pb are used in lithium ion batteries.

f) Longer cycle life.
Lithium ion batteries have longer cycles, which are shown in Table 1.

1.3 Contents of lithium ion batteries
Primary functional parts of a lithium-ion battery include anode, cathode, electrolyte, and separator (Figure 7). An outer case made of metal holds a long spiral comprising three thin sheets pressed together: positive electrode (anode), negative electrode (cathode), and separator. Inside the case these sheets are submerged in the electrolyte which is an
organic solvent. The separator is a very thin microperforated polymer sheet which separates the two electrodes allowing ions to pass through.

Lithium ion batteries use an intercalated lithium compound as the electrode materials. The commercial anode (negative) contains graphite/carbon and PVDF binder, coated on copper foil. The cathode (positive) electrode contains cathode material, carbon, and PVDF binder, coated on aluminium foil. The cathode material is generally one of three kinds of materials: a layered oxide (such as lithium cobalt or nickel oxide), a polyanion (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide) [15]. The electrolyte is typically a mixture of organic carbonates, generally use non-coordinating anion salts like lithium hexafluorophosphate (LiPF₆). An organic electrolyte acts as an ionic path between electrodes and separates the two electrode materials.

Figure 7: Structure of cylindrical lithium-ion battery [13].

1.4 Principles of lithium ion batteries
Lithium-ion battery (LIB) is a family of rechargeable battery. Lithium ions move from the negative electrode to the positive electrode during discharge, and reverse when charging (Figure 8).
Figure 8: Mechanism of discharging and charging in lithium ion batteries [16]. When a lithium-based cell is discharging, lithium ions are extracted from the anode, move through the electrolyte and inserted into the cathode. When the cell is charging, the reverse occurs.

The positive electrode half-reaction (cathode reaction), take LiCoO$_2$ as an example:

$$\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^-$$

The negative electrode half-reaction is:

$$x\text{Li}^+ + x\text{e}^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6$$

Overall cell reaction:

$$\text{C} + \text{LiCoO}_2 \rightleftharpoons \text{Li}_x\text{C} + \text{Li}_{1-x}\text{CoO}_2$$

During charging, the transition metal cobalt is oxidized from Co$^{3+}$ to Co$^{4+}$, and reduced from Co$^{4+}$ to Co$^{3+}$ during discharge.

1.5 The importance of recycling lithium ion batteries

“We do not need to exhaust materials, spoiling our environment and ending up with nothing to continue with. What we need do is to treat each material in a way similar to that in which Nature treats water: we should use it, then supply energy to its used (degraded) form to upgrade it to its original state”[17].

1.5.1 Demand for lithium ion batteries

Figure 9 shows the growth in the size of the rechargeable battery market by battery type over the years [18]. Up to date, most of the demand for lithium-ion batteries has been for
portable devices such as mobile phones and note PCs. The demand for such small devices is expected to steadily increase in the future. While with the help of other lithium-ion battery applications, such as solar panel systems, smart grids, electric tools and especially electric vehicles, the market of lithium ion batteries will flourish after a series of improvements. In 2014, the market of rechargeable battery for electric vehicle is expected to exceed two trillion yen, and the total market for the batteries surpasses three trillion yen (Figure 10).

Figure 9: Battery market between year 1991 and 2009[18].
1.5.2 Cell life of lithium ion batteries

Lithium ion batteries usually have certain life, normally 1-2 years. Over time, deposits inside the electrolyte formed during charging inhibit ion transport, the cell’s capacity decreases. Internal resistance increases with both cycling and age, reducing the cell’s ability to deliver current. Also, rising internal resistance causes the voltage at the terminals to drop under load. Thus, older batteries do not charge as much as new ones (charging time required decreases proportionally). It is predictable that lithium ion batteries will become an important part of solid waste, which must not be overlooked [7].

1.5.3 Dangerous & environment threat [19]

Lithium ion batteries are nontoxic, and rated safe for landfill disposal, as they don’t contain materials that are dangerous to the environment by themselves. However, if lithium ion batteries in a landfill rupture and come into contact with water, dangerous substances created will sink down into the groundwater, thus landfill will be dangerous to our environment. LiPF₆ in electrolyte can decompose and react with H₂O, releasing poisonous HF:

\[
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} + \text{LiF}
\]
In addition, during decomposing internal short circuits might happen and large heat and oxygen might be released, which cause explosion.

The concern about wildlife is that lithium ion batteries contain cobalt, copper, nickel and iron, which will leach into an animal’s system, causing great harm and likely death, also the same for people.

Additionally, throwing the batteries away means that fresh metals have to be mined, and mining has a much bigger environmental impact than simple recycling would.

While lithium ion batteries are completely recyclable, millions of tons of lithium ion batteries are added to landfill every year, taking up space that could be saved.

1.5.4 Sustainable development-lithium demand
While 97% lead acid batteries are recycled, over 50 percent of the lead supply comes from recycled batteries, lithium ion batteries are NOT being recycled widely. The increase of Lithium demand is huge, however, analysis of Lithium’s geological resource base shows that there is insufficient Lithium available in the Earth’s crust to sustain electric vehicle manufactures in the volumes required, based solely on Li-ion batteries [20]. Recycling can dramatically reduce the required lithium amount (Figure 11) [21]. Having a recycling infrastructure in place will ease concerns that the adoption of vehicles that use lithium-ion batteries could lead to a shortage of lithium carbonate and a dependence on countries such as China, Russia, and Bolivia, which control the bulk of global lithium reserves [22].
1.5.5 Benefits

Various chemical lithium ion batteries contain valuable metal elements such as cobalt, manganese, iron, and nickel. Table 2 shows the mass and approximate value (in year 2000) for the main components in a standard ICR18650 cell (Figure 12) whose cathode material is LiCoO$_2$. As more and more lithium ion batteries are being produced, recycling large numbers of lithium ion batteries in easy and cheap ways certainly will not only protect our environment, but also yield significant economic benefits.

Table 2 Approximate value for main components in a standard ICR18650 cell in year 2000 [23].

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass(g)</th>
<th>Approximate value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>£</td>
</tr>
<tr>
<td>Cobalt</td>
<td>6.5</td>
<td>0.16</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>5</td>
<td>0.151</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.6</td>
<td>0.002</td>
</tr>
<tr>
<td>Copper</td>
<td>28</td>
<td>0.003</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.8</td>
<td>0.004</td>
</tr>
<tr>
<td>Other</td>
<td>22.6</td>
<td>-</td>
</tr>
</tbody>
</table>
1.6 Current researches on recycling lithium ion batteries

1.6.1 Industrial Recycling Processes

Figure 13: Sony recycling process [24].

