



An innovative approach to recover the metal values from spent lithium-ion batteries



S.P. Barik*, G. Prabakaran, B. Kumar

Department of R&D, Attero Recycling Pvt. Ltd, Roorkee, Uttarakhand 247661, India

ARTICLE INFO

Article history:

Received 16 August 2015

Revised 29 October 2015

Accepted 1 November 2015

Available online 6 November 2015

Keywords:

Lithium-ion batteries

Recycling

Washing

Precipitation

Roasting

ABSTRACT

A new approach to recover metal values from spent lithium-ion batteries with a simple and environmentally friendly method is investigated. Two stages of water washing of the mixed black powder resulted in satisfactory separation of cobalt and lithium. Lithium in the wash liquor is precipitated using saturated sodium carbonate solution. Cobalt oxide in the residue is purified by removing organic matrix through roasting followed by dilute acid washing. The purities of the products obtained during the processes are analyzed by Microwave Plasma-Atomic Emission Spectrophotometer and confirmed from X-ray diffraction analysis. The overall process is safe, economic and can be scaled up for commercial production. Based on the process steps involved, a flow sheet is proposed for industrial application.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Managing electronic waste (E-waste) is one of the most rapidly growing pollution problems worldwide. E-waste consists of a large variety of materials, some of which contains a range of toxic as well as valuable metals that can contaminate the environment and threaten human health if not managed appropriately. Lithium-ion battery (LIB), one of such E-waste has grown rapidly due to dominating implementation of new technologies in electronics, consumer attractive designs and requirements of day-to-day life. In addition, enhanced performances of LIBs (high energy density, high power density and long service life than other rechargeable batteries) and restrictions on the use of Ni–Cd batteries have shown a rapid growth on the consumption of LIBs (Espinosa et al., 2004; Li et al., 2010). The growing rate of consumption of LIBs is an indication for environmental hazards at the end of life unless it is recycled properly (Hunt, 2015). In the recycling process of LIBs, major components such as cathode material (lithium metal oxide), anode (graphite), polymer electrolyte, separator (PVDF), metal casing, plastics and electronic control unit are to be separated and converted into a reusable material (Gaines and Cuenca, 2000; Wakiyara and Yamamoto, 1998; Contestabile et al., 2001). In addition, recycling of LIBs preserves the primary resources for the future by recovering valuable metals associated with it and

keeps the environment clean. Moreover, recycling of LIBs is attractive for commercial production as it is free from siliceous matrix and its high concentration of metal ions compared to the primary sources.

A wide variety of methods for recovering the valuable metals from spent LIBs using pyrometallurgical, hydrometallurgical and the combination of both processes have been reported (Kang et al., 2010; Espinosa et al., 2004; Ferreira et al., 2009; Provazi et al., 2011; Wang et al., 2009; Li et al., 2012, 2009). The pyrometallurgical processes are adopted and commercialized by different organizations (Inmetco, Xstrata, and Umicore). In this process, the binder and organic electrolyte are usually burnt off prior to further processing, which is not economical due to high energy consumption. In addition, lithium and aluminum are lost in the slag (Maschlara et al., 2012). In the case of hydrometallurgical processes, the steps generally involved are crushing, physical separation, acid leaching (inorganic or organic) with or without additives and precipitation or solvent extraction. Leaching of the cathodic active material with inorganic acids such as H₂SO₄ (Meshram et al., 2015; Kang et al., 2010; Jha et al., 2013), HCl (Wang et al., 2009) and HNO₃ (Lee and Rhee, 2003) have also been reported. Apart from inorganic acids, organic acids such as malic acid, oxalic acid, ascorbic acid and citric acid with or without H₂O₂ have also been investigated (Li et al., 2010, 2012, 2014; Sun and Qiu, 2012). More than 95% of leaching efficiency was achieved for all the metals and organic acids found to be better than inorganic acids. Though organic acids gave a better leaching efficiency, but no separation study of the dissolved metal ions was reported.

* Corresponding author.

E-mail addresses: spbarik@gmail.com (S.P. Barik), prabakaran_g@yahoo.co.in (G. Prabakaran).



