

The Evaluation of the Recovery of Cobalt in the Lithium-ion Batteries

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Abstract: In this work, the removal of cobalt has been precipitation separation in the form of cobalt oxalate by acid-soluble alkali leaching method. At first, the aluminum was selective removal by 5% sodium hydroxide, and then with the mixed solution of H_2SO_4 and H_2O_2 to achieved the precipitation of cobalt oxalate. The results of this study can be considered in making decision which conditions of achieved precipitation of cobalt can be efficiently applied in a real manufactory and recover valuable metals from waste lithium-ion batteries. The leaching rate of cobalt were evaluated by ultraviolet spectrophotometry.

Keywords: Waste Lithium-ion Battery; Recovery of Cobalt; CoC_2O_4 ; $LiCoO_2$

1. Introduction

Recently, the Lithium-ion battery anode material and electrolyte solution had caused a specific and serious environmental problem because of their toxicity and possible accumulation in the environment. Even a minor-scale batteries had contaminated thousand kilometers of river banks and damaged the terrestrial habitats, resulting in a direct threat to the survival of humans, animals and agriculture. Over the past several decades, with the continuous progress of the industrial and technologies, more and more lithium-ion battery products being used daily worldwide[1-3]. Extensive application increased the possibility of their contaminated the environment and loss of many precious metals, such as cobalt, manganese, lithium, etc. To date, the great risk from lithium-ion battery contamination into the groundwater environment remains an aesthetic issue towards the public health and food chain interference. Therefore, it is important to establish and develop techniques to recycle the waste lithium-ion secondary battery[4-6].

2. Experiment

All of the lithium-ion batteries used in experiment are provided by a battery factory in Tianjin.

Soak the battery in the amount of volume of 10% sodium hydroxide into the beaker, set temperature, time then split the battery; cut the will-split aluminum-cobalt film, weighed 5g sample into 10% sodium hydroxide solution, boiling, filtering, washing, and obtained residues, then add an appropriate amount of hydrogen peroxide for slurry, using sulfuric acid, sodium hydroxide to control the pH value to 5 or so, then mixed with ammonium oxalate adjusted pH value to 2, after two hours for water bath action, drying, then in a muffle furnace sintering five hours at $600\text{ }^\circ\text{C}$ to get Co_3O_4 .

Battery pack The synthetic lithium cobalt oxide samples and commercially available lithium cobalt oxide as the cathode material, carbon black as a conductive agent, PTFE emulsion as a binder, mixture according to the ratio of the mass 90:5:5, then adding an appropriate amount of anhydrous ethanol, ultrasound, using roll pressure method film the sample, and presses it with pressure on the aluminum foil, vacuum dried, assembly (CR2032) coin cell battery in the argon filled glove box, the electrolyte of 1 mol/L (1:1), then charge-discharge experiments test in Wuhan Li Xing PCB T-138-32D program-controlled battery.

Preparation of lithium cobalt oxide weighed Li_2CO_3 and Co_3O_4 in ratio of 1:1, then calcined 5 hours in a furnace, heat 2 hours, heated to $700\text{ }^\circ\text{C}$, then natural cooling get the lithium cobalt oxide.

3. Method and instruments

3.1. The effect of pH on the recovery of cobalt

In this case, the solution sample of cobalt ammonium was keeping with the oxalate solution ratio of 1:1 at $60\text{ }^\circ\text{C}$ for 2h and adjusting the reaction temperature to determine the effects of pH on the recovery of cobalt. As shown in Fig.3.1, the quality of sediment was obtained at different pH, the precipitation quality was increased with the pH increases from 1 to 2, When the pH=2, the quality of precipitation reached the maximum and it was 0.58g. However, when the pH is over a critical value of 4, the quality of precipitation was hindered. Therefore, this obtained results suggested that the recovery of cobalt must under the condition of acidic and the optimum pH value was 2.