The Sony process uses a high temperature that the cells are incinerated. By using standard hydro-metallurgical techniques, cobalt is recovered. However, the organic components, lithium and fluoride are lost, though a scrubbing system on the incinerator avoids emission problems [24].

Figure 14: Umicore recycling process [25-27].
The Umicore VAL’EAS™ developed a process of recycling lithium-ion batteries combined pyro- and hydrometallurgical process. The battery scrap is directly melted down in furnace without any pre-treatment. Cobalt and nickel are recovered in form of LiCoO$_2$ and Ni(OH)$_2$, ignoring metals like aluminum, and lithium while copper, iron and manganese are refined & purified in an aqueous solution. Organic materials and carbon are burned [25-27]. It is concluded that the recycling scenario result in a 51.3% natural resource savings because of decreased mineral ore dependency and reduced fossil resource and nuclear energy demand [28].

In the Toxco process [23], old batteries go into a hammer mill and are shredded, allowing components made of aluminum, copper, and steel to be separated easily. Larger batteries that might still hold a charge are cryogenically frozen with liquid nitrogen at -325 °F before being hammered and shredded. Lithium is then extracted by flooding the battery chambers in a caustic bath that dissolves lithium salts, which are filtered out and used to produce lithium carbonate. The remaining sludge is processed to recover cobalt, which is used to make battery electrodes.

1.6.2 Typical recycling processes in academy

Contestablile et al. [29] studied a recycling process (Figure 15) composing of sorting, crushing and riddling, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. The cobalt dissolved in the hydrochloric solution was recovered as cobalt hydroxide Co(OH)$_2$ by addition of NaOH solution. By filtration, the Co(OH)$_2$ precipitate can be separate easily, to be then recycled.
Nan et al. [30] developed a recycling process (Figure 16) comprising the dismantling of spent lithium ion batteries, the recovery of cobalt, copper and lithium using chemical deposition and solvent extraction methods, and the reuse of recovered compounds to synthesize LiCoO$_2$ cathode material. Acorga M5640 and Cyanex 272 extractants were applied to extract copper and cobalt in sulfate solution. The experimental results showed that valuable metals including cobalt, copper and lithium could be effectively recovered and reused, and the recovered products had high purities.
Castillo et al. [31] developed a combined process (Figure 17) aimed to the treatment and recycling of mixed spent lithium-ion batteries of different composition. After mechanical treatment, materials are put into a selective dissolution in dilute nitric acid. Then, it operates a solubilization and filtration. Mn(OH)$_2$ can be separated from solution by filtration at pH=10 with addition of NaOH solution. The solid residue, including an iron, cobalt and nickel hydroxides mixture and some traces of Mn(OH)$_2$ are introduced into a muffle furnace at 500 °C during 2 h to eliminate carbon and organic compounds and directly undergo beneficiation in metallurgical applications.
Figure 17: The flow-sheet of the recycling processes from spent lithium-ion batteries [31].

Wang et al. [32] developed a novel process to separate and recover valuable metals such as Co, Mn, Ni and Li from the cathode materials of lithium-ion secondary batteries (Figure 18). During the recovery process, cathode active materials LiCoO$_2$(A), LiMn$_2$O$_4$(B), and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$(C) were performed in an experiment of the leaching process. Metallic elements from the cathode active materials of the lithium-ion batteries are leached out in 4 M hydrochloric acid solution, at 80 °C leaching temperature. The manganese in the leaching solution processes a redox reaction selectively with a potassium permanganate reagent, and precipitates as MnO$_2$. The separation of Ni from the leaching solution after the recovery of Mn is performed by employing a dimethylglyoxime reagent (C$_4$H$_8$N$_2$O$_2$). After the separation of nickel, cobalt is performed by employing hydroxide precipitation. At last, the leaching solution is treated with a saturated solution of sodium carbonate to precipitate Li as lithium carbonate.
Figure 18: Experimental procedure of the leached and recovery process for the mixture [32].

Cathode active material
(A=B+C)

Hydrochloric acid concentration= 4M

Solid-to-liquid ratio= 0.02 g/ml

A glass extractor of 500 ml capacity was put into a thermostat (300 rpm), leaching temperature (T)= 80 °C and leaching time (t)= 1h.

Addition of 1M NaOH solution until pH= 1, 2, 3

Temperature (T)= 40, 50°C

Molar ratio of Mn²⁺ to KMnO₄= 3:0.5,
3:1, 3:1.5, 10 min

Filtration and separation

Precipitate (Mn hydroxide, MnO₂)

Leach liquor

Addition of 28% NH₃ solution until pH= 3 to 14

Molar ratio of C₆H₅NH₂ to [Mn(NH₃)₆]²⁺
= 1:1, 1:5:1, 2:1, 2:5:1, 3:1, 10 min

Filtration and separation

Precipitate (red solid complex)

Leach liquor (Ce(NH₃)₆³⁺)

Addition of 4M hydrochloric acid solution until pH= 0

Addition of 1M NaOH solution until pH= 11

Filtration and separation

Precipitate (Co hydroxide)

Leach liquor (LiF)

Addition of saturated Na₂CO₃ solution at 100 °C

Filtration and separation

Precipitate (Li₂CO₃)

Leach liquor (Na⁺ etc.)

Addition of 1M NaOH solution until pH= 11

Filtration and separation

Precipitate (Na hydroxide)

Leach liquor
Up until now, most of the research works focus on recycling LiCoO$_2$ spent lithium ion batteries. However, with the development of lithium ion batteries technologies, cathode materials with different chemistry for example LiFePO$_4$, LiNiO$_2$, LiMnO$_2$, and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are now being used to produce lithium ion batteries. It is complex to sort out lithium ion batteries based on the battery chemistry and previous methods cannot effectively recycle lithium ion batteries with these different chemistries.

1.7 Pretreatment separation processes

1.7.1 Mechanical crushing/shredding
Discharged Li-ion batteries are posted in an inert, dry atmosphere for mechanical crushing/shredding. This reduces the impact of internal short circuits which might release much heat when in contact with oxygen and also avoids exposing the materials with water vapour, which would hydrolyze the electrolyte. Plastics and container will be separated for recycling. Electrode and electrolyte will go to the next step for further processing [23].

