Production of Chemical Manganese Dioxide from Lithium Ion Battery Ternary Cathodic Material by Selective Oxidative Precipitation of Manganese

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We have conducted studies to produce chemical manganese dioxides (CMDs) from ternary cathodic materials by oxidative precipitation. In this study, a cathodic material was concentrated by pretreatment and leached with sulfuric acid to recover 1 L of a leachate containing 22.0 g/dm$^3$ of Ni, 24.2 g/dm$^3$ of Mn, 9.5 g/dm$^3$ of Li and 8 mg/dm$^3$ of Al as valuable metals. For selective oxidative precipitation of Mn (II), the leachate was reacted with 1 equivalent of Na$_2$S$_2$O$_8$ based on the Mn concentration with stirring at 500 rpm at a temperature of 363 K for 18000 s. As a result of the reaction, it was confirmed that the majority of Mn was precipitated from the solution. XRD, PSA, TG–DTA, LECO and ICP analyses were performed to characterize the precipitate. The analytical results revealed the production of a chemical manganese dioxide (CMD) having a chemical composition of 84.60% MnO, 1.40% CoO$_3$, 0.11% Li$_2$O, 0.25% NiO, 0.02% Al$_2$O$_3$, 0.06% S and 0.52% Na$_2$O, an average particle diameter of 10.7 µm, a crystal form of γ-MnO$_2$, and a purity of at least 98%. [doi:10.2320/matertrans.M2012379]

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1. Introduction

Manganese dioxide features high capacity and low toxicity and in particular, possesses good electrochemical capabilities. Due to these advantages, manganese dioxide has received considerable attention as a cathodic material for primary and secondary batteries.1–3) Synthetic manganese dioxides are used in a variety of production fields. From a commercial standpoint, the most important feature of manganese dioxide is that it is electrochemically active. Based on this feature, manganese dioxide is widely used as a cathodic material for dry batteries. Other commercial applications in electronic industries where high-purity manganese dioxide is required are ferrites and thermistors. Particularly, the use of manganese dioxide as an oxidative catalyst for the removal and decomposition of air pollutants, for example, the removal of volatile organic compounds and the decomposition of ozone, has been growing steadily.4–6)

Chemical manganese dioxides (CMDs) and electrolytic manganese dioxides (EMDs) as synthetic manganese dioxides can be produced from solutions or naturally occurring raw ores containing manganese or salts thereof by chemical processes and electrochemical methods, respectively.7–9) For example, a chemical manganese dioxide can be produced by heat treatment of MnCO$_3$ or oxidative precipitation from a sulfuric acid solution by using NaClO$_3$ (Sedema process).10)

Recently, there has been a continually increasing demand for lithium ion batteries. The application range of lithium ion batteries is expanded into power sources from hybrid electric vehicles (HEVs) and electric vehicles (EVs) to energy sources for electronic devices. It is anticipated that lithium ion batteries will be applied to robots, energy storage and aerospace industries in the near future. Thus, cobalt, lithium, nickel and manganese as major constituent components of lithium ion batteries will be consumed in enormous amounts, resulting in an exponential increase in the number of spent lithium ion batteries. Separation/recovery of rare metals, such as cobalt, manganese and lithium, from spent lithium ion batteries, reuse of the rare metals and recycling of such rare metals are of great importance in that, through such recycling processes, core materials of batteries, most of which are currently imported, can be stably supplied from the domestic market.11–14)

Previous research has suggested solvent extraction processes for recovery of cobalt from lithium ion batteries. With the recent development and commercialization of new Co–Mn–Ni-based lithium ion battery cathodic materials as replacements for very expensive Co-based cathodic materials, there is a growing tendency to use a larger amount of Mn in cathodic materials. In view of this tendency, the separation of Mn is a prerequisite for the recovery and separation of valuable metals.

The objective of this study was to selectively separate Mn, Co and Ni from Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$, a lithium ion battery ternary cathodic material that is currently used in mobile phones and electric vehicles, by sulfuric acid leaching, and to selectively precipitate Mn from the sulfuric acid reductive leachate by using Na$_2$S$_2$O$_8$ as an oxidant.

