

Preparation of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials from spent Li-ion batteries

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Abstract: A recycling process including separation of electrode materials by ultrasonic treatment, acid leaching, Fe-removing, precipitation of cobalt, nickel, manganese and lithium has been applied successfully to recycle spent lithium-ion batteries and to synthesize $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. When ultrasonic treatment with 2-nitroso-4-methylphenol(NMP) at 40 °C for 15 min, the electrode materials are separated completely. Above 99% of Co, Ni, Mn and Li, 95% of Fe in the separated electrodes are acid-leached in the optimized conditions of 2 mol/L H_2SO_4 , 1:2 H_2O_2 : H_2SO_4 (molar ratio), 70 °C, 1:10 initial S:L ratio, and 1 h. 99.5% of Fe and less than 1% of Co, Ni, Mn in the leaching solution can be removed in the conditions of initial pH value 2.0–2.5 adjusted by adding 18% Na_2CO_3 , 90 °C and stirring time 3 h. After adjusted to be equal by adding NiSO_4 , CoSO_4 and MnSO_4 solution, 97.1% of Ni, Co, Mn in the Fe-removing surplus leaching solution can be recovered as $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$. 94.5% of Li in the surplus filtrate after the deposition of Co, Ni and Mn can be recovered as Li_2CO_3 . The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, prepared from the recovered compounds, is found to have good characteristics of the layered structure and electrochemical performance.

Key words: recycling process; spent Li-ion batteries; cathode material; $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

1 Introduction

Lithium-ion batteries(LIBs) are widely used as electrochemical power sources in many portable apparatus. Because LIBs contain lots of valuable metals such as cobalt, lithium and aluminum, the spent LIBs increases the metal-containing hazardous waste. Therefore, the recycling of major components from spent LIBs is considered to be a beneficial way to prevent environmental pollution and as alternative resources of valuable metal.

Up to now, some processes for the recycling of spent LIBs have been proposed. Because LiCoO_2/C batteries are widely used, most of the reported processes concentrate mainly on the recycling and reuse of Co and Li. Hydrometallurgical and pyrometallurgical routes, such as chemical deposition[1–2], solvent extraction [3–4], ion-exchange[5] or electrolysis[6] have been widely used to recover valuable metals from the spent LIBs. In addition, several procedures for the direct regeneration of lithium cobalt oxide electrode from waste LIBs have published by KIM et al[7] and RA et al[8].

At the moment, LiCoO_2 is the most used active cathode material, however, the use of new cathode materials such as LiMn_2O_4 , LiFePO_4 , $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ and $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ have increased in the last few years due to cost and safety. Coexistence of Li, Fe, Co, Ni and Mn ions increases the difficulty of recycling valuable metals. Recently, LUPI et al[9] had reported a process for recycling Co and Ni from the spent LIBs by electrochemical process. NAN et al[10] had published a novel recycling process for the valuable metal from a mixture of spent LIBs and nickel-metal hydride batteries.

In this work, we present a new process for recycling the valuable metals from a mixture of spent LIBs, in which LiCoO_2 , $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$, LiFePO_4 and LiMn_2O_4 are used as cathode materials respectively. In view of the better electrochemical performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the new recycling process of spent LIBs bases on the preparation of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from the spent LIBs.

2 Experimental

Commercial LIBs used in this study were kindly

provided by Mike Battery Co. Ltd., in which LiCoO_2 , $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$, LiFePO_4 , LiMn_2O_4 were used as cathode materials respectively, graphite active materials as anode materials, carbon as conducting additives, and polyvinylidene fluoride (PVDF) as binder, Al and Cu foil as current collector, Celgard 2400 as separator. The batteries were opened by simply cutting their cases and extracting the internal rolls. The rolls were submitted to a series of tests defining their recycling and treating process. Finally, an overall recycling process, as shown in Fig.1, was designed and studied. The determination of the concentration of lithium, cobalt, nickel, manganese, iron in aqueous solutions were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 2100DV spectrophotometer. Powder X-ray diffraction was used to characterize the structure of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders. The charge-discharge performance of the synthesized materials was tested in a half-cell type of coin cell by using a computer controlled battery test system.