1.7.2 Electrolyte extraction
Electrolyte is one of the most valuable components in lithium ion batteries. Recently, the widely used electrolyte in commercial lithium ion batteries is LiPF$_6$ and its organic solvent. The liquid electrolyte is dispersed in the pores of the electrodes and separator. By immersing in suitable solvent, the electrode can be extracted. Several liquids could be used as the extraction solvent. The boiling point of solvent should be below the decomposition temperature of lithium salt (~80°C), and that also available in an anhydrous state. Figure 19 shows the leaching efficiency of electrolyte in various solvents. Among them, propylene carbonate (PC) has the best performance to fully extract electrolyte in 2 hours. After separation from the residual solids, the solvent can be recovered by evaporation at reduced pressure, leaving pure electrolyte and PC can be reused many times [5,23].
1.7.3 Electrode dissolution

The electrodes are cast on foils using PVDF binder, and cannot be separated easily by physical processes. By immersing in the suitable solvent, the binder re-dissolves, and the electrode particles can be separated from copper, aluminium current collector [23]. Table 3 shows the separation efficiency for different solvents at varied temperature. N-methyl-2-pyrrolidone (NMP), an efficient solvent (solubility around 200g/kg of solvent) for PVDF, whose boiling point is about 200°C, can dissolve all binder at 70°C, while for acetone, the separation efficiency is acceptable but with the increase of temperature, acetone evaporates fast [5]. Thus, the cell pieces are immersed in the solvent NMP, which is stirred, heated to around 70°C.

Table 3: Separation efficiency of active materials from current collectors in various solvents at varied temperature for 1 h [5].

<table>
<thead>
<tr>
<th>Solvents</th>
<th>20°C</th>
<th>40°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>27.06</td>
<td>80.66</td>
<td>70(50°C)</td>
</tr>
<tr>
<td>NMP</td>
<td>27.12</td>
<td>60.52</td>
<td>100</td>
</tr>
<tr>
<td>DMSO</td>
<td>20.83</td>
<td>50.73</td>
<td>80.17</td>
</tr>
<tr>
<td>DMF</td>
<td>10.64</td>
<td>30.22</td>
<td>50.44</td>
</tr>
<tr>
<td>DEF</td>
<td>10.59</td>
<td>35.79</td>
<td>70.69</td>
</tr>
</tbody>
</table>
The electrode particles are filtered from the solution to recover the valuable metals, while the solution can be reused to dissolve the binder. This treatment achieves effective separation of the films, the recovery of both copper and aluminum in their metallic form by simply filtering them out from NMP solution. After adequate cleaning, the two metals can be directly reused.
2 Objectives

With the development of lithium ion battery technologies, different chemistries are now being used to produce lithium ion batteries. Currently, the cathode materials in widely used commercial lithium ion batteries include LiCoO$_2$, LiMn$_2$O$_4$, LiNiO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiFePO$_4$. Even the same battery company may use different battery materials for different applications. For example, LiCoO$_2$ is used for high energy density applications; however, LiFePO$_4$ is used for high power density applications. It is too complex to sort out lithium ion batteries based on the battery chemistry. In order to recycle lithium ion batteries effectively, we need to consider all the various battery chemistries. The research being carried out on recycling lithium ion batteries only considers LiCoO$_2$ as the cathode material. However, this is not the case in the commercial world. Thus, it is important to develop a simple and environmentally acceptable recycling process to recover lithium ion batteries widely used. The objective of this project is to extract useful elements Co, Ni, Mn, Li, Fe from mixed cathode materials and utilize the recycled materials to synthesize active materials for batteries.
3 Experimental

3.1 Materials and equipment
During the recovery process, mixed cathode materials of LiCoO$_2$, LiMn$_2$O$_4$, LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ and LiFePO$_4$, with Ni(OH)$_2$ were employed in the recovery materials process. The cathode materials LiCoO$_2$ and LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ were supplied by Umicore. LiMn$_2$O$_4$ and LiFePO$_4$ were from MTI. 30wt% Hydrogen peroxide was from Columbus Chemical Industries Inc.. Lithium carbonate was from Alfa Aesar Company. All of the reagents were utilized as received without any further purification. Other chemicals were of reagent grade. Ball milling was done by Labmill 8000.

3.2 Experimental procedure
Step 1: Cathode materials from spent lithium ion batteries can be obtained by pretreatment separation. Firstly, discharged Li ion batteries are crushed/shredded. Mechanical separation processes are applied to treat the outer cases and shells, and the metallic fraction will be conducted to a hydrometallurgical recycling process. Electrode and electrolyte will be soaked into propylene carbonate (PC) to recycle the salt (mainly LiPF$_6$) in the electrolyte since LiPF$_6$ has a high solubility in PC, which can be evaporated to obtain LiPF$_6$. LiPF$_6$ can be used to make new electrolyte. Undissolved materials including electrode and current collectors will be filtrated. The cell pieces are immersed in the NMP at about 70°C to separate the electrode particles from the residual current collector. The electrode particles are filtered from the binder solution.

Step 2: The electrode particles were leached by 4M sulfuric acid and 29-32% hydrogen peroxide for about 2-3 hours at 70-80°C. Carbon could not be dissolved, and it floated on solution. After filtration, residual LiFeO$_4$ can be purified by burning to remove carbon and graphite. The metals of interest were transferred to the aqueous liquor.

Step 3: NaOH solution was added to adjust pH number around 3-5 to deposit Fe(OH)$_3$ and keep Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ in the solution, then Fe(OH)$_3$ are recovered by filtration.

Step 4: The concentration of Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ in the solution were tested, and adjusted the ratio of them to 1:1:1 with additional CoSO$_4$, NiSO$_4$, MnSO$_4$. Stirred the solution for
2h.NaOH solution was added to increase the pH to 11, Co(OH)₂, Ni(OH)₂, Mn(OH)₂ can be fully coprecipitated and the mole ratio of them was 1:1:1. The mixture was rinsed by distilled water.

Step 5: Na₂CO₃ was added in the solution to deposit Li₂CO₃ at about 40°C. After filtrating, Li₂CO₃ can be recycled as the starting material to synthesize the active cathode material LiNi₁/₃Mn₁/₃Co₁/₃O₂.

Step 6: The coprecipitate materials Co(OH)₂, Mn(OH)₂, Ni(OH)₂ and recovered Li₂CO₃ with additional Li₂CO₃ in molar ratio 1.1 of Li versus M (M=Ni₁/₃Mn₁/₃Co₁/₃) were mixed and grinded in mortar. The precursor was subject to ball-milling for 48 hours and pressed into pellets (Pressure=15000lbs, 12.96mm diameter). The pellets were sintered at 900°C for 15 h in air and temperature increasing rate is 9°C/min from room temperature. The reaction product was ground into powder using a mortar and pestle. The LiNi₁/₃Mn₁/₃Co₁/₃O₂ was sintered by high temperature solid-state method at 900°C for 15 hours.
3.3 Characterization and analysis

The recycled product Li$_2$CO$_3$ and sintered LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ were characterized by X-ray diffraction (XRD) using an X-ray diffractometer by Bruker D8 Focus; S/N 203207 with copper K$_\alpha$ radiation (Cu target: S/N 07/03-1120). X-ray detector is from Scintillation detector SD 650 NaI (TI).