Fig. 1. Different components of dismantled spent lithium-ion battery.

Table 1

Basic components and weight distribution of battery.

Sl. no.	Components	Weight (g)	%
1	External covering	11.57	2.31
2	Aluminum casing	85.70	17.14
3	Aluminum foil with paste	180.18	36.03
4	Copper foil	36.09	7.21
5	Plastics	8.94	1.78
6	Electronic parts (PCB)	5.47	1.09
7	Black powder	94.36	18.87
8	Others	77.69	15.53

Table 2

Composition of black powder.

Element	Co	Li	Ni	Mn	Al	Cu	Fe	Acid insoluble
%	19.25	2.36	0.09	0.05	0.57	0.61	0.05	74.33

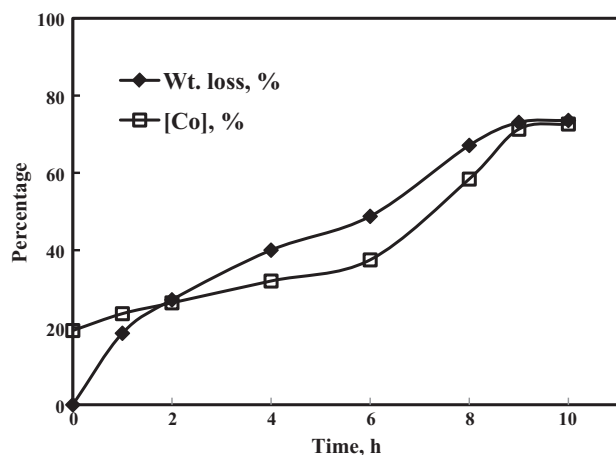


Fig. 2. Effect of roasting of the dried black powder.

Most of the reported hydrometallurgical processes aimed to recover the target metals like Co, Ni and Mn from the cathodic active material (LiCoO_2) without considering the other metals (Li, Cu and Al) of spent LIBs. Thus, there is need for a process which meets the following requirements: (i) methods for recovering all the metal values, (ii) economically feasible, (iii) environmentally safe, (iv) simple and easily scalable.

Table 3

Effect of dilute acid on washing of impure cobalt oxide.

Sample	Element	Co	Li	Ni	Mn	Al	Cu	Fe
Impure Cobalt oxide	%	72.63	2.41	BDL	BDL	0.45	0.49	0.25
HCl washing	g/L	0.39	1.33	BDL	BDL	0.84	0.29	0.12
H_2SO_4 washing	g/L	0.32	1.36	BDL	BDL	0.46	0.03	0.03

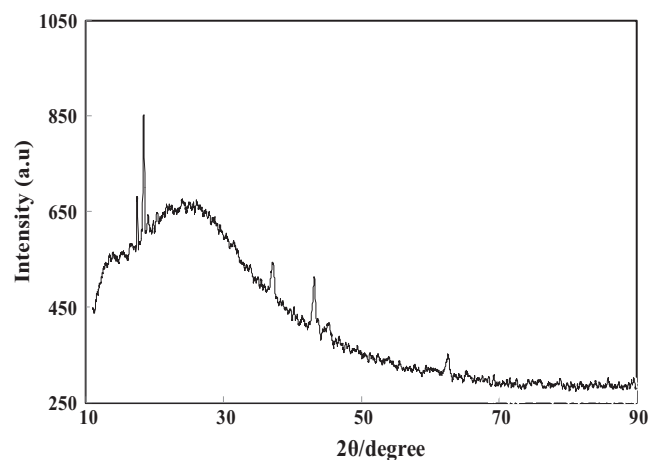


Fig. 3. X-ray diffraction pattern (XRD) of recovered cobalt oxide from spent lithium-ion battery.

Based on the above issues raised in the existing methods, this study is focused on finding an environmentally friendly and commercially feasible recycling process to recover all the metal values from LIBs.

2. Materials and methods

2.1. Materials

The spent lithium-ion batteries (LIBs) of 500 g having different mAh values used for the study were collected from the dismantling section of the Attero Recycling Pvt. Ltd., India. Commercial grade of soda ash, sulphuric acid and hydrochloric acid were used for the study. All chemical analyses were done by using LR grade acids. Activated charcoal used was of laboratory reagent grade (M.B. value 220).