2. Materials and Methods

2.1 Leaching

Mn was selectively precipitated from a solution containing Li, Co, Mn, Ni, etc., from which Al had already been removed from a scrap ternary cathodic material by physical treatment and pH adjustment, using Na$_2$S$_2$O$_8$ as an oxidant. Specifically, a leachate (500 ml) of a ternary cathodic material was reacted with 0.1 M Na$_2$S$_2$O$_8$ as an oxidant at 500 rpm while varying the equivalents of the oxidant (1, 1.1 and 1.2) to determine the precipitation behaviors of Mn and the coprecipitation behaviors of Co, Ni and Li at different
reaction temperatures of 343, 353, 363 and 368 K. A reaction system for selective oxidative precipitation of Mn from the ternary cathodic material leachate is illustrated in Fig. 1.

3. Results and Discussion

3.1 Leaching process using 2 M sulfuric acid solution

Leaching experiments were conducted on a cathodic material concentrated from a ternary cathodic material by physical treatment. The cathodic material was leached under the following conditions: 2 M H₂SO₄, 5 vol% H₂O₂, 333 K, S/L ratio of 50 g/500 ml, 200 rpm, 7200 s. Table 1 shows the concentrations of valuable metals after leaching and with 2 M sulfuric acid.

The concentrations of Co, Mn, Ni and Li as the valuable metals in the leachate after leaching were 22.0, 21.6, 24.2 and 9.5 g/dm³, respectively.

3.2 Predominance diagrams for manganese species: discussion of Eh vs. pH

pH-Eh diagram was drawn with HSC program of 5.11 version under condition 1 atm, 298 K, and concentration of 0.37 M Co, 0.39 M Mn, 0.41 M Ni, 0.14 M Li.

Figure 2 shows pH-Eh diagrams of the Mn–Co–Li–Ni–S–H₂O system. This graph reveals that Mn (II) can be oxidized to Mn (IV) as a precipitate while maintaining the Eh at 1–1.5 V in the pH range of 0–6. From the behaviors of Co, Ni and Li on the Eh-pH diagrams, it is determined that Mn can be precipitated in the form of MnO₂ at a pH not higher than 2 and an Eh not lower than 1.5 V. Co₃O₄ is the dominant Co species in this zone. Thus, a discussion on the precipitation of Mn and Co is needed on a thermodynamic basis.

The following are precipitation reactions of Mn (II), Co (II), Ni (II) and Li (I) by the use of Na₂S₂O₈ as an oxidant used in this study:

\[
\begin{align*}
\text{MnSO}_4 + \text{Na}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} &\rightarrow \text{Na}_2\text{SO}_4 + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 \\
\text{3CoSO}_4 + \text{Na}_2\text{S}_2\text{O}_8 + 4\text{H}_2\text{O} &\rightarrow \text{Na}_2\text{SO}_4 + \text{Co}_3\text{O}_4 + 4\text{H}_2\text{SO}_4 \\
\text{2NiSO}_4 + \text{Na}_2\text{S}_2\text{O}_8 + 4\text{H}_2\text{O} &\rightarrow \text{Na}_2\text{SO}_4 + 2\text{NiOOH} + 3\text{H}_2\text{SO}_4 \\
\text{Li}_2\text{SO}_4 + 5\text{Na}_2\text{S}_2\text{O}_8 + 6\text{H}_2\text{O} &\rightarrow 5\text{Na}_2\text{SO}_4 + 2\text{LiO}_3 + 6\text{H}_2\text{SO}_4 \\
2\text{MnSO}_4 + \text{Na}_2\text{S}_2\text{O}_8 + 4\text{H}_2\text{O} &\rightarrow \text{Na}_2\text{SO}_4 + 2\text{MnOOH} + 3\text{H}_2\text{SO}_4 \\
3\text{CoSO}_4(a) + \text{NaClO} + 3\text{H}_2\text{O} &\rightarrow \text{Co}_3\text{O}_4 + \text{NaCl} + 3\text{H}_2\text{SO}_4 \\
\end{align*}
\]

To get standard free energy of change, above all reaction was calculated with HSC program of 5.11 version. ΔG values of the reactions as a function of reaction temperature are shown in Fig. 3. As can be seen from the graph of Fig. 3, all reactions except the reactions (1) and (2) had negative ΔG values. Therefore, it is concluded that the precipitation reactions of Co, Ni and Li will not take place, unlike Mn.