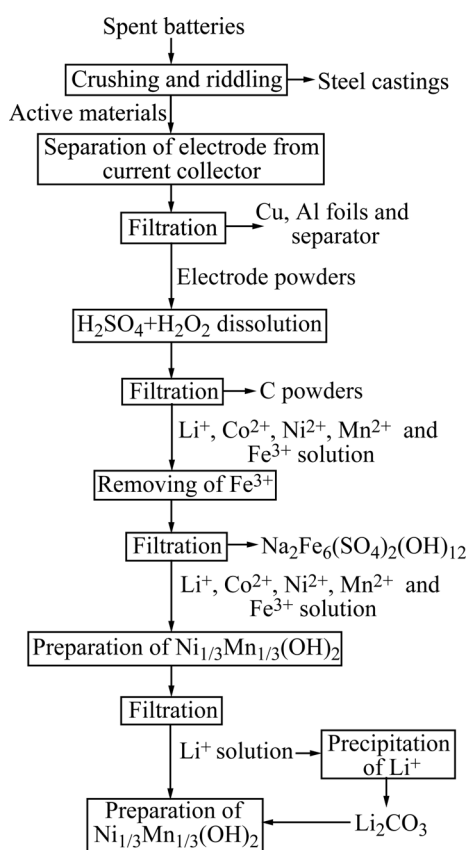


Fig.1 Flow-sheet of recycling process

3 Results and discussion

Fig.1 shows the flow-sheet of the process designed in this work, the various step operations are described below.

3.1 Separation of electrode materials

To simplify the recycling process, separation of electrode materials from the current collector is necessary. The ultrasonic vibration is applied in this study to assist this treatment and improve the effect of separation. Fig.2 shows the effect of organic solvents on the separation. The results indicate that the effect of organic solvent on the separation decreases in the order of 2-nitroso-4-methylphenol (NMP) > N, N-dimethyl formamide (DMF) > Dimethyl sulfoxide (DMSO) >> acetone. In view of good solvent for PVDF and high boiling point, NMP is a good choice for liberating the active materials from current collectors. The optimized process is ultrasonic treatment with NMP at 40 °C for 15 min. The separation temperature and time are respectively lower and lesser than those reported by CONTESTABILE et al[2]. To identify if ultrasonic vibration improves the separation, we compare the treatment effect by ultrasonic vibration with those by magnetic stirring in DMF and NMP respectively. As shown in Fig.3, the separation effect by ultrasonic vibration is better than that by magnetic stirring. Ultrasonic treatment lowers the temperature of organic solvent for dissolution of PVDF, and shortens the separation times.