Table 4

Chemical specification of cobalt oxide (a) and lithium carbonate (b).

	Co	Cu	Li	Pb	Mn
Commercial product (a) ^a (%)	78	0.005	NA	0.005	0.005
		Al	Ni	Fe	Zn
		NA	0.01	0.01	0.005
Purified product (%) (a) (This work)	76.2	0.35	1.09	BDL	BDL
		Al	Ni	Fe	Zn
		0.31	BDL	0.19	BDL
Commercial product (b) ^b (%)	18.72	0.0002	0.0005	0.0005	0.0002
		Ni	Fe	Zn	Co
		NA	0.0002	NA	NA
Purified product (%) (b) (This work)	18.68	BDL	BDL	BDL	0.1
		Ni	Fe	Zn	Co
		BDL	BDL	BDL	BDL

BDL – Below detection limit; NA – Not available.

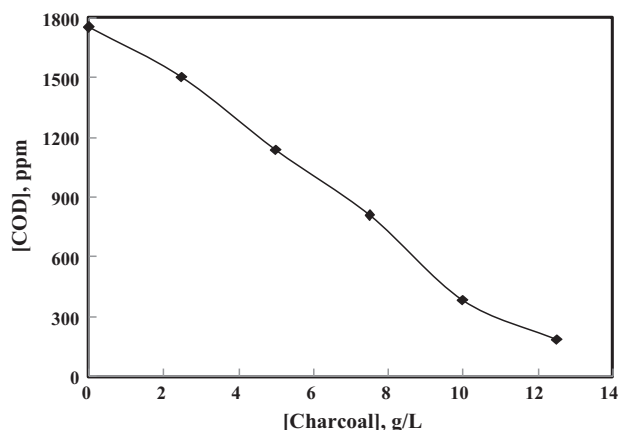
^a <http://www.huayou-intl.com/cobalt-oxide-78.htm>.^b http://lithium-chemical.com/product/?32_320.html.

2.2. Component collection and sample preparation

The collected LIBs were opened by simply removing the external covers followed by cutting their cases. The different components of LIBs such as plastics, PCBs, Teflon, aluminum covering and foil, copper foil and the electrode material (black powder) were separated manually. Fig. 1 represents the different components of the manually dismantled and separated from spent batteries. The basic components and weight distribution (%) in batteries are given in Table 1. The black material (LiCoO₂) that pasted on the copper and aluminum foils was removed by scraping manually and taken for the further study.

2.3. Analytical methods

The cobalt and lithium contents in the collected wash liquor and residue were analyzed by Microwave Plasma-Atomic Emission

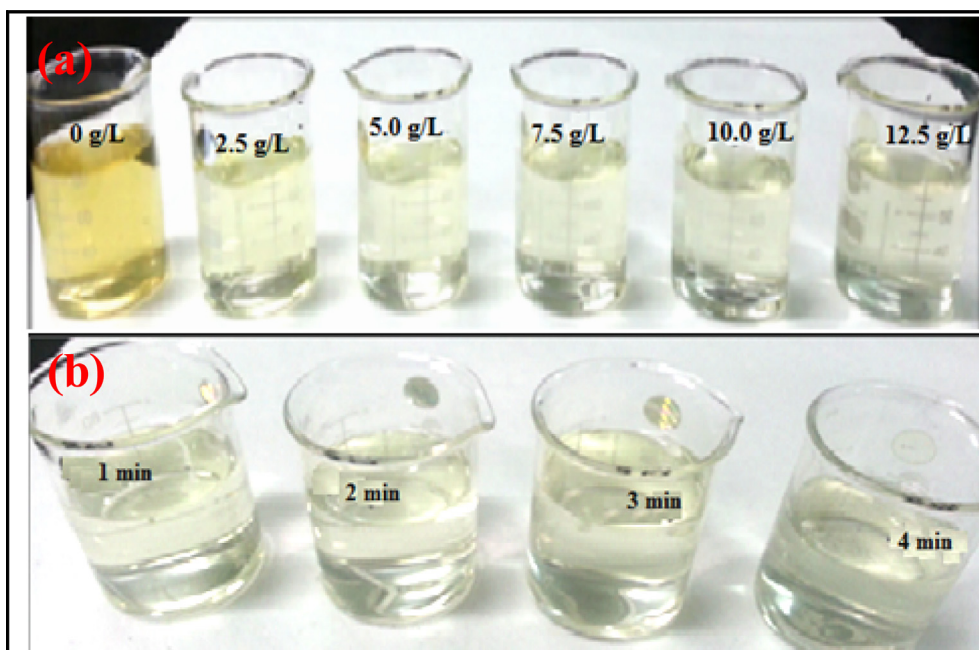
**Fig. 5.** Effect of charcoal on removing COD from lithium rich wash liquor.