3.3 Precipitation of Mn using Na₂S₂O₈ as oxidant

3.3.1 Precipitation behaviors of Mn and coprecipitation behaviors of Co, Ni and Li depending on reaction time

After the oxidant was used in an amount of 1 equivalent relative to the Mn (II) concentration in the leachate, the precipitation behaviors of Mn was observed with stirring at a rate of 500 rpm at 363 K. Figure 4 shows that as the reaction time increased, the precipitation efficiency of Mn increased.

Table 1 Concentrations of valuable metals (mg/dm³) in the leachate after leaching with 2 M sulfuric acid.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ni</th>
<th>Al</th>
<th>Li</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.34</td>
<td>5.34</td>
<td>5.34</td>
<td>5.34</td>
<td>5.34</td>
</tr>
<tr>
<td>Conc. (mg/dm³)</td>
<td>24,200</td>
<td>8.1</td>
<td>9,470</td>
<td>22,000</td>
<td>21,600</td>
</tr>
</tbody>
</table>

Fig. 1 A reaction system for selective oxidative precipitation of Mn from a leachate of a ternary cathodic material.

Fig. 2 pH-Eh diagrams of Mn–Co–Li–Ni–S–H₂O system at 298 K.
and the precipitation efficiencies of Co, Ni and Li also increased to about 20%.

### 3.3.2 Precipitation behaviors of Mn and coprecipitation behaviors of Co, Ni and Li with varying reaction temperatures and equivalents of oxidant

The precipitation behaviors of Mn and coprecipitation behaviors of Co, Ni and Li were examined at different reaction temperatures of 343, 353, 363 and 368 K under the same conditions as in Section 3.3.1. Figure 5 shows the precipitation behaviors of Mn at different reaction temperatures.

As can be seen from Fig. 5, a steep increase in the precipitation efficiency of Mn was observed with increasing reaction temperature. 99.5% or more of Mn was precipitated at reaction temperatures of 363 and 368 K despite a slight difference in precipitation reaction rate. Variations in Eh and pH as a function of reaction time are shown in Fig. 6. Eh increased rapidly in the beginning of the reaction and was thereafter maintained at 1.4 V or higher. As the precipitation reaction proceeded after the addition of the oxidant, sulfuric acid was formed, as depicted in the reactions explained above. As a result, the pH decreased to 0.5.

The contents of valuable metals (%) in the precipitates formed at the different reaction temperatures were analyzed (condition: agitation speed of 500 rpm, Na2S2O8 1 equiv., 18000 s). The results are shown in Table 2. As is apparent from the results in Table 2, the precipitation efficiency of Mn increased rapidly with increasing reaction temperature. 99.7% or more of Mn was precipitated at 363 K or higher but Co, Ni and Li, which are target metals for separation, were not substantially precipitated, demonstrating selective precipitation of Mn. Exceptionally, the precipitation efficiency of Co increased from 0.5% up to 2.4% with increasing reaction temperature, suggesting the need for further treatment of co-precipitated Co after the precipitation reaction.

The precipitation behaviors of Mn and coprecipitation behaviors of Co, Ni and Li were examined with increasing equivalents of the oxidant (1, 1.1 and 1.2) at a temperature of
Fig. 7 Influence of the equivalents of the oxidant Na2S2O8 on the precipitation of Mn as a function of reaction time.