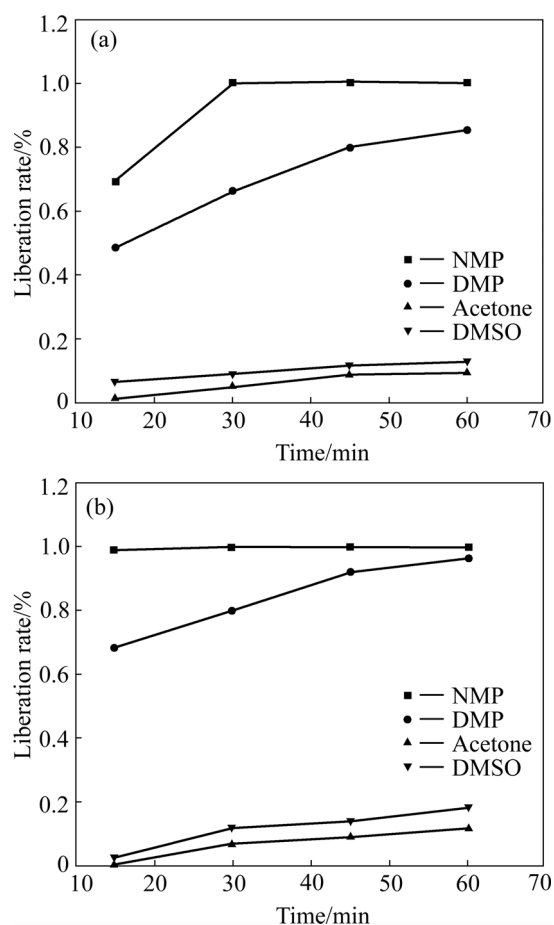


Fig.2 Effect of organic solvent on liberation of electrode from current collector at 30 °C (a) and 40 °C (b), respectively

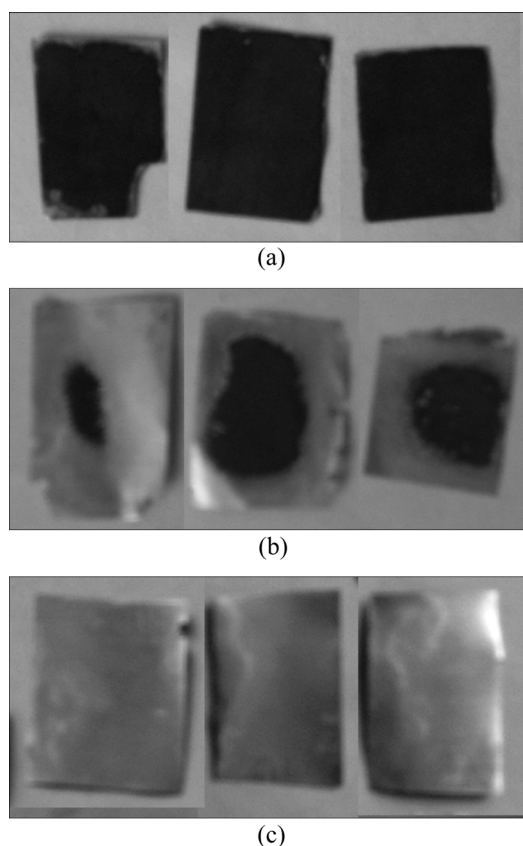


Fig.3 Appearance of electrode after magnetic stirring in DMF for 60 min at 30 °C by ultrasonic vibration (a), in DMF for 60 min at 30 °C by ultrasonic vibration (b) and in NMP for 15 min at 40 °C (c)

After the separation of electrode materials, the recovery of both Al and Cu foil in their metallic form are carried out by simply filtrating them out from the NMP solution. The electrode powders, such as carbon additive and active materials settling on the bottom, are separated and recovered by solution decantation. The decanted NMP can be reused for many times owing to its high solubility for PVDF.

3.2 Dissolution of separated electrode powders

Then $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ is chosen as acid leaching reagent to dissolve Co, Fe, Ni, Mn and Li from the separated electrode powders, in which some iron can precipitate as FePO_4 and be filtrated out. Based on several leaching experiments results, the optimum conditions are determined to be 2 mol/L H_2SO_4 , 1:2 H_2O_2 : H_2SO_4 molar ratio, 70 °C, 1:10 initial S:L ratio, and 1h. Above 99% of Co, Ni, Mn and Li, 95% of Fe are leached under this condition.