Spectrophotometer (4100 MP-AES), an Agilent instrument. X-ray diffraction pattern of products obtained were investigated using a powder diffractometer (Bruker, D8 Advance) in the range of 10–80° (2θ) at a scanning rate of 2°/min. The pH values of the aqueous solutions were measured with a pH/mV meter (Model CL 54+, TOSHCON Industries Pvt. Ltd., and India). Chemically oxygen demand (COD) analysis was performed by open reflux method (APHA-5220 B). All the experiments were carried out in duplicate and the results generally agreed within ±3%.

3. Results and discussion

3.1. Washing of black material (LiCoO₂)

The black material obtained (100 g) after scrapping was washed with water (PD = 20% w/v and room temperature) in two stages. The total wash liquor and the residue obtained after washing were taken for the recovery of lithium and cobalt, respectively. The detailed composition of the residue (black powder) is shown in Table 2.

**Fig. 4.** Effect of concentration of charcoal (a) and time (b) on removing organic matrix.

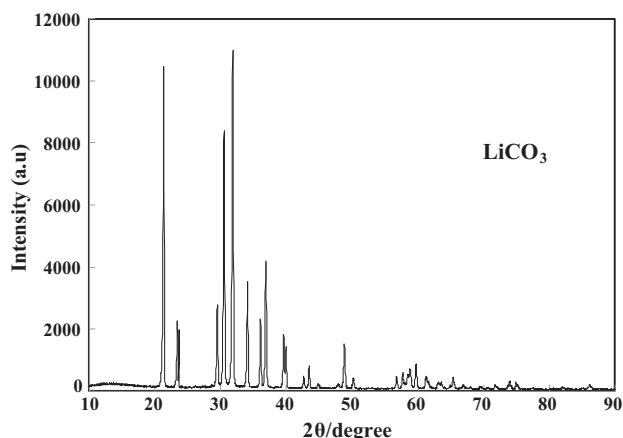


Fig. 6. X-ray diffraction (XRD) pattern of pure lithium carbonate obtained from spent lithium-ion battery.

3.2. Cobalt recovery

The primary objective is to recover cobalt and lithium from the spent LIBs. The residue obtained (as described in Section 3.1) was taken for cobalt recovery study. In the preliminary studies, the dried black powder is treated with different dilute acid solutions for removing the impurities. However, loss of cobalt along with some impurities was observed. Hence, to avoid the cobalt loss dilute acid washing was carried out after roasting.

3.2.1. Effect of roasting on cobalt recovery

Roasting study of the dried black powder was conducted by varying reaction time (1–10 h) at 900 °C. From Fig. 2, the weight of the black powder was gradually decreased from 18.5% to 73.6% with increase of reaction time from 1 h to 9 h and remained same beyond 9 h, while the cobalt content increased from 19.21% to 72.63%. The loss of weight of the black powder and the increase in cobalt content could be attributed to the decomposition of organic matter and conversion of Co_3O_4 to CoO (Brauer, 1963; Greenwood and Earnshaw, 1997).