3.2. The effect of temperature on the recovery of cobalt

In this case, the solution sample of cobalt ammonium was keeping with the oxalate solution ratio of 1:1 at PH= 2 for 2 h and adjusting the reaction temperature to determine the effects of temperature on the recovery of cobalt. As shown in Fig.3.2, the quality of sediment was obtained at different temperatures, the tendency of precipitation quality was much similar with the temperature increased from 30 °C to 60 °C. When the temperature reached 60 °C, the quality of precipitation reached the maximum and it was 0.92g. However, when the temperature is over a critical value, the quality of precipitation was hindered, Therefore, this obtained equilibrium temperature of 60°C was selected for the next experiments.

3.3. The effect of the ratio of cobalt/ ammonium oxalate on the recovery of cobalt

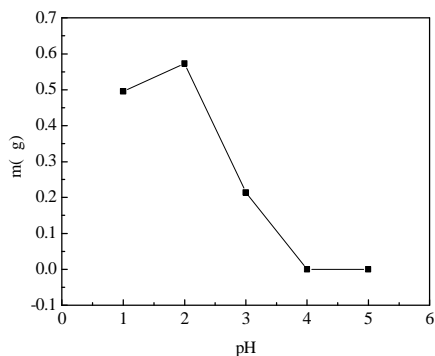


Figure 3.1. The effect of pH on the recovery of cobalt.

In this study, the effect of the ratio of cobalt/ ammonium oxalate on the recovery of cobalt was adjusted by added different amount of ammonium oxalate was used at 60°C, pH=2 for 2h. As shown in Fig3.3, the quality of precipitation increased with the ratio of cobalt/ammonium oxalate increase from 1:0.5 to 1:1.5, When the ratio of cobalt/ammonium oxalate reached 1: 1.5, the reached the maximum value of 1.07g. However, the precipitation quality was not substantially increased with ratio increased, which leading to an asymptotic saturation of the cobalt precipitation. Therefore, the obtained equilibrium data suggested that the optimal experiments factor for cobalt recovery was the ratio of 1:1.5 at 60°C and pH 2.00.

3.4. The standard curve of cobalt²⁺

The scanning for cobalt solution sample was by ultraviolet spectrophotometry, the maximum absorption wavelength of the standard solution is λ = 516.0nm, then measured the values of absorbance with different concentration of cobalt²⁺, drawn the standards curve in accordance with the data. A typical standards curve recipe is shown in Fig. 3.4.

3.5. The calculation of quality and recovery ratio for cobalt

$m_{\text{standard}} = C_{\text{cobalt}^{2+}} \times V_0 = 0.1504\text{g}$ then the m_0 was 0.1418g. The recovery ratio for cobalt was calculated as $A = (m_0 / m_{\text{standard}}) \times 100\% = 94.3\%$.

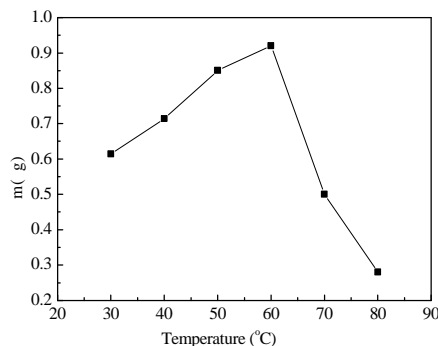


Figure 3.2. The effect of temperature on the recovery of cobalt.

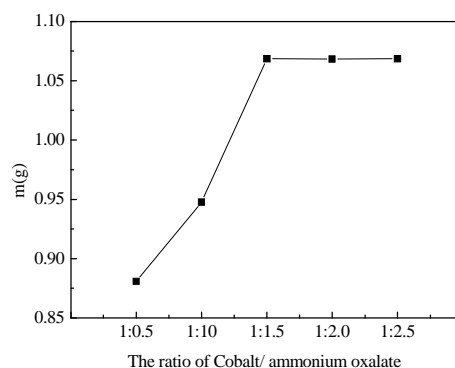


Figure 3.3. The effect of the ratio of cobalt/ ammonium oxalate on the recovery of cobalt.

