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Characterization of spent lithium ion batteries in the process of recovery of value metals

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ABSTRACT

Component parts of two different types (M 660 and V 83) of spent lithium ion batteries were examined to determine the amount and nature of metal values contained. The outer casing of these batteries was found to be of aluminum alloy. Lithium and cobalt in the form of $LiCoO_2$ was the most prominent phase in the material pasted on a thin foil of Aluminium that formed the cathode while graphite pasted on a thin foil of copper formed the anode of the spent lithium ion batteries. In the paste of cathode electrode, lithium and cobalt constituted 7.09 and 60.25 percent respectively. Irrespective of the brands investigated, the average content of metal values, aluminum, lithium, copper and cobalt was 45.99 percent of the total weight of the spent batteries. The remainder was electrolyte solvent, adhesive and other impurity elements.

KEYWORDS

Li-ion battery;
Characterization;
Spent batteries;
Waste management.

INTRODUCTION

Lithium ion batteries are widely used in mobile telephones, laptops, video cameras, and other modern life appliances. Due to their characteristics of light weight, high energy and good performance these batteries are increasingly substituting for other batteries[1,2]. The lifespan of a LIB is 1-3 years. The tremendous growth in the use of LIBs has resulted in the generation of a large amount of wastes in the form of spent LIBs. Improper disposal of these batteries may cause serious environmental problems.

A LIB comprises a cathode, an anode, organic electrolyte and a separator. The cathode is a thin Aluminium foil coated with a mixture of active cathode material, electric conductor, binder and adhesives. Most lithium systems use a material like $LiXMA_2$ at the positive electrode. Some materials used at the cathode include $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ and the electrolyte is an organic liquid with dissolved substances like $LiClO_4$, $LiBF_4$ and $LiPF_6$[3-5]. The anode is a thin copper foil coated with a mixture of carbon graphite, conductor, binder and adhesives. The heavy metals, organic chemicals and plastics are in the proportions of 5 – 20% cobalt, 5 – 10% nickel, 5 – 7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers[6]. In 2000, the worldwide production of LIBs reached about 500 million cell and from this LIB waste is estimated at 200 to 500 MT, with a metal content of 5 to 15 wt.% Co and

2 to 7 wt.% Li[7]. Spent lithium batteries thus represent a valuable source for the metals present (Co, Li, Mn and Ni) or their compounds. Recycling of spent batteries may result in economic benefits[8,9]. At the same time, development of a suitable method for the recovery of values from spent LIBs can decrease the amount of wastes to be disposed and thus reduce the disposal and treatment problems.

A lot of research has been done on the development of recycling technologies of LIBs. Most of the proposed processes are based on hydrometallurgical chemistry[10,11] and recovery of lithium and cobalt is one of the primary objectives in the recycling of LIBs[12,13].

Detailed information on the exact nature and content of metal values and other component parts of a lithium ion battery is useful for the development of a suitable process for recovery of metal values from the spent LIBs. This study focuses on the determination of the nature and amount of different metals contained in two commercial type LIBs. It was expected that the results obtained will be useful for the subsequent development of a suitable process for extraction of the metal values contained is such batteries.

EXPERIMENTAL

Samples of spent lithium ion batteries of two commercially available types (M 660 and V 83) were collected from various sources. The potential voltage of all the batteries used in this study was 3.7V. The collected batteries were dismantled manually. The plastic cover of the batteries was removed by using a sharp cutting edge. It was then fixed in a vice and the metallic outside shell of the battery was removed mechanically. The different component parts were carefully separated and grouped on the basis of appearance and information available in the published literature. The weights of the different components (casing. chips, electrode etc) of five randomly selected samples were measured and the average weights were calculated. The weight proportions of the different component parts reported in this presentation are the average of the values determined on five samples. The composition of the external casing in the spent batteries was determined by optical emission spectroscopy (Shimadzu PDA 7000). The composition of the Aluminium foil of the cathode was determined by atomic absorption spectroscopy (Varian AA 240), while the amount of copper in the copper conductor was determined by wet chemical analysis. The phases present in the cathode and anode were identified by x-ray diffraction analysis. X-ray diffraction patterns were recorded in a Bruker X-Pert diffractometer using a Cu K_α (λ=1.54056 A^o) radiation source.