The concentration of metals in solution was tested by atomic absorption spectroscopy (Perkin-Elmer AA Analyst 300). The scanning electron microscope (SEM) images and
energy disperse spectroscopy (EDS) results were obtained by JEOL JSM-7000F electron microscope.

The pH of the solution was tested by pH meter-Milwaukee MW102. The resolution is about 0.01 pH, and its range is from -2.00 to 16.00 pH.

3.4 Battery assemble and test

In preparing the electrodes, polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) solution was used as a binder. The black slurry consisting of 80 wt.% LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, 10 wt.% conductive carbon, and 10% PVDF was cast on an aluminum foil with blade. Then, NMP was evaporated at 70°C for 12 hours. A lithium electrode was prepared by pressing a lithium metal onto a stainless steel sheet (12.84mm diameter). Two sheets of porous polypropylene membrane (Celgard 2500) were used as a separator. The electrolyte used was 1M LiPF$_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethylcarbonate (DMC) in a 1:1:1 volume ratio.

Swagelok cell was then assembled in an argon filled dry box (<0.1ppm H$_2$O, 4.6 ppm O$_2$) at room temperature. This cell was discharged until 2.5 and charged up to 4.6 by battery cycler (Bio-Logic SAS, VMP3). Cell first cycled twice at current density of 11.67mAg$^{-1}$, and then the rate capability was measured by varying the charging and discharge density at 23.33, 46.67, 116.67, 233.34mAg$^{-1}$, and kept cycling at 46.67mAg$^{-1}$ for 50 cycles. All the measurements were performed at ambient temperature (25±2°C).
4 Results and discussion

4.1 Leaching process

4.1.1 Acid leaching

The residual electrode particles are cathode materials LiCoO$_2$, LiMn$_2$O$_4$, LiNiO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiFePO$_4$, and graphite and conductive carbon. The leaching of cathode materials from spent lithium ion batteries has been investigated using H$_2$SO$_4$, HCl and HNO$_3$, as leaching agents. Table 4 summaries some operational conditions for the leaching by different acidic media. The leaching reaction of LiCoO$_2$ of lithium ion batteries in HCl is as follows:

$$2\text{LiCoO}_2 + 8\text{HCl} \rightarrow \text{CoCl}_2 + \text{Cl}_2 + 2\text{LiCl} + 4\text{H}_2\text{O}$$

Although HCl has better leaching rate [7], this leaching process will result in serious environmental problem if special equipment for treating with chlorine (Cl$_2$) is not installed, while installing these equipment will result in much more recycling cost. In this research, the leaching of cathode materials is studied by the use of H$_2$SO$_4$ to substitute HCl with the addition hydrogen peroxide as a reducing agent.
Table 4: Summary of some operational conditions for the leaching of spent lithium-ion secondary rechargeable batteries by different acidic media [32].

<table>
<thead>
<tr>
<th>References</th>
<th>Sample</th>
<th>Leaching agent</th>
<th>Temperature (°C)</th>
<th>Time</th>
<th>Reduction agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhang et al. (1998)</td>
<td>LiCoO₂</td>
<td>4M HCl</td>
<td>80</td>
<td>1h</td>
<td></td>
</tr>
<tr>
<td>Castillo et al. (2002)</td>
<td>Li Mn Ni</td>
<td>2 M HNO₃</td>
<td>80</td>
<td>2h</td>
<td></td>
</tr>
<tr>
<td>Lee and Rhee (2003)</td>
<td>LiCoO₂</td>
<td>1 M HNO₃</td>
<td>75</td>
<td>1h</td>
<td>1.7 vol.% H₂O₂</td>
</tr>
<tr>
<td>Bok et al. (2004)</td>
<td>LiCoO₂</td>
<td>35% HNO₃ +18% H₂SO₄ +5% HCl</td>
<td>room temp.</td>
<td>24h</td>
<td></td>
</tr>
<tr>
<td>Shin et al. (2005)</td>
<td>LiCoO₂</td>
<td>H₂SO₄</td>
<td>75</td>
<td>10min</td>
<td>15 vol.% H₂O₂</td>
</tr>
<tr>
<td>Nan et al. (2005)</td>
<td>LiCoO₂</td>
<td>3 M H₂SO₄</td>
<td>70</td>
<td>4h</td>
<td>H₂O₂</td>
</tr>
<tr>
<td>Aktas et al. (2006)</td>
<td>LiCoO₂</td>
<td>4 M H₂SO₄</td>
<td>80</td>
<td>4h</td>
<td></td>
</tr>
<tr>
<td>Nan et al. (2006)</td>
<td>LiCoO₂</td>
<td>3 M H₂SO₄</td>
<td>70</td>
<td>5h</td>
<td>3wt.% H₂O₂</td>
</tr>
</tbody>
</table>

4.1.2 Effect of hydrogen peroxide on leaching and recovery

Acid leaching of lithium cobalt oxide is difficult, as the chemical bond between cobalt and oxygen is extremely strong. The dissolution of cobalt oxides in acid solution was researched by Vu et al. [33]. In these experiments, the concentration of sulfuric acid was 2 mol/L and pulp density was 50g/L, the leaching temperature was 75 °C with an agitation of 300 rpm. A concentration of 15 vol.% was enough for the full leaching of both metal components. Figure 21 (a) and (b) illustrated the effect of hydrogen peroxide on leaching efficiency. The leaching rate was fast in the initial stage regardless of the hydrogen peroxide concentration, the increase of the concentration of hydrogen peroxide will lead to higher efficiency in a shorter time. The hydrogen peroxide helps the dissolution of cobalt, manganese and nickel because when hydrogen peroxide is added, it converts Co(III) to Co(II) to help the dissolution [34]. The same effect for LiMn₂O₄, LiNiO₂, and LiNi₁/₃Mn₁/₃Co₁/₃O₂. The dissolution of lithium is promoted because the metals (Li and Ni, Mn, or Co) are contained in the same oxide compound.