3.2.2. Effect of dilute acid on washing

The obtained cobalt oxide was found to be consisting of some minor impurities like lithium, copper, aluminum, manganese and iron. In order to remove these impurities, washing was carried out with water (PD 20% w/v) by maintaining pH 2.5 using two different dilute acids (hydrochloric and sulphuric acid, 10% v/v). The results are presented in Table 3. From the results, it is observed that larger fraction of impurities are removed in the case of hydrochloric acid than that of sulphuric acid and around 0.5% loss of cobalt was observed in both the cases of acid washing. Hence, dilute hydrochloric acid was chosen for the purification of impure cobalt oxide. The obtained pure cobalt oxide was subjected to X-ray diffraction analysis which is shown in Fig. 3. The major peaks at 2θ values (36.86), (42.82) and (62.17) correspond to the hkl values (111), (200) and (220), respectively are of CoO . It is a cubic type structure and the pattern is in good agreement with the JCPDS card No. 43-1004. The other two peaks at 2θ values (18.21) and (18.34) are due to the traces amount of LiCoO_2 (Jha et al., 2013), which was again confirmed from the chemical analysis of the

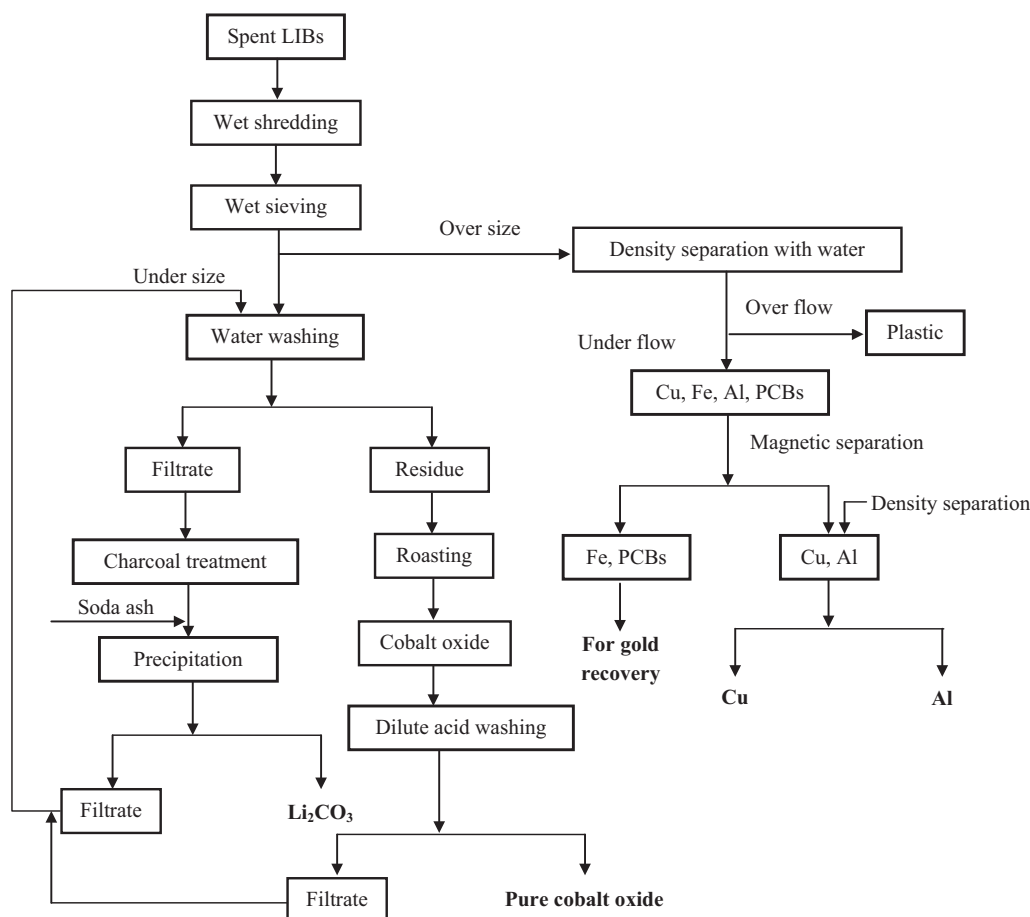


Fig. 7. Proposed flow sheet for the processing of spent lithium-ion batteries.

obtained cobalt oxide (Table 4). The purity of the obtained cobalt oxide was analyzed by MP-AES which was found to be 97%.

