Room Temperature Extraction of Co and Li from Ground Lithium-ion Secondary Battery Scrap*

by Jaeryeong LEE¹, Qiwu ZHANG² and Fumio SAITO³

Lithium-ion secondary battery scrap, which contains LiCoO₂, graphite and PVDF (poly vinyliden fluoride), was subjected to dry grinding using a planetary mill with and without quartz powder as a grinding aid, following its room temperature leaching using 1N HCl solution. The scrap material becomes amorphous state as grinding time and the quartz additive ratio increase. Accordingly, Co and Li in the scrap can be easily extracted from the ground product, and the former yield reaches about 90 mass% at 4-hour grinding with 50 wt% additive. Only about 2 mass% of F in PVDF in the scrap can be extracted under the same grinding condition.

KEY WORDS: Mechanochemistry, Room Temperature Extraction, Lithium-ion Secondary Battery, Grinding Aid

Table 1 Chemical composition of the scrap sample (mass%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>O</th>
<th>C</th>
<th>Li</th>
<th>PVDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%</td>
<td>52.6</td>
<td>28.6</td>
<td>10.7</td>
<td>6.2</td>
<td>1.9</td>
</tr>
</tbody>
</table>

1. Introduction

Lithium-ion secondary battery is known to have high power and rechargeable feature which enables us to use as energy sources for electric products such as personal computers and generators for vehicles. The battery consists of positive and negative electrodes with insulator. The positive substance is normally composed of LiCoO₂ powder with poly vinyliden fluoride (PVDF) as an adhesive reagent, and the negative one is composed of graphite.

In 1993, about 7 million unit / yr of the lithium-ion secondary battery have been manufactured (in Japan), and its amount will increase in the future. Accordingly, the enormous amount of the battery has run to waste. This induces another environmental problem, so that, proper technique for processing it with recovering valuable metals such as Co and Li from the scrap is needed. At this moment, there has been a process for recovering Co and Li from the scrap by its leaching at high temperature. However, it generates toxic gas such as HF although the high Co yield is attained. The authors have developed another process, which is a grinding aided leaching of the waste battery containing LiNi₁₋ₓCoₓO₂ with PVDF.

The main purpose of this paper is to provide information on grinding the scrap of lithium-ion secondary battery, following its room temperature leaching to extract Co and Li. This paper has included the data on F extracted in the leaching.

2. Experiments

2.1 Sample

The sample used in this study was the scrap of lithium-ion secondary battery, supplied from Dowa Mining Co. Ltd., Japan. This sample consists of LiCoO₂, graphite and PVDF. The chemical composition of the scrap is shown in Table 1.

2.2 Grinding

Grinding of the scrap sample was conducted with and without quartz powder as a grinding aid by a planetary ball mill (Fritsch, Pulverisette-7) at rotational speed of approximately 700 rpm under dry atmospheric condition. 4 g of the sample (the mixture of scrap and quartz powder) was put in a zirconia pot of 50 cm³ inner volume with 7 zirconia balls of 15 mm diameter. Weight percentage of quartz powder in the scrap sample was ranged from 0 to 50 wt%. The grinding time was varied from 0 to 240 min. The grinding was stopped every 15 minutes for 10 minutes to avoid excess temperature increase.

2.3 Leaching

0.5 g of the ground / unground scrap samples were dispersed in 50 ml of 1N HCl solution in a vial (100 ml), and the slurry was stirred mechanically at 300 rpm by a magnetic stirrer to extract the valuable metals. During the leaching, small amount of the slurry was taken out for characterization, and it was filtered to separate solid from liquid phases by using a filter paper (5C).

2.4 Characterization

The unground / ground scrap samples were characterized by X-ray diffraction (XRD, RAD-B system, Rigaku, Japan) using Cu-Kα radiation with a pyrolytic graphite monochromator to identify phases formed in the sample during grinding. The crystallite size was determined by the Scherrer's equation given by Eq.(1), based on the diffraction plane (104) in the XRD pattern.

\[
t = \frac{0.9 \lambda}{B \cos \theta_B} \quad \text{----------------------------------------------- (1)}
\]

Where, \( t \), \( B \), \( \theta_B \) and \( \lambda \) denote crystallite size, broadening of diffraction line measured at half of its maximum intensity, diffraction angle and wave length of X-ray (Cu-Kα : 1.54 Å).

Chemical analysis of Co and Li in the filtrate after the leaching was carried out by inductively coupled plasma-atomic..
emission spectroscopy (ICP-AES) (Optima 3300SYS, Perkin Elmer). Concentration of F⁻ in the filtrate was also determined by an ion-chromatography instrument (IC, LC-10ADvp series, SHIMADZU).

3. Results and Discussion

3.1 Grinding

Fig. 1 shows the crystallite size of LiCoO₂ as a function of grinding time, depending on quartz additive ratio. The crystallite size decreases rapidly in the early stage of grinding from about 560 Å to 330 Å within 60 min when the grinding aid is absent. Subsequently, the size decreases gradually as the grinding progresses and reaches about 260 Å at 120 min. However, further grinding does not reduce the size at all. Similar trend can be seen in the relation between the crystallite size and the grinding time for the case of the grinding with the grinding aid, however, the crystallite sizes are mostly lower than that in the case of the absent of the grinding aid. In addition, it seems that the crystallite size tends to decrease with an increase in the additive ratio, although the correlation between the additive ratio of the grinding aid and the crystallite size is still indistinct.