In this research, the mixed cathode powder includes LiCoO₂, LiMn₂O₄, LiFePO₄ and LiNi₁/₃Mn₁/₃Co₁/₃O₂ and Ni(OH)₂ were put into acid with hydro peroxide. The reactions are as following:

\[
2\text{LiCoO}_2 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{CoSO}_4 + \text{O}_2 + 4\text{H}_2\text{O}
\]
\[2\text{LiMn}_2\text{O}_4 + 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Li}_2\text{SO}_4 + 4\text{MnSO}_4 + 2\text{O}_2 + 6\text{H}_2\text{O}\]
\[2\text{LiNiO}_2 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{NiSO}_4 + \text{O}_2 + 4\text{H}_2\text{O}\]
\[6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2 + 9\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow 2\text{MnSO}_4 + 2\text{NiSO}_4 + 2\text{CoSO}_4 + 3\text{Li}_2\text{SO}_4 + 2\text{O}_2 + 10\text{H}_2\text{O}\]

The hydrogen peroxide transfer all Co(III), Mn(III), Ni(III) to Co(II), Mn(II), Ni(II), also all Fe(II) to Fe(III). These can be verified by experiments, which will be demonstrated in 4.3. This is a very important step to separate iron from solution in next step.

All Mn, Ni, Co, Li are dissolved in solution; however, most of LiFePO_4 cannot be dissolved in the solution with sulfuric acid and hydrogen peroxide. This might because of the high bond energy between Fe and O. Also, carbon does not dissolve in acid solution, and instead it floats on the solution. Thus, carbon can be separated and by filtration LiFePO_4 is separated. In order to have high purity of LiFePO_4, the mixture can be burn to remove carbon.
4.2 Separating iron
Controlling pH can completely separate iron ions from solution. For M(OH)$_n$, according to solubility equilibrium and the definition of pH,

\[
K_{sp} = [M^{n+}] [OH^-]^n
\]

\[
K_w = [H^+][OH^-] = 10^{-14}
\]

\[
pH = -\log_{10}(a_{H^+})
\]
According to the reactions above, the maximum ion concentration of metals $C_{\text{max}}(M^{n+})$ for Fe, Ni, Co, Mn are 1M (only very small amount of LiFePO$_4$ dissolved in the solution, treat 1M as the highest concentration), 2.667M, 2.667M, 3.2 M respectively when the concentration of sulfuric acid is 4 M. Regard $C_{\text{min}}(M^{n+})=10^{-5}$ as the concentration of all $M^{n+}$ fully precipitated, $C_{\text{max}}(M^{n+})$ as the concentration of $M^{n+}$ begins to precipitate. Table 5 shows pH number of metal ions began to precipitate and fully precipitate.

Table 5: The pH number of start and end of precipitating for various metals

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K_{sp}$</th>
<th>$C_{\text{max}}$</th>
<th>$C_{\text{min}}$</th>
<th>pH$_{\text{start}}$</th>
<th>pH$_{\text{end}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_3$</td>
<td>2.79E-39</td>
<td>1.000</td>
<td>1.00E-05</td>
<td>1.149</td>
<td>2.815</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>5.48E-16</td>
<td>2.667</td>
<td>1.00E-05</td>
<td>5.156</td>
<td>8.869</td>
</tr>
<tr>
<td>Co(OH)$_2$</td>
<td>5.92E-15</td>
<td>2.667</td>
<td>1.00E-05</td>
<td>6.673</td>
<td>9.386</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>2.00E-13</td>
<td>3.200</td>
<td>1.00E-05</td>
<td>7.398</td>
<td>10.151</td>
</tr>
<tr>
<td>*Fe(OH)$_2$</td>
<td>4.87E-17</td>
<td>1.000</td>
<td>1.00E-05</td>
<td>5.844</td>
<td>8.344</td>
</tr>
</tbody>
</table>


Figure 22: pH number of start and end of precipitating for different ions.

From Figure 22, if all Fe ions are exist in the state of +3, while all other metal ions- Mn, Ni, Co are in divalent state, then controlling the pH of leach liquor between 2.815 and 5.156 (this number various with the concentration of Co in the solution) can separate all iron ions from solution. As mentioned above, H$_2$O$_2$ can help transfer all Fe(II) to Fe(III), and other metals to divalent state. Experiments are conducted to verify the effect and test the separating result.

Firstly, separating Fe and Co was done: 0.2262g LiFePO$_4$ and 0.2343g LiCoO$_2$ were mixed in 20mL 4M H$_2$SO$_4$ and 4mL H$_2$O$_2$ at about 74°C for 2h. Undissolved LiFePO$_4$
was filtrated from solution and NaOH was added into the solution until pH=3.5. The residue separated from the solution by filtration was test by EDS. EDS result (Figure 24) showed that there was no Co in the residue. The concentration of Fe in the solution, after filtrating, was tested by atomic absorption spectroscopy (AAS). The concentration of Fe was too low to be tested by AAS, and no iron was showed in the solution. AAS result demonstrated all Fe were completely separated from this solution.

Figure 23: EDS analysis for precipitation filtrated from acid solution for mixed LiFePO₄ and LiCoO₂.
Secondly, the same experiment to separate Fe and Mn: 0.2355g LiFePO$_4$ and 0.2635g LiMn$_2$O$_4$ were treated as mentioned above, the controlling pH number was 3.0. The EDS result (Figure 24) proved that no Mn existed in the residue. And 200ppb of iron was determined by AAS in the solution. This means that all Fe existed in state of +3, and others were in state of +2, and separating Fe from other metals in this method was good.

Figure 24: EDS analysis for precipitation filtrated from acid solution for mixed LiFePO$_4$ and LiMn$_2$O$_4$. 
Co and Ni have similar physical and chemical properties. So it has the same results on separating Fe and Ni with separating Fe and Co.

Thirdly, separate Fe and Ni, Co from LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2: 0.2350g LiFePO_4 and 0.2759g LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 were put into acid solution. LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 can all dissolve in the solution of sulfuric acid and hydrogen peroxide, Mn, Co and Ni were existed as divalent metal ions in solution. So we can use this method to separate iron ions from other metal ions in the solution. AAS test showed that by controlling pH=3.22, the Fe ions left in solution was 0.162ppm. EDS results (Figure 25) showed that the precipitate filtrated from solution did not contain Co, Ni and Mn.

Figure 25: EDS analysis for precipitation filtrated from acid solution for mixed LiFePO_4 and LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2.
Finally, 0.083g LiFePO$_4$, 0.0996gLiCoO$_2$, 0.1074g LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, 0.1021g LiMn$_2$O$_4$, were mixed in acid solution with hydro peroxide. Controlled pH=3.43, the Fe ions left in solution tested by AAS was 0.041ppm. EDS results (Figure 26) showed that the precipitate filtrated from solution did not contain Co, Ni and Mn.

