

STUDY ON THE MECHANISM OF COBALT RECOVERY FROM WASTE LITHIUM COBALTATE BATTERIES IN CITRIC ACID SYSTEM

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The waste lithium cobalt acid batteries were utilized as raw materials to separate out LiCoO_2 cathode material. Citric acid was used to leach cathode material, and LiCoO_2 leaching solution was electrodeposited to obtain cobalt plating, in the meantime the Li^{2+} ions were enriched. The optimized conditions of leaching process are 1,2 mol/L citric concentration and 0,35 mol/L sodium thiosulfate concentration, the leaching efficiency of cobalt and lithium is 97,5 % and 97,0 % respectively. At pH 4, the smooth cobalt coating with fine grains can be obtained on the surface of the stainless-steel cathode.

Key words: cobalt recovery, battery, citric acid, electrocrystallization, X-ray research

INTRODUCTION

Lithium cobalt oxide batteries are the leading cathode material for 3C electronic products due to their high rated voltage, high energy density, excellent multiplying capacity, and good cycle performance[1-2]. After a certain cyclic charge-discharge period, the active material of batteries is deactivated due to structural changes[3-4]. Waste lithium cobalt acid batteries have the dual attributes of hazardous solid waste and available resources. which cause great harm to the environment if not suitably treated. At the same time, rare strategic metals such as cobalt, lithium, and nickel are enriched in the batteries[5]. Recovering the metals has significant resource and environmental economic benefits.

Electrodeposition technology can obtain high-purity metal products, and has the advantages of low production cost and low secondary pollution. In this paper, the mixed solution of Citric acid and sodium thiosulfate was used to leach the cathode material of waste lithium cobalt acid batteries, and Co and Li ions were enriched into the solution. Using the difference of deposition potential between Co^{2+} and Li^+ , cobalt is deposited onto the surface of the stainless steel cathode. Effective separation of cobalt and lithium metals is achieved, at the same time, the cobalt coating of anti-corrosion and high temperature oxidation resistant is constructed on the surface of the stainless steel.

EXPERIMENTAL MATERIALS AND METHODS

For discharging, The waste lithium cobalt acid battery was soaked in 10 % mass concentration of NaCl

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solution for 48 hours, and then the positive and negative electrode active materials were separated through physical disassembly and screening. The LiCoO_2 cathode material is calcined in a muffle furnace at 550 °C to decompose the adhesion of the adhesive, and then added to a mixed solution of citric acid and sodium thiosulfate. Acid leaching is conducted under the conditions of a solid liquid ratio of 10 g/L, a temperature of 80 °C, magnetic stirring of 600 r/min, and a leaching time of 70 minutes. The leaching solution is filtered to obtain a pure LiCoO_2 leaching solution. In the electrodeposition experiment, a 2cm*2cm stainless steel plate was used as the cathode, and a platinum plate electrode was used as the anode. In the LiCoO_2 leaching solution, the electrodeposition conditions used were a current density of 400 A/m², a temperature of 63 °C, and a time of 150 min. Scanning Electron Microscopy (SEM) was used to analyze the morphology of the coating, and X-Ray Diffraction (XRD) was used to the coatings phase structure. The chemical composition of the coating was analyzed by Energy Dispersive Spectrum (EDS).

RESULTS AND DISCUSSION

Figure 1 is the SEM image of the micro-morphology of the calcined LiCoO_2 cathode material. As can be seen from Figure 1, Before roasting, the agglomeration of lithium cobalt oxide particles is relatively serious caused by the organic binder between the lithium cobalt oxide particles. After roasting, lithium cobalt oxide particles exist in the form of single particles, with good dispersion and no obvious agglomeration, indicating that the organic binder has been completely decomposed during the roasting process.

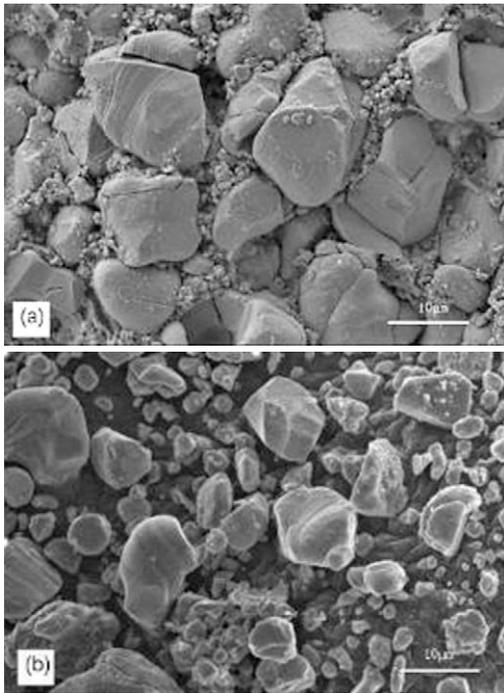


Figure 1 SEM image of LiCo₂ cathode material; (a) before roasting; (b) after roasting.

Figure 2 shows the XRD energy spectrum analysis diagram of the cathode material. From the figure, it can be seen that the main phase of the cathode material is composed of oxidized LiCo₂, CoO₂, CoO, and Co₃O₄, with a small amount of carbon remaining.