3.2 Leaching

Fig. 2 shows concentration/yield of Co and Li extracted from the samples unground and ground without the grinding aid (quartz) as a function of leaching time, depending on the grinding time. The concentration/yield increases rapidly within 60 min, subsequently it levels off, and keeps almost constant at certain values over 120 min in leaching time. This implies that 120 min in the leaching time is enough to extract Co and Li from the unground/ground samples. Hereinafter, the leaching time for the unground and ground scrap was fixed at 120 min.

Fig. 3 shows the yields of Co and Li extracted from the samples by 1N HCl solution as a function of grinding time. The Co−yield increases from about 35 mass% to about 90 mass% within 240 min in grinding time when the grinding aid is added by 50 wt%. The yield is improved as the additive ratio increases. On the other hand, the yield of Li reaches about 70 mass% for the unground sample and increases further as the grinding progresses. For the sample ground with the grinding aid, the Li−yield is measured at high values, depending on the additive ratio. However, there is no significant difference in the data with and without grinding aid and its ratio.

Fig. 4 shows the Co−yield extracted from the samples ground for different periods of time as a function of additive ratio of grinding aid. The yield tends to increase with an increase in additive ratio as well as grinding time, and reach about 90 mass% at 240 min in grinding time. In the present work, only about 1.9 mass% of F⁻ in the PVDF existed in the scrap sample was extracted in the leaching of the sample ground for 240 min with 50 wt% additive ratio. This implies
that the PVDF in the scrap sample is seldom dissociated at all under the present grinding condition. According to the previous work done by the authors\(^6\), almost 100 mass% in the Co–yield can be achieved in the leaching of the scrap sample with LiNi\(_{1-x}\)Co\(_x\)O\(_2\). It is somewhat difficult to compare the present data with the previous ones because of the different samples, grinding aids and its ratio. In the present work, about 90 mass% in the Co–yield can be attained, and it seems to be comparable to the previous datum, despite quartz powder is used as a grinding aid and its ratio is lower than 80 mass%. This means that addition of quartz powder to the scrap up to 50 wt% enables us to disorder the structure of the LiCoO\(_2\) in the scrap selectively, without rupturing the bond of PVDF. In addition, the grinding aid plays a significant role to improve the Co–yield in the leaching of the scrap.

Fig. 5 shows the relationship between the crystallite size of LiCoO\(_2\) in the scrap sample shown in Fig. 1 and the Co yield. The Co yield is inversely proportional to the crystallite size regardless of the additive ratio, and the relation seems to be expressed by a quadratic equation. Therefore, the crystallite size of LiCoO\(_2\) calculated by the Scherrer’s equation may be a monitor for estimating the Co–yield in the grinding aided leaching of the scrap sample, irrespective of the additive ratio and grinding time.

4. Conclusion

Room temperature leaching of the lithium-ion secondary battery scrap, which contains LiCoO\(_2\) as a positive substance was conducted using 1N HCl solution after its dry grinding. Quartz powder was added to the scrap sample at different amounts as a grinding aid. The experimental result is summarized as follows.

1) The crystallite size of LiCoO\(_2\) in the scrap tends to decrease with an increase in grinding time as well as the additive ratio of the grinding aid.

2) About 90 mass% of cobalt and lithium can be extracted from the scrap ground for 240 min under the presence of 50 wt% additive ratio by its room temperature leaching. The quartz powder plays a significant role to disorder the structure of LiCoO\(_2\) in the scrap, leading to the improvement of Co yield.

3) Co–yield is inversely proportional to the crystallite size of LiCoO\(_2\). The crystallite size would be an indicator for estimating the yield extracted from the scrap irrespective of grinding time and additive ratio.

4) PVDF in the scrap does not dissociate at all under the present grinding and leaching conditions.

References

粉砕したリチウムイオン二次電池スクラップからのCoとLiの室温下抽出

李载宰¹ 張其武² 齊藤文良³

LiCoO₂、黒鉛、ポリフッ化ビニリデン(PVDF)で構成されるリチウムイオン二次電池のスクラップに粉砕助剤として石英粉末を添加し、遊星ミルにより乾式粉砕した後、1規格の塩酸により室温下でCo、Liの抽出を試みた。粉砕時間が長いほど、また、粉砕助剤添加量が多いほど、スクラップのLiCoO₂結晶の無定形化が進行する。これより、粉砕物からCoとLiが抽出されやすくなり、石英粉末50wt%添加で4時間粉砕した場合、90wt%以上のCo、Liが抽出できた。しかし、PVDF中のフッ素は、同一条件下でも、わずかに2%程度しか抽出されなかった。

１．東北大学大学院生 工学研究科博士課程
２．正会員 工博 東北大学助手 素材工学研究所
３．正会員 工博 東北大学教授 素材工学研究所

キーワード：メカノケミストリー、室温下抽出、リチウムイオン二次電池、
粉砕助剤、抽出