![Figure 26: EDS analysis for precipitation filtrated from acid solution for mixed LiFePO$_4$, LiCoO$_2$, LiMn$_2$O$_4$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.](image)

4.3 Co-precipitate of cobalt, manganese, and nickel

After separating iron ions, other metals-cobalt, manganese and nickel has no lose and coexist in the solution. In this project, the final object is to synthesize
LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. Then proper amount of NiSO$_4$, MnSO$_4$, CoSO$_4$ is added to make the molar ratio of Ni, Mn, and Co 1:1:1. One of the innovations in this process is that Co, Mn, Ni are recycled and re-introduced into the battery production chain without separation, and they were directly utilized to synthesize the cathode material LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.

NaOH was added to co-precipitate Ni, Mn and Co as Ni(OH)$_2$, Mn(OH)$_2$, Co(OH)$_2$. The precipitate was utilized to synthesize LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. The concentration of metal ions left in the solution determines the purity of lithium precipitated. Figure 23 shows the relationship between the concentration of metals in solution and pH number. The concentration decreases as pH increases. Almost 100% metal ions can co-precipitate when the pH value equals to 11 or above. After filtration, resin the precipitate with much distilled water by air pump filtration to remove impurities and liquor. Materials were distributed evenly and the particles were small. The coprecipitate would be used as the starting materials to synthesize LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.

![Figure 27: Concentration of metals ions left in solution at various pH numbers.](image-url)
4.4 Lithium recovery

After co-precipitating, the leaching liquor was treated with sodium carbonate at about 40°C to precipitate Li as lithium carbonate, since the solubility of lithium carbonate in an aqueous solution is inversely proportional to its temperature. The proper amount of sodium carbonate is directly added to the leach liquor. The lithium carbonate is recovered after filtration and washed by hot water to remove the residual liquor.

The results showed that about 80% lithium was recovered as precipitate, because aqueous solution dissolves some Li$_2$CO$_3$. This result is similar to others’ recovery ratio [35]. In theory, according to reaction equations, assuming there is 1 g LiCoO$_2$,

$$2\text{LiCoO}_2\sim3\text{H}_2\text{SO}_4\sim\text{Li}_2\text{CO}_3$$

$$1/98 \quad 1.5/98 \quad 0.5/98$$

Thus, 3.8265 mL ($1.5x/98/4*1000$) 4M/L H$_2$SO$_4$ is needed for reaction fully. So just suppose the solution contains 10 mL H$_2$O (compare to the volume of H$_2$SO$_4$, more than 2.33 times of NaOH are needed to control the pH number to 11). From table 5, at 40°C, there is $(0.5/98*1.17%*10)$ mol Li$_2$CO$_3$ dissolved in the solution while the total amount of Li ions in solution is 1/98. The recycling efficiency of Li ions is 88.3%. The hot water used to resin the recycled Li$_2$CO$_3$ will also reduce the efficiency.

Lithium carbonate recovered from spent lithium ion batteries can be used as precursors to produce LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. Figure 29 shows the XRD patterns of recycled Li$_2$CO$_3$ and standard product. The lattice parameters are $a=8.34802$ Å, $b=4.96058$ Å, $c=6.1819$ Å. The recycled Li$_2$CO$_3$ has high purity.
Table 6: Variation of solubility of different substances in water with temperature, under 1 atm pressure, units of solubility in g/100g H₂O.

<table>
<thead>
<tr>
<th>Formula</th>
<th>0°C</th>
<th>10°C</th>
<th>20°C</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>70°C</th>
<th>80°C</th>
<th>90°C</th>
<th>100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>11.9</td>
<td>12.1</td>
<td>12.3</td>
<td>\</td>
<td>12.7</td>
<td>\</td>
<td>13.2</td>
<td>14.6</td>
<td>16.6</td>
<td>17.8</td>
<td>19.1</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>7</td>
<td>12.5</td>
<td>21.5</td>
<td>39.7</td>
<td>49</td>
<td>\</td>
<td>46</td>
<td>\</td>
<td>43.9</td>
<td>43.9</td>
<td>\</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>1.54</td>
<td>1.43</td>
<td>1.33</td>
<td>1.26</td>
<td>1.17</td>
<td>\</td>
<td>1.01</td>
<td>\</td>
<td>0.85</td>
<td>\</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Data from NIST Solubility Database, distributed by the Measurement Services Division of the National Institute of Standards and Technology (NIST)

Figure 28: Solubility of Na₂CO₃ and Li₂CO₃ at different temperature.
4.5 Synthesis of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode material

Comparing to LiCoO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ combines lower cost as well as greater safety and performance. When it was charged to 4.6 V and then discharged to 2.5 V, the specific capacity can reach 200mAh$^{-1}$ [38], which was higher than LiCoO$_2$ without sacrificing circle life. It also had much less heat flow and higher onset temperature than LiCoO$_2$.

Homogeneous precursors can not only accelerate the formation of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, but also significantly improve the electrochemical performances [36]. So during the recycling process, precipitate including Ni(OH)$_2$, Mn(OH)$_2$, Co(OH)$_2$ while stirring can help the starting materials distributed uniformly. Precursors were grinded by mortar and pestle and ball-milled for 3 days to make them mixed well and particles small.

Figure 30 shows the XRD patterns of synthesized LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and standard product from Umicore. The lattice parameters of sample were calculated form the d-value of 10 strong diffraction peaks. The All peaks of sample can be indexed as α-NaFeO$_2$ structures with a space group of R 3 m. Distinct splitting of (006)/(012) and (018)/(110)
peaks indicates that the sample possesses a well-developed layered-structure [37]. No other impurity peaks were present in these patterns which means that no impurity phase appeared. The recycled materials were pure enough to produce high purity products LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2.

Figure 30: XRD patterns of LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 (a=2.8553 Å; c=14.1312 Å)
Figure 31: SEM images of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ at different magnification sintered at 900°C for 15h in air.

From the SEM images of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (Figure 31), homogenous spherical particles are well distributed. The particle size ranges from 100-200 nm. No agglomeration appears in the sample. Uniform particle size and homogenous particles are critical factors for synthesis of high quality materials. Smaller size allows shorter diffusion length, which can provide higher rate performance.