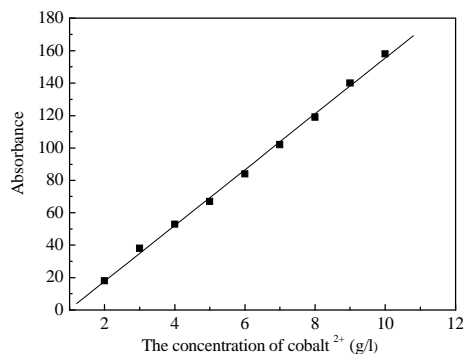


Figure 3.4. The standard curve of cobalt²⁺. Curve equation : $y = 17.216x - 16.744$

3.6. The batteries performance measurement

Fig.3.5.Line A is the capability curve of LiCoO₂ battery purchased from market. Line B is the capability curve of LiCoO₂ battery made by laboratory t.

Fig.3.5 A shows that the discharge platform of LiCoO₂ purchased from market is about 3.5v, and the specific capacity is about 82mAh/g. The discharge platform of LiCoO₂ made by laboratory is about 3.5v too, but the specific capacity is lowed to about 52mAh/g. However, Because of personal reasons, the performance of assembled LiCoO₂ batteries purchased from market did not behaved good, and so as the LiCoO₂ batteries made by laboratory t. So we need do more works in this aspect.

Fig.3.6 Line A is the discharge specific capacity attenuation curve of LiCoO₂ battery purchased from market. Line B is the discharge specific capacity attenuation curve of LiCoO₂ battery made by laboratory.

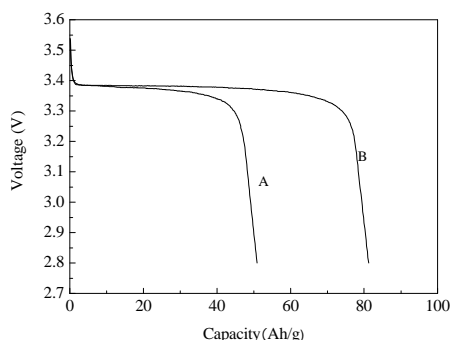


Figure 3.5. The first discharge curves.Line A is the capability curve of LiCoO₂ battery purchased from market. Line B is the capability curve of LiCoO₂ battery made by laboratory.

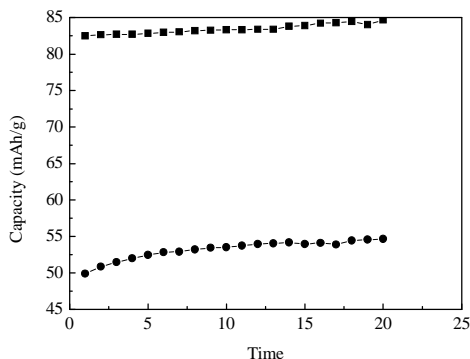


Figure 3.6. cycling performance.Line A is the discharge specific capacity attenuation curve of LiCoO₂ battery purchased from market. Line B is the discharge specific capacity attenuation curve of LiCoO₂ battery made by laboratory.

Fig.3.6 shows that specific capacity of LiCoO₂ batteries, both purchased from market all made by laboratory, did not decay after discharged 20 circulations. And the specific capacity of LiCoO₂ made by laboratory trend to increasing, it is show that the LiCoO₂ made by laboratory has a good performance of circulation. It is worth to research.

4. Conclusion

This paper main uses the precipitation separation of Alkali dip dissolve acid to recycling cobalt. Researched PH value, reaction temperature, the proportion of cobalt and ammonium oxalate and electrochemical performance of battery etc., affected to cobalt precipitate. The best conditions to depositing cobalt are blending cobalt and ammonium oxalate to the proportion of 1:1.5, then regulating pH value to 2, reacting 2h in water bath at temperature of 60, according to the experiment. Come to the concentration of Co²⁺ in the specimen on the basis of standard absorbency curve of Co²⁺, and calculate the quality of the cobalt, thereby the leaching rate of cobalt. The leaching rate of Co²⁺ is 94.3% according to experimentation. The method of alkali dip dissolve acid epositing cobalt give a easy but fast way to the research of reovering cobalt due to the advantages of no pollution to environment, lower cost, and higher recovery rate.

References

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