Effect of Different Reductants on Leaching Lithium and Cobalt from Lithium Ion Batteries in Tartaric Acid Solution

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Abstract. The cathode active materials of spent lithium ion batteries contain significant amounts of lithium and cobalt, which is worthy of recycling. The cathode active materials were employed as raw materials. The effect of reduction on the leaching efficiency of Li+ and Co2+ was compared among glucose, ascorbic acid and hydrogen peroxide with tartaric acid as the acid leaching solution. The results show all three reducing agents can convert the Co3+ of the cathode active materials to soluble Co2+. The complex of Co(III) can also be found during the reduction process. All three reductants can promote the leaching efficiency of Co2+, while having a marginal effect on the leaching efficiency of Li+. The maximum leaching efficiency of Co2+ is 36.94% for 20 g/L glucose, 47.22% for ascorbic acid, and 69.66% for 15% hydrogen peroxide, respectively. Among the three, hydrogen peroxide exhibits the best reduction effect.

1. Introduction
Presently, the production of lithium-ion batteries (LIBs) continues to increase with the rising popularity of new energy vehicles and portable electronic devices [1]. Therefore, it is predicted that a large number of spent LIBs will be produced in the coming years, as their service life is only three years [2]. These spent LIBs contain large amounts of heavy metals and organic compounds which could pose a serious threat to biological health and are hazardous to the environment [3]. However, these spent LIBs are important secondary sources of metals, such as cobalt and lithium. It is reported that the amount of cobalt found in the spent LIBs is 15%, which is higher than that found in some ores from which it is extracted [4]. Thus, the recycling of spent LIBs is crucial, not only from an environmental point of view, but also from an economic standpoint as they are quite valuable. Hydrometallurgical processes can be used as a recycling technique to recover the metal with high efficiency. Acidic leaching has been proposed as the main method for the leaching process. Inorganic acids can efficiently leach metal ions, however, they often result in the emission of toxic gas [5, 6]. Recent studies have been focusing on organic acids as they are more environmentally-friendly. Pure organic acids, such as citric acid, oxalic acid, malic acid, aspartic acid, and tartaric acid can be used as the leaching agent, but they do not provide efficient leaching [7-9]. To improve the leaching efficiency, reductants (e.g., glucose [10], hydrogen peroxide [9], NaHSO3 [11]) are typically introduced to the leaching solutions to convert the metals of higher valency, from the cathode active material (e.g. Co3+), to lower valence metals (e.g. Co2+). The reduction process and the effect of the reduced products on the environment depend considerably on the chosen reducing agent. Therefore, this paper presents the tartaric acid leaching process of cathode active materials with a series of reducing agents (i.e., glucose, aspartic acid, and hydrogen peroxide) with the objective of comparing the three reductants and their
effect on the leaching efficiency. The results can provide further insight towards developing a more efficient leaching process.

2. Materials and methods

2.1. Materials

The spent LIBs were collected from a recycling factory. N-methyl-2-pyrrolidone (NMP) was used as the solvent to extract the cathode materials from aluminum foil. The leaching reagents used in the following studies consisted of HCl for characterization of the total lithium and cobalt content in the cathode material, while a mixture of tartaric acid and reducing agent (glucose, aspartic acid and hydrogen peroxide) was used for the battery leaching experiments. All solutions were prepared using distilled water and all reagents were analytical grade.

2.2. Pretreatment process

The cathode active materials were obtained using a series of techniques including crushing, sieving, magnetic separation and fine crushing. The initial dismantling procedure was accomplished using a 100 mL beaker in a magnetic heating agitator in a fume hood. The scraps and the NMP solution were added under the following optimal experimental conditions: 1 mol/L tartaric acid, solid-to-liquid ratio 10 g/L, reaction time 90 min, since preliminary results have shown there is no significant leaching after 90 min. The reaction mixture was then filtered and washed with solvent three times to provide the resulting residue and the leachate solution. The leaching efficiencies were investigated by varying the reductants and reductant concentrations.

2.3. Experimental procedure

The leaching experiments were conducted in a 100 mL three-necked round-bottomed flask on a heated, magnetic heating agitator. The flask was fitted with a thermometer, piston, and condenser to minimize the loss of water by evaporation. The crude LiCoO₂ powder from the spent LIBs was added to the flask and stirred at a rate of 300 rpm. The reported concentrations of tartaric acid solutions and reducing agent were then added to the flask. The reaction time for all leaching experiments was 90 min, since preliminary results have shown there is no significant leaching after 90 min. The reaction mixture was then filtered and washed with solvent three times to provide the resulting residue and the leachate solution. The leaching efficiencies were investigated by varying the reductants and reductant concentrations.