3.3. Lithium recovery

Lithium rich wash liquor (LiOH) was pale brown in color which was peculiar. Shuva and Kurny (2013) reported regarding the impurities (binder, adhesives, etc.) in lithium carbonate. Based on the abnormal color and earlier report by Shuva and Kurny (2013), the lithium rich wash liquor might be associated with some amount of organic matter. To remove the organic content, it was treated with activated charcoal.

The consumption of amount of charcoal and the time required for removing organic content from the lithium rich wash liquor was studied in the range of 2.5–12.5 g/L and 1–4 min, respectively. The results are presented in Fig. 4a. From the results (Fig. 4a), it is observed that the intensity of the color¹ of the wash liquor decreased with increase in concentration of charcoal and became colorless at 12.5 g/L of activated charcoal. To quantify the effect of charcoal, COD analysis was carried out which was presented in Fig. 5. The time required for chemisorptions of the organic content from the wash liquor was varied (1–4 min) by keeping the charcoal concentration of 12.5 g/L. The results are presented in Fig. 4b. As can be seen from Fig. 4b, the intensity of color of the wash liquor was decreased and became colorless at 4 min. Thus 12.5 g/L of charcoal and 4 min of time is sufficient for complete removal of the organic content which was confirmed by COD analysis.

Lithium from the charcoal treated wash liquor (Li, 2.5 g/L) was precipitated by heating with saturated sodium carbonate solution (Shuva and Kurny, 2013). The precipitation efficiency was 91%. The solid obtained was washed with hot water and dried at 110 °C for 2 h. The dried solid mass was characterized by X-ray diffraction analysis and the diffraction pattern is shown in Fig. 6. The major peaks at 2θ values (21.32), (30.61), (31.80) and (36.95) correspond to the hkl values (110), (202), (002) and (311), respectively are of Li_2CO_3 . It is a monoclinic type structure and this pattern is in good agreement with the JCPDS card No. 22-1141 and the previous reports (Zemann, 1957; Swanson et al., 1970). The diffraction pattern was much better compared to the earlier report by Shuva and Kurny (2013), which is due to the removal of other matrices (binder, adhesives, etc.) from lithium carbonate. The purity was analyzed and found to be 99.7%.

Finally, the specifications of both commercially available and the products obtained by this study are compared and the results are listed in Table 4. Based on the above study, a complete process flow sheet (Fig. 7) has been proposed to recover other components of the LIBs such as Teflon, plastics, aluminum, steel and PCBs for commercial application.

4. Conclusions

We studied the processing of the spent lithium-ion batteries in detail. The preliminary results suggest that the process developed in our laboratory is of practical interest since it gives promises of obtaining a good recovery of the battery components by efficient and easily achievable operations. The following conclusions were drawn from the above study.

- (i) Lithium and cobalt from the spent LIBs are separated through a two stages of water washing.
- (ii) Residue containing cobalt was roasted to remove the organic content and the optimum roasting condition was 9 h at 900 °C.

- (iii) Other minor impurities are removed by acid washing and hydrochloric acid was the better washing medium compared to sulphuric acid.
- (iv) 12.5 g/L of char coal and 4 min of time was sufficient for the removal of organic content from the lithium rich wash liquor.
- (v) X-ray diffraction patterns confirm the monoclinic and cubic structures of Li_2CO_3 and CoO, respectively.

Further studies for testing the commercial feasibility of the above process are under progress.

Acknowledgement

The authors are grateful to Mr. Nitin Gupta, CEO, Attero Recycling Pvt. Ltd., Roorkee for providing facilities to carry out the study and his kind permission to publish this article.