3.3 Separation of iron from leaching solution

Because $\text{Fe}(\text{OH})_3$ precipitates at lower pH values of

about 2–4, Fe ions must be separated from the leaching solution before the Ni, Co, Mn ions are recycled as hydroxide precipitates. Separation of iron in the form of jarosite, goethite, and $\text{Fe}(\text{OH})_3$ is widely used[11–12], and separation of iron by extraction method also has been reported[13]. Based on several Fe-removing experiments, separation of iron in the form of jarosite is chosen in this work because of enough amounts of SO_4^{2-} in the leaching solution and easy filtration of the formed precipitates $\text{Na}_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}$. The procedure is as follows: adjusting the initial pH of the leaching solution by adding 18% (mass fraction) Na_2CO_3 aqueous solution, and then stirring for 0.5–3.0 h at a stable temperature. After that, the solution is readjusted to pH 2.5–3.1 by adding 18% (mass fraction) Na_2CO_3 aqueous solution, and the formed precipitates are filtrated out. The total reaction is

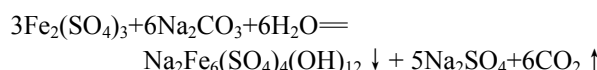


Table 1 lists the effect of initial pH value on the separation of iron in the condition of 90 °C and stirring time 4 h. The Fe-removing rate enhances with increasing the initial pH value. However, filtrating out the precipitates becomes difficult while $\text{pH} > 2.5$ because small amounts of Fe^{3+} precipitate in the form of $\text{Fe}(\text{OH})_3$. Table 2 lists the effect of temperature on the separation of iron in the condition of pH 2.0 and stirring time 4 h. The effect of stirring time on the separation of iron in the condition of pH 2.0 and 90 °C is also investigated, as listed in Table 3. Based on the results mentioned above, the separation condition is optimized to be initial pH value 2.0–2.5, temperature 90 °C and stirring time 3 h. Under this condition, above 99.5% of iron is removed and the loss of Co, Ni, Mn is less than 1%, respectively.

Table 1 Effect of initial pH value on separation of iron

Initial pH value	Filtration of precipitate	Fe-removing rate/%
1.0	No precipitate	—
1.5	Easy	90.91
2.0	Easy	99.55
2.5	Normal	99.76
3.0	Difficult	—

Table 2 Effect of temperature on separation of iron

Temperature/°C	Filtration of precipitate	Fe-removing rate/%
60	No precipitate	—
70	No precipitate	—
80	Easy	87.02
90	Easy	99.66

Table 3 Effect of stirring time on separation of iron

Stirring time/ h	Filtration of precipitate	Fe-removing rate/ %
0.5	Normal	14.38
1	Normal	50.36
2	Easy	89.09
3	Easy	99.55
4	Easy	99.60

3.4 Preparation of $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$

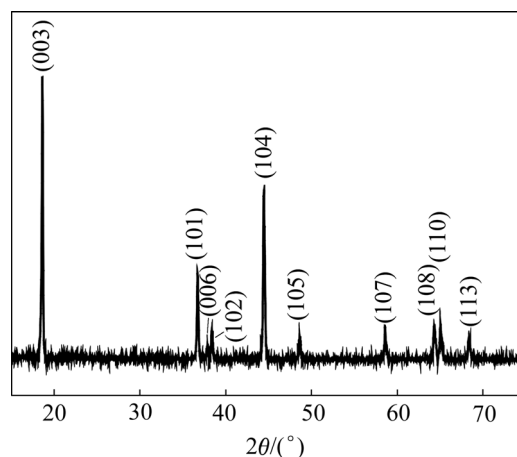
After filtrating out $\text{Na}_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}$, the content of Ni, Co, Mn in the surplus leaching solution is determined, and adjusted to be equal by adding NiSO_4 , CoSO_4 and MnSO_4 solution. Following that, the spherical $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ is prepared by controlled precipitation with NaOH solution under N_2 atmosphere. The precipitation condition is optimized to be pH 10.5 (± 0.2), 55 °C, and 6 h of reaction time under stirring intensely. The recovery of Ni, Co, Mn in the adjusted leaching solution reaches 97.1% under this condition.