4.6 Electrochemical performance of synthesized material

The first two cycles of the cell was charged and discharged at 0.0729C (11.67mA/g, C=160mAh/g), the discharge capacity for the first two cycles are 173.96 mAh/g and 172.92mAh/g, the coulombic efficiency (discharge capacity over charge capacity) of first two cycles are 81.07% and 94.86%. Comparing with the commercial product, the performance is good.
Table 6: Initial charge and discharge capacities at different charge and discharge rates*

<table>
<thead>
<tr>
<th>Discharge Rate</th>
<th>Current density</th>
<th>Charge capacity (mA.h)</th>
<th>Discharge capacity (mA.h)</th>
<th>Coulombic Efficiency</th>
<th>Discharge specific Capacity (mA.h/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0729C</td>
<td>0.011 mA/cm²</td>
<td>0.206</td>
<td>0.167</td>
<td>81.07%</td>
<td>173.96</td>
</tr>
<tr>
<td></td>
<td>11.67 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0729C</td>
<td>0.011 mA/cm²</td>
<td>0.175</td>
<td>0.166</td>
<td>94.86%</td>
<td>172.92</td>
</tr>
<tr>
<td></td>
<td>11.67 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.146C</td>
<td>0.022 mA/cm²</td>
<td>0.163</td>
<td>0.151</td>
<td>92.64%</td>
<td>157.29</td>
</tr>
<tr>
<td></td>
<td>23.34 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.292C</td>
<td>0.044 mA/cm²</td>
<td>0.142</td>
<td>0.129</td>
<td>90.85%</td>
<td>134.38</td>
</tr>
<tr>
<td></td>
<td>46.68 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.729C</td>
<td>0.11 mA/cm²</td>
<td>0.105</td>
<td>0.089</td>
<td>84.76%</td>
<td>92.71</td>
</tr>
<tr>
<td></td>
<td>116.7 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.458C</td>
<td>0.22 mA/cm²</td>
<td>0.067</td>
<td>0.054</td>
<td>80.60%</td>
<td>56.25</td>
</tr>
<tr>
<td></td>
<td>233.4 mA/g</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1. Standard product Li Ni₁/₃Mn₁/₃Co₁/₃O₂ by Lin Yi GeLon New Battery Materials Co., Ltd, the first discharge capacity is about 155-158 mAh/g (0.2C, 4.2-2.7V, button half open cell), first coulombic efficiency is 83-85%.

*2. Other commercial cathode material LiFePO₄ by Lin Yi GeLon New Battery Materials Co., the first discharge capacity is 135 mAh/g (0.2C).

Figure 32: Capabilities of the cell at different charge and discharge rate.
Figure 33: Rate-capability tests of synthesized LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. The cell was charged up to 4.6V and then discharged to 2.5V at (a) 11.67, (b) 23.33, (c) 46.67, (d) 116.67, (e) 233.34 mA/g.

As shown in Figures 32 and 33, the rate capability tests were carried out to examine the lithium-ion transfer in the solid state. The cell was charged until it was at 4.6V and discharged to 2.5V at different C rates. The discharge capacity decreases rapidly with increasing C rate. The rate performance was not great compared to the published results. From SEM images, particles are interconnected together, and are not separated well. Although the single particles are nearly nano scale, diffusion length of the tightly connected single particles was still high. Well grinded powders might have a better high performance. The low carbon content in the electrode, or a lack of skill in electrode preparation might also attribute to it. In addition, the material sintering has no preheat treatment.
Figure 34: The cycling performance of synthesized LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ from recycled materials.

Figure 34 shows specific capacity and coulombic efficiency (discharge capacity over charge capacity) as a function of cycle number for the LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cell cycled through voltage ranges 2.5-4.6V at 46.6mA/g and 25°C. The initial capacity is 130.20 mAh/g, and the reversible capacity after 50 cycles is 107.29mAh/g (82.40% of the first discharge capacity). The decrease of the capacity is probably due to the increase of the impedance of lithium foil. The coulombic efficiency is nearly 100% which demonstrates that the cell has good charge and discharge performance.

4.7 Commercial value in this recycling process

4.7.1 Cost & profit

Cathode materials, as the essential part of lithium ion batteries, determine performances of lithium ion batteries. Currently, LiCoO$_2$ are widely commercialized as a cathode material, because of its simple producing process, high specific capacity and long cycle life. But its relatively high cost, safety issues when abused and the relatively low specific
capacity had led to the research of other cathode materials, such as LiNi$_{1-x}$Mn$_x$Co$_{1-y}$O$_2$ (NMC), LiFePO$_4$ (LFP), LiMn$_2$O$_4$ (LMO), and LiNiO$_2$ (LNO). Table 7 compares these cathode materials.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Average potential difference(V)</th>
<th>Specific capacity (mA·h/g)</th>
<th>Specific energy (kW·h/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>3.7 V</td>
<td>140</td>
<td>0.518</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>4.0 V</td>
<td>100</td>
<td>0.400</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>3.5 V</td>
<td>180</td>
<td>0.630</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>3.3 V</td>
<td>150</td>
<td>0.495</td>
</tr>
<tr>
<td>LiNi$<em>{1/3}$Mn$</em>{1/3}$Co$_{1/3}$O$_2$</td>
<td>3.6 V</td>
<td>160</td>
<td>0.576</td>
</tr>
</tbody>
</table>

a) LiCoO$_2$ currently is most successful commercial cathode materials in lithium-ion batteries. Comparing with other materials, LiCoO$_2$ has better performance in reversibility, capacity, charging efficiency, and voltage stability. However, cobalt is very expensive given its limited resources, and has safety issue to the environment.

b) The performance of LiNiO$_2$ is quite similar to LiCoO$_2$, while its price is lower. But it should be synthesized at severe condition and slight changes will lead to produce nonstoichiometric lithium nickel oxide, which lithium and nickel random distribute, make electrochemical performance worse and decrease the energy density. In addition, it may cause fire or explosion when it is overcharged. Because the decomposition temperature of product after desertion of lithium is low, a lot of heat and oxygen releases during decomposing.

c) As iron is plentiful and cheap, LiFePO$_4$ has low cost. It also has very high thermal stability (better than LiCoO$_2$), and is friendly to our environment. This is most potential cathode materials. A problem for LiFePO$_4$ is that the conductivity is not high.

d) Lithium manganese oxide has the same advantages with LiFePO$_4$: low cost, plenty resource, environment-friendly. But at high temperature, electrolyte
will cause manganese dissolve, making the amount of cathode materials decrease.

e) Comparing to LiCoO₂, LiNi₁/₃Mn₁/₃Co₁/₃O₂ combines lower cost as well as greater safety and performance. When it was charged to 4.6 V and then discharged to 2.5 V, the specific capacity reached about 200mAhg⁻¹[38], which was higher than LiCoO₂ without sacrificing circle life. It also had much less heat flow and higher onset temperature than LiCoO₂.

