Recovery of Metal Values From Spent Lithium-ion Batteries

LI Jian-gang, ZHAO Ru-song, LIU Hua-chen
(Department of Applied Chemistry, Beijing Institute of Petrochemical Technology, Beijing 102617)

Abstract: A new process involving ultrasonic separation of electrode materials, acid dissolution, precipitation of cobalt and lithium has been applied to recover metals values from spent lithium-ion batteries. The effect of organic solvent on separation of electrode decrease as the order: NMP > DMF > DMSO ≫ Acetone. Ultrasonic treatment can reduce the separation temperature and times. In the optimized process, electrode materials can be separated completely when ultrasonic-treated with NMP at 40℃ for 15 min. 99.4% of Co and Li of separated electrode materials can be acid-leached. 99.5% of cobalt ion in acid solution can be recovered easily as spherical CoC_2O_4 powders, and 94.5% of Li in the surplus filtrate can be recovered as Li_2CO_3 after the deposition of cobalt. The $LiCoO_2$ prepared from the recovered compounds of cobalt and lithium is found to have good electrochemical performance.

Key words: spent lithium-ion batteries; recycling; metal values; ultrosonic; precipitation
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The recycling of metal values from spent lithium-ion baterries (LIBs) is a beneficial way to prevent environmental pollution and as alternative resources of cobalt, copper, aluminum, lithium. By now, several processes for the recycling have been proposed[1-4]. In this study, a new process has been applied to recover metals values from spent LIBs.

1 Experimental

Cylindrical 18650 size $LiCoO_2$/LiCx spent LIBs were opened. The internal rolls were treated under the following process: ① Separation of electrode from current collector by ultrasonic treatment with organic solvent; ② Acid leaching of $LiCoO_2$; ③ Recovery of the cobalt in the leaching solution; ④ Recovery of lithium in the surplus filtrate after the deposition of cobalt; ⑤ Preparation of $LiCoO_2$ with the recovered compounds.

The concentration of lithium and cobalt in solutions were determined using a PerkinElmer Optima 2100DV spectrophotometer. Morphology of the $LiCoO_2$ powders was observed using HITCHI S-3500 SEM. The charge-discharge performance of $LiCoO_2$ was tested in a half-cell.

2 Results and discussion

As shown in Fig. 1, the separation effect by ultrasonic vibration is better than that by magnetic stirring.

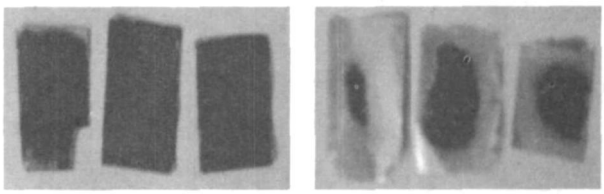

Fig. 1 Appearance of electrode after magnetic stirring (left) and ultrasonic vibration (right) in DMF for 30 min at 40℃

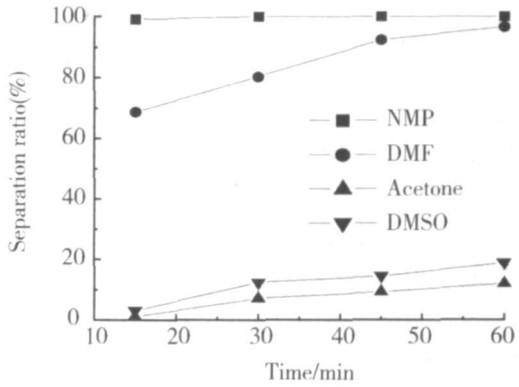

Fig. 2 Effect of organic solvent on separation of electrode from current collector at 40℃

Fig. 2 shows that the effect of organic solvent on the ultrasonic separation decrease as the order: NMP > N, N-dimethyl formamide (DMF) > Dimethyl sulfoxide (DMSO) ≫ Acetone. The optimized process is ultrasonic treatment with NMP at 40℃ for 15 min. The

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作者简介: 李建刚 (1966年生), 男, 博士, 副教授; 通讯联系人: E-mail: lijiangang@bipt.edu.cn

separation temperature and time are smaller than that reported[3], which can lessen harm of organic solvent.

$H_2SO_4+H_2O_2$ were chosen to dissolve Co and Li from the separated electrode powders. Based on leaching experiments results, the conditions were optimized to be 3 mol/L H_2SO_4, 1∶2 H_2O_2∶H_2SO_4 molar ratio, 70℃, 1∶10 initial S∶L ratio and 1 h. 99.4% of Co and Li were leached.

The cobalt in the leaching solution was recovered at 50℃ by precipitation. The recovery of Co reached 97.1%, 99.5%, 94.4% when using 2 mol/L NaOH, 1 mol/L $Na_2C_2O_4$, 1 mol/L Na_2CO_3 as precipitator respectively. Because spherical CoC_2O_4 was prepared easily which is beneficial for filtration of precipitates and preparation of high density $LiCoO_2$, the cobalt is recovered as CoC_2O_4.

The surplus filtrate after the deposition of cobalt was concentrated to contain about 3 mol/L Li, and then treated with a saturated Na_2CO_3 solution. Results indicate that 94.5% of Li can be recovered with 100% excess saturated Na_2CO_3 solution.

2.5 Preparation of $LiCoO_2$

The recovered Li_2CO_3 and CoC_2O_4 (Li∶Co molar ratio 1.05∶1) were mixed uniformly and heated at 900℃ for 10 h to obtain $LiCoO_2$. As shown in Fig. 3, the synthesized $LiCoO_2$ shows close spherical morphologies with about 10 μm particle size, a specific capacity of 153 mA·h·g^{-1} and good cycleability at 0.2 C current.

3 Conclusion

In the new simple LIBs recyching process, ultrasonic treatment can reduce the separation temperature and times of electrode materials. Co and Li can be effectively recovered and reused to prepare high density spherical Li_2CoO_2 with good electrochemical performance.

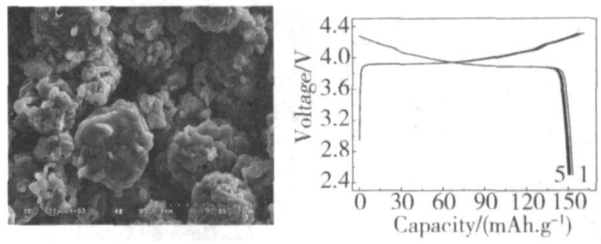

Fig. 3　Morphology (left) and charge-discharge curves (right) of $LiCoO_2$

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废旧锂离子电池中有价金属的回收

李建刚，赵如松，刘华臣

（北京石油化工学院应用化学系，北京 102617）

摘　要：采用超声波分离电极材料—酸浸—钴锂沉淀新工艺分离并回收了废旧锂离子电池中的有价金属。超声波分离中所研究溶剂的分离效果为：NMP＞DMF＞DMSO≫丙酮。超声波处理可降低分离温度与时间。采用该工艺，电极材料用NMP于40℃超声波处理15 min可完全剥离；所剥离电极材料中99.4%的钴锂可酸浸出；酸浸液中99.5%的钴离子可以高密度球形CoC_2O_4回收；钴沉淀分离后，滤液中94.5%的锂离子可以Li_2CO_3沉淀回收。以所回收钴锂化合物制备的$LiCoO_2$具有良好的电化学性能。

关键词：废旧锂离子电池；回收；有价金属；超声波；沉淀

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