3.5 Recovery of lithium

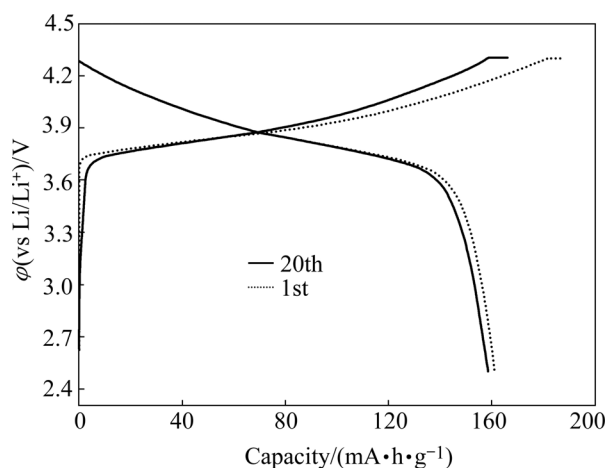
Lithium is left in the surplus filtrate after the removal of $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$. The filtrate is concentrated to be about 3 mol/L of Li, and then treated with a saturated Na_2CO_3 solution. The amount of Na_2CO_3 on the recovery of Li is investigated, the results indicate that the recovery of Li can reach 94.5% when adding 100% excess saturated Na_2CO_3 solution.

3.6 Synthesis of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

The $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$ precipitates are filtrated out, heated at 600 °C for 5 h to transform to metal oxides, then mixed with Li_2CO_3 in a molar ratio of $\text{Li}:(\text{Ni}+\text{Co}+\text{Mn})=1.03:1.00$ and annealed at 850 °C in air for 10 h to prepare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials, successively. As shown in Fig.4, the XRD pattern of as-prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ reveals that the sample presents the typical layered $\alpha\text{-NaFeO}_2$ structure. No impurity-related reflection peaks can be observed in this XRD pattern. The clear splitting of the lines assigned to the Miller indices (006, 102) and (108, 110) in Fig.4 indicates that the sample presents good characteristics of the layered structure. The ratio I_{003}/I_{104} of 1.62 is obtained, indicating no undesirable cation mixing[14]. The lattice parameters a and c of the sample are determined to be 0.286 0 nm and 1.423 7 nm, respectively. These data match well with the values observed by Ohzuku and Makimura ($a=0.286$ 7 nm and $c=1.424$ 6 nm) [15] and SHAJU et al[16]($a=0.286$ 4 nm and $c=1.423$ 3 nm).

**Fig.4** XRD pattern of as-prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

The charge-discharge characteristic of as-prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is tested in a coin cell, which is consisted of a cathode with the composition of 88% (mass fraction, the same below) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, 6% carbon black, and 6% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film, and electrolyte composed of 1 mol/L $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{DMC}$ (1:1:1 by volume). Fig.5 shows that $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ synthesized from the recovered compounds of spent LIBs presents a specific capacity of 161.1 mA·h/g and good cycleability at 0.3C over 2.5–4.4 V range.

**Fig.5** Charge-discharge curves of as-prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

4 Conclusions

1) A sequential recycling process including separation of electrode materials by ultrasonic treatment, acid leaching, Fe-removing, and precipitation of cobalt, nickel, manganese and lithium has been applied successfully to recycle spent lithium-ion batteries and to synthesize $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

2) Ultrasonic treatment can lower the temperature of organic solvent for dissolution of PVDF, and shorten the

separation times, which can lessen harm of organic solvent to people. The optimized process of separating electrode from current collector is ultrasonic treatment with NMP at 40 °C for 15 min.

3) The optimum leaching conditions for the separated electrode materials are 2 mol/L H_2SO_4 , 1:2 H_2O_2 : H_2SO_4 molar ratio, 70 °C, 1:10 initial S:L ratio, and 1h. Above 99% of Co, Ni, Mn and Li, 95% of iron are leached in this condition.