According to the report Lithium-ion Battery Market: Cell & Components 2011 by Yano Research Institute, the market share forecast in 2012 of lithium ion batteries cathode materials are as follows:

Table 8: LIB Cathode Materials: World Market Size Transition by Material (2012/Forecast in Volume)

<table>
<thead>
<tr>
<th>LiNi₁/₃Mn₁/₃Co₁/₃O₂</th>
<th>LiCoO₂</th>
<th>LiNiO₂</th>
<th>LiMn₂O₄</th>
<th>LiFePO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.00%</td>
<td>37.20%</td>
<td>7.20%</td>
<td>21.40%</td>
<td>5.20%</td>
</tr>
</tbody>
</table>

Suppose 1000kg cathode materials from recycled batteries, according to market share, there are 290kg LiNi₁/₃Mn₁/₃Co₁/₃O₂, 372kg LiCoO₂, 72kg LiNiO₂, 214kg LiMn₂O₄, 52kg LiFePO₄.

According to reactions and calculation:

\[
\begin{align*}
2\text{LiCoO}_2 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow \text{Li}_2\text{SO}_4 + 2\text{CoSO}_4 + \text{O}_2 + 4\text{H}_2\text{O} \\
2\text{LiMn}_2\text{O}_4 + 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow \text{Li}_2\text{SO}_4 + 4\text{MnSO}_4 + 2\text{O}_2 + 6\text{H}_2\text{O} \\
2\text{LiNiO}_2 + 3\text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow \text{Li}_2\text{SO}_4 + 2\text{NiSO}_4 + \text{O}_2 + 4\text{H}_2\text{O} \\
6\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2 + 9\text{H}_2\text{SO}_4 + \text{H}_2\text{O} & \rightarrow 2\text{MnSO}_4 + 2\text{NiSO}_4 + 3\text{Li}_2\text{SO}_4 + 2\text{O}_2 + 10\text{H}_2\text{O}
\end{align*}
\]

The prices and cost of chemicals needed for recycling in this process (all following prices data are from a business website Alibaba):
Table 9: Price and cost of raw materials by one ton cathode materials from spent lithium ion batteries in this recycling process.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Price($/ton)</th>
<th>Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·H₂O</td>
<td>600</td>
<td>265</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>6,000</td>
<td>4,831</td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
<td>7,500</td>
<td>0</td>
</tr>
<tr>
<td>H₂O₂, 30%</td>
<td>500</td>
<td>62</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>300</td>
<td>222</td>
</tr>
<tr>
<td>NaOH</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>8,000</td>
<td>2,621</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>150</td>
<td>210</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>8,611</strong></td>
<td></td>
</tr>
</tbody>
</table>

The products producing in the recycling includes LiFePO₄, and LiNi₁/₃Mn₁/₃Co₁/₃O₂. The weight and value of products from one ton of cathode materials recycled are as follows:

Table 10: Prices and Value of products by one ton cathode materials from spent lithium ion batteries.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Price($/ton)</th>
<th>Weight(ton)</th>
<th>Value($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO₄</td>
<td>35,000</td>
<td>0.04733</td>
<td>1,656</td>
</tr>
<tr>
<td>LiNi₁/₃Mn₁/₃Co₁/₃O₂</td>
<td>40,000</td>
<td>1.3899</td>
<td>55,596</td>
</tr>
</tbody>
</table>

So producing products via this method from recycling one ton of cathode materials, the profit=55,596+1,656-8,611=48,642($/ton) (ignore labor cost, equipment cost).

Thus, recycling one ton of cathode materials, it can earn $ 48,642. This account does not include other recycled materials such as carbon, electrolyte, Al foil, Cu foil.

4.7.2 Save

The cost of using fresh materials instead of recycled materials to synthesize the same amount of LiNi₁/₃Mn₁/₃Co₁/₃O₂ from one ton of cathode materials by coprecipitation is calculated:
Table 11: Prices and cost of raw materials in a normal method.

<table>
<thead>
<tr>
<th></th>
<th>Price($/ton)</th>
<th>Cost($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSO₄·H₂O</td>
<td>600</td>
<td>487</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>6,000</td>
<td>7,575</td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
<td>8,000</td>
<td>10,801</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>8,000</td>
<td>4,259</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>23,121</strong></td>
<td></td>
</tr>
</tbody>
</table>

The cost = $23,121/1.3899 ton = 16635$/ton.

While using recycled materials, the cost is 8610.688$/1.3899 ton = 6,195$/ton.

The save = 16635$/ton - 6195$/ton = 10,440$/ton.

This means that to produce one ton of LiNi¹/₃Mn¹/₃Co¹/₃O₂, it only need $6195 by utilizing the recycled materials via this method. While in normal ways by using fresh materials, it costs $16,635. Producing product LiNi¹/₃Mn¹/₃Co¹/₃O₂ via recycling, it saves $10,440.

In addition, recycling of batteries obviously help save natural resources. Dewulf et.al. [36] studied resource savings of recycling rechargeable lithium ion batteries. It turns out that recycling result in natural resource savings by decreasing mineral ore dependency and reduced fossil resource and energy demand.

Recycling lithium ion batteries can not only save cost of production, but also save energy and reduce resource consumption.
5 Conclusions

Combining synthesis of NMC cathode materials, a novel recycling process dedicated all spent commercial lithium-ion batteries has been developed. Battery components including different cathode materials, such as LiCoO$_2$, LiMn$_2$O$_4$, LiNiO$_2$, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and LiFePO$_4$ are recovered as much as possible in the form of marketable materials or as directly utilized to synthesize. Analysis results show that almost 100% of Ni, Mn, Co are recovered, and experiment demonstrated that about 80% Li are recycled in the form of Li$_2$CO$_3$. The synthesized material has good quality and excellent electrochemical performance.

Commercial value in this process is calculated, which illustrated that recycling one ton of cathode materials from spent lithium ion batteries can obtain $48,642, and synthesis NMC by recycled materials in this way can save $10,440/ton without considering the saved energy and byproducts such as Al, Cu, electrolyte, carbon. Nevertheless there are still some improvements can be made to synthesize better performance NMC products. And lithium ion batteries industries are growing fast, new types of lithium ion batteries will be presented in market. However, this might not challenge this method, if some process step is adjusted to the new chemical systems. The future work might be done is to develop an assembly line which contains the mechanical crushing machine, electrolyte extraction and electrode dissolution, acid leaching, separation and sintering all together, to recycle large amount of spent lithium ion batteries.
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