2.4. Analytical method.

The UV-vis spectra of the leaching solutions were recorded using a UV-visible spectrophotometer (UV-2540A, SHIMADZU Corporation, Japan) with distilled water as the reference solution. The concentration of Li and Co in the leachate was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES Optima 7000, Perkin Elmer Instruments, U.S.A.). The fraction of Li and Co in the original cathode material was obtained by dissolving the cathode completely in concentrated hydrochloric acid, which yielded 6.23% and 68.43% (wt.%), respectively. The leaching efficiency of M (M = Li and Co) was calculated as follows:

\[
\text{Leaching Efficiency} \% = \frac{\text{Content of } M \text{ in the leachate}}{\text{Total content of } M \text{ in the cathode}} \times 100\% \quad (1)
\]

3. Results and discussion

3.1. UV-visible spectra characteristics of tartaric acid, glucose, aspartic acid and hydrogen peroxide

UV-visible spectra of tartaric acid, glucose, aspartic acid (H₂A) and hydrogen peroxide were collected in the range of 200-800 nm, as shown in Figure 1A. The spectra (a), (b), (c), and (d) correspond to 1
mol/L tartaric acid, 10 g/L glucose, 0.5 g/L aspartic acid and 0.24% hydrogen peroxide, respectively. Spectrum (a) shows a strong UV absorption occurring at a wavelength of 230 nm, which is potentially induced by the tartrate. No peaks can be observed in spectrum (b), as glucose has no absorbance in the 200-800 nm range. Spectrum (c) shows the presence of two shoulders at the wavelengths of the 230 and 290 nm, which can be ascribed to the H$_2$A and HA$^-$ forms of aspartic acid, respectively [14]. The spectrum (d) of hydrogen peroxide exhibits a strong UV absorption at approximately 230 nm.

The spectra (a), (b), (c), and (d) in Figure 1B correspond to 1 mol/L tartaric acid, a mixture of 1 mol/L tartaric acid and 10 g/L glucose, a mixture of 1 mol/L tartaric acid and 0.5 g/L aspartic acid, and a mixture of 1 mol/L tartaric acid and 0.24% hydrogen peroxide, respectively. The maximum absorption peaks of the solution are exhibited in the Table I. Spectrum (b) exhibits no new peaks compared with the spectra (a) and (b) in Figure 1A, which suggests that there are no by-products formed. The same phenomenon can be observed in the spectra (c) and (d), which is indicative that the mixture will not generate any by-products.

**Table 1.** The maximum absorption peaks of the UV-vis spectra of the solution before leaching

| Solution                     | Maximum absorption peaks(nm) |
|------------------------------|-------------------------------|
| tartaric acid                | 230                           |
| glucose                      | none                          |
| ascorbic acid                | 230, 290                      |
| hydrogen peroxide            | 230                           |
| tartaric acid + glucose      | 230                           |
| tartaric acid + ascorbic acid| 230, 290                      |
| tartaric acid + hydrogen peroxide | 230                        |

3.2. Comparison of varying reductants in the tartaric acid leaching solution

Figure 2 shows the UV–visible spectra of the leaching solution. The spectrum (a) corresponds to the leaching solution with 1 mol/L tartaric acid, and the spectra (b), (c), and (d) contain the same concentration of tartaric acid along with varying reducing agents with concentrations of 10 g/L.
glucose, 0.2 g/L \( \text{H}_2\text{A} \), and 2.5% hydrogen peroxide, respectively. The inset in Figure 2 is the enhancement of spectrum (c) in the range of 400-800 nm. The maximum absorption peaks of the leaching solution are exhibited in the Table II. A significant UV-visible absorption occurred at around 514 nm in all spectra (a), (b), (c), and (d), which appears to be due to the the production of Co(II) [15]. This demonstrates that the Co(III) of LiCoO_2 is successfully reduced to the Co(II) in the solution. Comparing the spectrum (b) with (a), a weak shoulder can be observed and occurs in the range of 270-320 nm, which may be ascribed to the UV absorbance of a complex of Co(III) [15]. The same phenomenon can be observed in the spectrum (d). As for the spectrum (e), there are three peaks that can be observed in the 200 - 400 nm range, located at approximately 210, 240, and 290 nm, respectively. The peaks at 210 and 240 nm may be ascribed to the UV absorbance of \( \text{H}_2\text{A} \) and \( \text{HA}^- \). Compared to spectrum (c) in the Figure 1A, the peaks are blue shifted which may be due to the decrease in the concentration of \( \text{H}_2\text{A} \) and \( \text{HA}^- \) [14]. The shoulder which occurs at 290 nm may be due to Co(III) complexation with \( \text{HA}^- \).

![Figure 2. UV-visible spectra of leaching solution: tartaric acid(a), tartaric acid + glucose(b), tartaric acid + ascorbic acid(c), and tartaric acid + hydrogen peroxide(d).](image)

**Table 2. The maximum absorption peaks of the UV-vis spectra of the leaching solution**

| Leaching solution                  | Maximum absorption peaks(nm) |
|------------------------------------|-----------------------------|
| tartaric acid                      | 230, 514                    |
| tartaric acid + glucose            | 230, 270-320, 514           |
| tartaric acid + ascorbic acid      | 210, 240, 290, 514          |
| tartaric acid + hydrogen peroxide  | 230, 270-320, 514           |