4) The Fe-removing condition is optimized to be initial pH value 2.0–2.5 adjusted by adding 18% Na_2CO_3 solution, temperature 90 °C and stirring time 3h. In this condition, above 99.5% of iron is removed and the loss of Co, Ni, Mn is less than 1%, respectively.

5) After adjusted to be equal by adding NiSO_4 , CoSO_4 and MnSO_4 solution, 97.1% of Ni, Co, Mn in the Fe-removing surplus leaching solution can be recovered as $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}(\text{OH})_2$. 94.5% of Li in the surplus filtrate after the deposition of Co, Ni and Mn can be recovered as Li_2CO_3 . The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, prepared from the recovered compounds, is found to be having good characteristics of the layered structure and electrochemical performance.

References

- [1] CASTILLO S, ANSART F, LABERTY-ROBERT C, et al. Advances in the recovering of spent lithium battery compounds [J]. *J Power Sources*, 2002, 112(1): 247–254.
- [2] CONTESTABILE M, PANERO S, SCROSATI B. A laboratory-scale lithium-ion battery recycling process [J]. *J Power Sources*, 2001, 92(1): 65–69.
- [3] ZHANG Ping-wei, YOKOYAMA T, ITABASHI O, et al. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries [J]. *Hydrometallurgy*, 1998, 47: 259–271.
- [4] NAN Jun-min, HAN Dong-mei, ZUO Xiao-xi. Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction [J]. *J Power Sources*, 2005, 152(1): 278–284.
- [5] WANG Xiao-feng, KONG Xiang-hua, ZHAO Zeng-ying. Recovery of noble metal lithium ion batteries [J]. *Battery Bimonthly*, 2001, 31(1): 14–15. (in Chinese)
- [6] SHEN Yong-feng. Recovery cobalt from discarded lithium ion cells [J]. *Nonferrous Metals*, 2002, 54(4): 69–71. (in Chinese)
- [7] KIM D S, SOHN J S, LEE C K, et al. Simultaneous separation and renovation of lithium cobalt oxide from the cathode of spent lithium ion rechargeable batteries [J]. *J Power Sources*, 2004, 132(1/2): 145–149.
- [8] RA D, HAN K S. Used lithium ion rechargeable battery recycling using Etoile-Rebatt technology [J]. *J Power Sources*, 2006, 163(1): 284–288.
- [9] LUPI C, PASQUALI M. Electrolytic nickel recovery from lithium-ion batteries [J]. *Minerals Engineering*, 2003, 16(6): 537–542.
- [10] NAN Jun-min, HAN Dong-mei, YANG Min-jie, CUI Ming, HOU Xian-lu. Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries [J]. *Hydrometallurgy*, 2006, 84: 75–80.
- [11] XIE Fu-biao. Practice on comprehensive recovery of valuable metals from cobalt-bearing wastes [J]. *Mining & Metallurgy*, 2001, 10(3): 61–64. (in Chinese)
- [12] WANG Yan, ZHOU Chun-shan. Study on the separation of cobalt, iron and manganese from the leach solution of sulphated calcined cobalt residue [J]. *Chemical World*, 2001(6): 289–305. (in Chinese)
- [13] XIAO Jin-e. Quality control for production of cobalt oxide [J]. *Non-ferrous Smelting*, 1994(2): 26–29. (in Chinese)
- [14] OHZUKU T, UEDA A, NAGAYAMA M. Electrochemistry and structural chemistry of LiNiO_2 (R3m) for 4 volt secondary lithium cells [J]. *J Electrochem Soc*, 1993, 140(7): 1862–1870.
- [15] OHZUKU T, MAKIMURA Y. Layered lithium insertion material of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for lithium ion batteries [J]. *Chem Lett*, 2001, 642–644.
- [16] SHAJU K M, SUBBA RAO G V, CHOWDARI B V R. Performance of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as cathode Li-ion batteries [J]. *Electrochim Acta*, 2002, 48(2): 145–151.

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