References

- Brauer, G., 1963. *Handbook of Preparative Inorganic Chemistry*, second ed. Academic Press, NY, pp. 1520.
- Contestabile, M., Panero, S., Scrosati, B., 2001. A laboratory-scale lithium battery recycling process. *J. Power sources* 92, 65–69.
- Espinosa, D.C.R., Bernardes, A.M., Tenório, J.A.S., 2004. An overview on the current processes for the recycling of batteries. *J. Power Sources* 135, 311–319.
- Ferreira, D.A., Prados, L.M.Z., Majuste, D., Mansur, M.B., 2009. Hydrometallurgical separation of aluminum, cobalt, copper and lithium from spent Li-ion batteries. *J. Power Sources* 187 (1), 238–246.
- Gaines, L., Cuenca, R., 2000. Costs of Lithium-Ion Batteries for Vehicles. United States Department of Energy, Center for Transportation Research: Energy Systems Division, Argonne National Laboratory, Argonne.
- Greenwood, N.N., Earnshaw, A., 1997. *Chemistry of the Elements*, second ed. Butterworth-Heinemann, pp. 1118. ISBN 0080379419.
- Hunt, T., 2015. <<http://www.greentechmedia.com/articles/read/Is-There-Enough-Lithium-to-maintain-the-Growth-of-the-Lithium-Ion-Battery-M>>.
- Jha, M.K., Kumari, A., Jha, A.K., Kumar, V., Hait, J., Pandey, B.D., 2013. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *Waste Manage.* 33 (2013), 1890–1897.
- Kang, J.G., Senanayake, G., Sohn, J., Shin, S.M., 2010. Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272. *Hydrometallurgy* 100, 168–171.
- Lee, C.K., Rhee, K.I., 2003. Reductive leaching of cathodic active materials from lithium ion battery wastes. *Hydrometallurgy* 68 (1–3), 5–10.
- Li, L., Ge, J., Chen, R., Wu, F., Chen, S., Zhang, X., 2010. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manage.* 30, 2615–2621.
- Li, J.H., Shi, P.X., Wang, Z.F., Chen, Y., Chang, C.C., 2009. A combined recovery process of metals in spent lithium-ion batteries. *Chemosphere* 77 (8), 1132–1136.
- Li, L., Zhai, L., Zhang, X., Lu, J., Chen, R., Wu, F., Amine, K., 2014. Recovery of valuable metals from spent lithium-ion batteries by ultrasonic-assisted leaching process. *J. Power Sources* 262, 380–385.
- Li, L., Lu, J., Ren, Y., Zhang, X., Chen, R., Wu, F., Amine, K., 2012. Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. *J. Power Sources* 218, 21–27.
- Maschlara, T.G., Friedricha, B., Weyheb, R., Heegnc, H., Rutzc, M., 2012. Development of a recycling process for Li-ion batteries. *J. Power Sources* 207, 173–182.
- Meshram, P., Pandey, B.D., Mankhand, T.R., 2015. Recovery of valuable metals from cathodic active material of spent lithium ion batteries: Leaching and kinetic aspects. *Waste Manage.* 45, 306–313.
- Provazi, K., Campos, B.A., Espinosa, D.C.R., Tenorio, J.A.S., 2011. Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. *Waste Manage.* 31, 59–64.
- Shuva, A.H., Kurny, A.S.W., 2013. Hydrometallurgical recovery of value metals from spent lithium ion batteries. *Am. J. Mater. Eng. Technol.* 1, 8–12.
- Sun, L., Qiu, K., 2012. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. *Waste Manage.* 32, 1575–1582.
- Swanson, H.E., McMurdie, H.F., Morris, M.C., Evans, E.H., 1970. Standard X-ray Diffraction Powder Patterns. Nat. Bur. Stand. (U.S.), Monogr. 25 Sections 8, pp. 42.
- Wakihara, M., Yamamoto, O., 1998. *Lithium Ion Batteries Fundamentals and Performance*. Kodansha Ltd., Tokyo.
- Wang, R.C., Lin, Y.C., Wu, S.H., 2009. A novel recovery process of metal values from the cathode active materials of the lithium-ion secondary batteries. *Hydrometallurgy* 99 (3–4), 194–201.
- Zemann, J., 1957. Die Kristallstruktur von Li_2CO_3 . *Acta Cryst.* 10, 664–666.

¹ For interpretation of color in Fig. 4, the reader is referred to the web version of this article.