Table 3 Precipitation efficiencies of valuable metals (%) with varying equivalents of the oxidant. (condition agitation speed of 500 rpm, 363 K, 18000 s)

<table>
<thead>
<tr>
<th>Equivalents of oxidant</th>
<th>Ni</th>
<th>Li</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.2</td>
<td>0.005</td>
<td>1.4</td>
<td>93.5</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.002</td>
<td>1.8</td>
<td>99.4</td>
</tr>
<tr>
<td>1.1</td>
<td>0.2</td>
<td>0.06</td>
<td>2.9</td>
<td>99.9</td>
</tr>
<tr>
<td>1.2</td>
<td>0.3</td>
<td>0.02</td>
<td>3.9</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Table 4 Precipitation efficiencies (%) obtained from the calculated mass balances of the final solution and precipitate relative to 500 ml of the initial solution.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Li</th>
<th>Co</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation efficiency (%) based on final solution</td>
<td>20.8</td>
<td>23.4</td>
<td>20.3</td>
<td>100.0</td>
</tr>
<tr>
<td>Precipitation efficiency (%) based on precipitate</td>
<td>0.3</td>
<td>0.074</td>
<td>2.7</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Table 5 Removal efficiencies (%) of the impurities from the precipitate by acid washing.

<table>
<thead>
<tr>
<th></th>
<th>Co2O3</th>
<th>MnO</th>
<th>Li2O</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue before washing (%)</td>
<td>2.86</td>
<td>79.41</td>
<td>0.002</td>
<td>0.25</td>
</tr>
<tr>
<td>Residue after washing (%)</td>
<td>2.18</td>
<td>87.55</td>
<td>0.002</td>
<td>0.13</td>
</tr>
<tr>
<td>Final washing solution (mg/dm³)</td>
<td>341.2</td>
<td>714</td>
<td>5.74</td>
<td>70.72</td>
</tr>
<tr>
<td>Removal efficiency of impurities (%)</td>
<td>24.8</td>
<td>—</td>
<td>—</td>
<td>45.6</td>
</tr>
</tbody>
</table>

363 K. Figure 7 shows the precipitation behaviors of Mn and precipitation efficiencies of valuable metals like Co, Ni, Li, and Mn were in Table 3 at different equivalents of the oxidant under condition agitation speed of 500 rpm, 363 K, 18000 s.

As can be seen from Fig. 7, the precipitation efficiency of Mn increased with increasing equivalents of the oxidant. In addition, when the oxidant was used in an amount of 1 equivalent or more, the majority of Mn was precipitated 18000 s or more post reaction.

Based on the analytical results in Tables 2 and 3, it could be confirmed that only negligible amounts of Co, Li and Ni were precipitated simultaneously with Mn precipitation. However, the concentrations of the valuable metals in the solution were reduced by about 20% during oxidative precipitation of Mn. The reason for the concentration reduction of the valuable metals is that the cations present in the solution were adsorbed to the surface of the manganese dioxide having a negative surface potential. In order to selectively recover the manganese dioxide produced under optimal conditions (1 equivalent of Na2S2O8, 363 K, 500 rpm, 18000 s), the adsorbed Ni, Co and Li ions were separated by solid-liquid separation and water washing. Thereafter, an examination was made to determine how much Ni, Co and Li could be recovered.

As is apparent from the results in Table 4, the precipitation efficiencies of the valuable metals except Mn were from about 20 to about 23% based on the solution, and Ni and Li were not substantially precipitated and the precipitation efficiency of Co was about 2.7% based on the precipitate.

Since some of the valuable metals were adsorbed to the surface of the precipitate during precipitation reaction, washing was required to recover the same. Reuse of a solution containing the valuable metals after washing, for example, by adding the solution to the leachate, is considered important for the recovery of the valuable metals.

3.4 Removal of impurities from the precipitate

The precipitate was washed to remove Co, Ni and Li contained therein under the following conditions: 4 M H2SO4, 10 g/100 ml, 80°C, 500 rpm and 7200 s. The results are shown in Table 5.