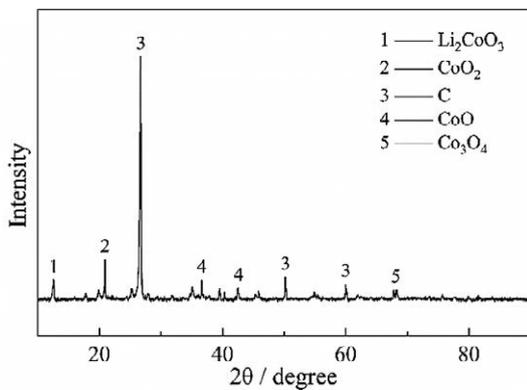


Figure 2 Phase composition of battery cathode material

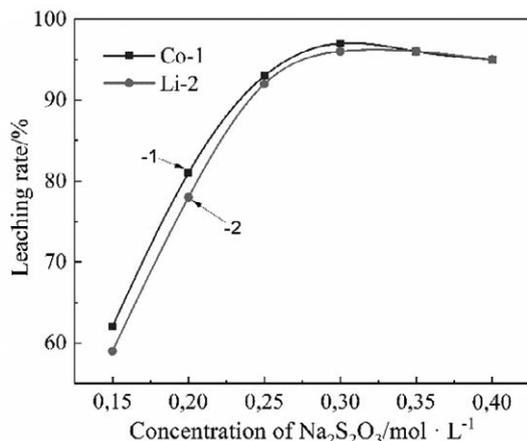


Figure 3 Effect of sodium thiosulfate concentration on leaching rate of cobalt and lithium.

Figure 3 shows the effect of citric acid concentration on leaching rate of cobalt and lithium. When the concentration of citric acid is in the range of 0,2 mol/L-0,4 mol/L, the leaching rates of Co and Li increase significantly with the increase of citric acid concentration. When the concentration of citric acid was above 1,4 mol/L, the leaching rates of cobalt and lithium metals decreased.

Figure 4 is the effect of sodium thiosulfate concentration on leaching rate of cobalt and lithium. As we can see from Figure 4, The leaching rates of Co and Li increase with the increasing concentration of Na₂S₂O₃. When the concentration of Na₂S₂O₃ gradually increases from 0,15 mol/L to 0.30 mol/L, the leaching rate of cobalt ions increases from 62 % to 97,5 %, while the leaching rate of lithium ions increases from 58 % to 97 %. When the concentration of Na₂S₂O₃ is above 0,3 mol/L, the leaching rate decreases, mainly due to the occurrence of side reactions during the leaching process. The by-products are wrapped around the lithium cobalt oxide powder, thereby impeding the progress of the leaching reaction, and reducing the Co and Li leaching rates.

Figure 5 shows SEM image of the micro-morphology of cobalt coating, and Figure 6 is the XRD diffraction pattern of cobalt coating.

From Figure 5, it is known that under the conditions of current density of 2.5 A/m², temperature of 50 °C, time of 1 h, and pH = 4, the cobalt grains in the plating

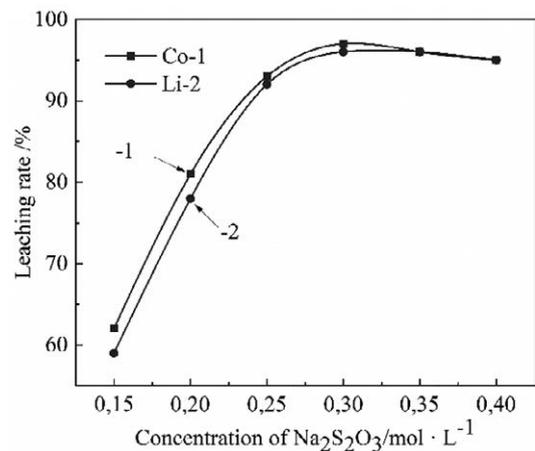


Figure 4 Effect of sodium thiosulfate concentration on leaching rate of cobalt and lithium



Figure 5 SEM image of cobalt coating

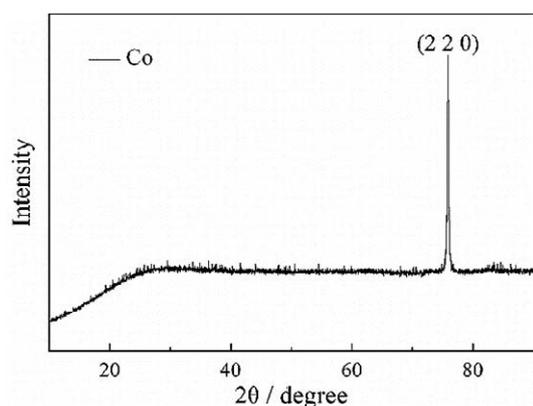


Figure 6 XRD diffraction pattern of cobalt coating

layer present a sharp pyramid shaped arrangement, and the cone tips grow outward, closely arranged on the surface of the substrate, forming a fine and compact metallic cobalt plating layer. In the XRD diffraction pattern of the cobalt coating, only the (220) crystal surface of Co was found at $75,82^\circ$, with a sharp peak pattern and high crystallinity. This indicates that the coating is composed of well-defined metallic cobalt crystals.

CONCLUSION

The process of citric acid leaching and electrodeposition was used to recover cobalt from waste lithium cobalt acid battery cathode materials. When the concentration of citric acid was 1,2 mol/L and $\text{Na}_2\text{S}_2\text{O}_3$ was 0,35 mol/L, the Co leaching rate could reach 97,5%; under the conditions of current density of $2,5 \text{ A/m}^2$, temperature of 50°C , time of 1h, and $\text{pH} = 4$, A smooth

and fine Co coating can be obtained, with a Co grain size of 26,34 nm and growing along the (220) direction.

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Note: H. Jin is responsible for English language, Anshan, Liaoning, China.