Figure 3 shows the UV–visible spectra of the leaching solution of different reductant at different concentrations with 1 mol/L tartaric acid, 10 g/L of the cathode active material in suspension, and a reaction temperature of 80 °C. Figure 3A demonstrates the five different glucose concentrations that were examined (5, 10, 20, 30, and 40 g/L) to investigate the effect on the absorbance and the change of peaks. It can be observed that the peaks at 200 - 400 nm and 514 nm did not shift but the intensity of the peak firstly increased and then decreased as the glucose concentration increased. This is because glucose can promote the Co(III) of LiCoO_2 reduced to the Co(II) in the solution. But the high concentration of glucose does not favor the conversion of high valence metal ions to their low valence state [16, 17]. Figure 3B demonstrates the four different \( \text{H}_2\text{A} \) concentrations that were examined (0.5, 1, 3 and 4 g/L) to investigate the effect on the absorbance and the change of peaks. As the absorbance
will exceed the detection line, the concentrations were all diluted 10 times. The inset is the absorption spectrum at 400 - 800 nm of different H$_2$A concentrations (5, 10, 30 and 40 g/L). The intensity and the spectrum peak do not change as the H$_2$A concentration increased, while the peak at 514 nm firstly increased and then decreased. The same phenomenon can be observed in the Figure 3C. The H$_2$O$_2$ concentrations were set as 0.25, 0.5, 0.75, and 1% for the UV experiment. They were all diluted 20 times as the absorbance of the primary concentration will exceed the detection line in the wavenumber of 400 - 800 nm.

3.3. The leaching efficiency of Li$^+$ and Co$^{2+}$ of different reductants with tartaric acid

The extractions were carried out at different reductant concentrations while the other variables were fixed at 1 mol/L tartaric acid in the leaching solution, 10 g/L of the cathode active material in suspension, and a reaction temperature of 80 °C. Figure 4A demonstrates the six different glucose concentrations that were examined (0, 5, 10, 20, 30, and 40 g/L) to investigate its effect on the leaching efficiencies of Li$^+$ and Co$^{2+}$. Figure 4B shows the effect of H$_2$A concentrations (0, 2.5, 5, 10, 20, and 30 g/L) on the leaching efficiencies of Li$^+$ and Co$^{2+}$. Figure 3C shows the effect of hydrogen peroxide concentrations (0, 5, 10, 15, and 20%) on the leaching efficiencies of Li$^+$ and Co$^{2+}$. From the experimental data, it can be observed that the leaching efficiencies of Li$^+$ only changed slightly as the reductant concentrations increased in the Figure 4A, 4B, and 4C. Meanwhile, the leaching efficiencies of Co$^{2+}$ increase initially and then decrease as the concentration continues to increase. This is due to the presence of Li ions which exist in a free state in the LiCoO$_2$ layered structures and are readily available for leaching. The stronger chemical bonds of Co-O in the layered structure make the leaching of Co difficult. However, the reaction can be promoted through addition of a reducing agent for converting Co(III) to Co(II) [10, 17]. Increasing the reductant concentration promote the formation of the metal-ion products which diffuse through the diffusion layer to the liquid-liquid interface. Thus, enhancing the ion transfer to the solution which leads to an increase in leaching efficiency [17]. However, the rate of formation of the metal-ion product is too rapid to prevent the reaction from further progress, leading to an excess of metal-ion products attaching to the solid-liquid interface. Therefore, the leaching efficiencies of Co$^{2+}$ decrease when increasing reductant concentrations. The maximum leaching efficiencies of Li$^+$ and Co$^{2+}$ are 82.7% and 46.6%, respectively, for a glucose concentration of 20 g/L; 84.3% and 47.3%, respectively, for a H$_2$A concentration of 30 g/L; and 82.4% and 53.2%, respectively, for a hydrogen peroxide concentration of 10%. Hydrogen peroxide shows stronger reducibility as it can provide more activation energy under the same reaction conditions [18].

4. Conclusion

The leaching process and the effect of a reductant on the leaching efficiency of Li$^+$ and Co$^{2+}$ was investigated using glucose, ascorbic acid and hydrogen peroxide with tartaric acid as the acid leaching solution. The analysis of the UV-visible spectra shows that there are no undesired by-products generated when mixing the reactants with tartaric acid. All three reducing agents can convert Co$^{3+}$ of the cathode active materials to soluble Co$^{2+}$. The complex of Co(III) can also be observed during the reduction process. The leaching efficiencies of Co$^{2+}$ exhibits a trend of increasing initially and decreasing at higher concentrations, while the leaching efficiencies of Li$^+$ changed only slightly as the reductant concentrations increased. Hydrogen peroxide shows the strongest reducing ability among the three reductants.
Figure 3. UV-visible spectra of leaching solution of different reductant at different concentrations with 1 mol/L tartaric acid, 10 g/L of the cathode active material in suspension, and a reaction temperature of 80 °C. (A) glucose; (B) ascorbic acid; (C) hydrogen peroxide.

Figure 4. The relationship between the leaching efficiency of Li+ and Co2+ and glucose concentration(A), ascorbic acid concentration(B), and hydrogen peroxide concentration(C) in a 1 mol/L tartaric acid solution.
5. References

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