As is evident from the results in Table 5, the removal efficiencies of Co and Ni were 24.8 and 45.6%, respectively. There was little change in the content of Li before and after acid washing, implying that none or a very small amount of Li was adsorbed to the surface of the precipitate. These results lead to the conclusion that the acid washing had difficulty in completely removing the impurities but was effective in recovering the precipitate in a purity of at least 98%.

3.5 Results of XRD analysis on the precipitate

XRD analysis was used to determine the chemical crystal form of the precipitate, from which the impurities had been washed off. The results are shown in Fig. 8. As can be seen from Fig. 8, the chemical crystal form of the precipitate was found to be γ-MnO2.

Thermogravimetric analysis was performed under U.H.P. (ultra high purity) N2 gas atmosphere to examine the weight loss behaviors of the precipitate during heat treatment. As can be seen from Fig. 9, weight losses were observed at temperatures of 775.08, 863.02 and 1053 K.

XRD analysis was performed to observe phase changes resulting from the weight losses. For XRD analysis, samples of the precipitate were heat-treated at 523, 773, 893 and 1053 K. As can be seen from Fig. 10, the Mn precipitate samples, heat-treated at temperatures of 773 K or below, were found to have a crystal form of γ-MnO2 and the Mn precipitate samples heat-treated at temperatures higher than 773 K were found to have a crystal form of Mn3O4. As is evident from the results in Table 6, the Mn content of the
original sample was 84.06%, indicating that the composition of the original sample was MnO₂. Also, concentration of S analyzed by LECO (Model: CS230-Carbon/Sulfur) in the original sample was 0.06%.

The Mn content increased with increasing heat treatment temperature. Co as a major impurity was present in an amount of 1.4 – 1.5%. The manganese dioxide had an average particle diameter of 10.7 µm, as determined using a particle size analyzer. The recovered MnO₂ is showed below photo (Fig. 11).

Based on the above results, the following process can be proposed for recycling ternary cathodic materials. The content of Mn in lithium ion battery cathodic materials is continually increasing. Under such circumstances, hydrometallurgy is currently used to separate and recover valuable metals from lithium ion battery cathodic materials. According to hydrometallurgy, oxidative precipitation is used to selectively produce Mn in the form of CMD, solvent extraction is performed to recover Co from the filtrate containing Co, Ni and Li, additional solvent extraction is performed to recover Ni from the raffinate containing Ni and Li, and carbonate precipitation with sodium carbonate is performed to recover lithium in the form of a lithium carbonate from the Li solution remaining after the secondary solvent extraction.

### 4. Conclusions

Mn was selectively recovered from the cathodic material leachate, and Co, Ni and Li remained in the solution. To this end, Na₂S₂O₈ was used in an amount of 1 equivalent relative to the Mn (II) concentration in the leachate at 90°C. As a result, Mn was precipitated and recovered in the form of manganese dioxide. The recovered precipitate was found to have a chemical composition of MnO₂%

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Original Sample</th>
<th>523 K</th>
<th>773 K</th>
<th>893 K</th>
<th>1053 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>MnO</td>
<td>84.06</td>
<td>86.25</td>
<td>89.74</td>
<td>95.94</td>
<td>100.46</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>95.94</td>
<td>100.46</td>
</tr>
<tr>
<td>Li₂O</td>
<td>0.11</td>
<td>0.11</td>
<td>0.09</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The precipitate was washed with a 4 M sulfuric acid solution to separate the impurities Co and Ni therefrom. The acid washing allowed for the removal of 25% of Co and 48% of Ni. XRD and thermogravimetric analyses revealed the production of a chemical manganese dioxide (CMD) having a crystal form of γ-MnO₂ and a purity of at least 98%. Through this study, we were able to present a process (Fig. 12) for the separation and recovery of Mn in high purity from a leachate of a lithium ion battery ternary cathodic material by utilizing the selective precipitation behavior of Mn and other valuable metal like Co, Ni and Li can be recovered by solvent extraction.
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REFERENCES


Fig. 12 Development process for recovery of CMD and Co, Ni and Li from lithium ion battery ternary cathodic material.