RESULTS AND DISCUSSION

Identification of the structural components

A dismantled lithium ion battery with its different component parts is shown in Figure 1. TABLE 1 lists the materials used in the construction of the different component parts of the batteries. This identification of the materials was based on the appearance and information available in the published literature[3].

TABLE 1 : Materials used in the construction of the different component parts (M660 and V83).

No.	Component Parts	Materials
1	External Case	Aluminum Alloy, Paper
2	Cathode	$LiCoO_2$
3	Anode	Graphite conductor
4	Electrolyte*	$LiClO_4$, $LiPF_6$
5	Electrolyte Solvent*	PC, DMC or DMC
6	Separators*	Plastics generally Polypropylene (PP), Polyethylene (PE)
7	Current Collector	Aluminum & Copper Foil
8	Current Joining*	Gold Plated Pad
9	Printed circuit board(PCB)	Component etc

*Identified on the basis of information available[3].

Weight percentage analysis

TABLES 2 and 3 give the weight and the relative proportions of the different component parts in spent lithium ion batteries of the types M 660 and V83 respectively. TABLE 4 shows a comparison of weights of the different components parts of the two types of batteries. Variations in the weight proportions of the different component parts of the two types of batteries were noted. The weights of the different component parts of the same type of spent batteries were also found to vary. These variations in the weight of the whole battery and in the weight proportions of the different component parts of the spent batteries could be attributed to the difference in the physical condition of the battery when collected and mechanical loss and contamination during the manual dismantling of the batteries.

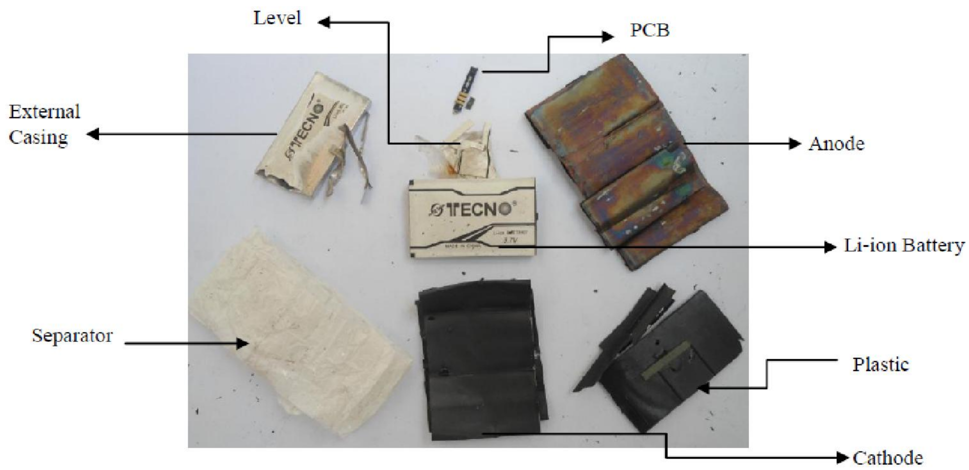

Figure 1 : A dismantled spent lithium ion battery.

TABLE 2 : Percentage weight analysis of different parts in M 660 type spent lithium ion battery.

SL.NO	Potential Voltage	Weight (gm)	Level for Branding (gm)	Ext. Casing (gm)	Chip of Circuit (gm)	Plastic Material (gm)	Cathode (gm)	Al-Foil (gm)	Anode (gm)	Cu-Foil (gm)
1	3.7V	29.599	0.504	4.821	0.399	3.574	10.551	1.107	7.284	0.869
2	3.7V	30.341	0.507	4.823	0.401	3.643	10.735	1.213	7.714	0.988
3	3.7V	30.807	0.497	5.063	0.387	3.663	10.953	1.113	7.936	1.092
4	3.7V	30.891	0.493	4.912	0.391	3.625	10.961	1.019	8.023	1.126
5	3.7V	31.065	0.529	4.826	0.397	3.630	11.354	1.158	8.163	1.195
Av.Wt	-	30.540	0.506	4.889	0.395	3.627	10.910	1.122	7.824	1.054
Wt%	-0.75	100	1.66	16.01	1.29	11.88	35.73	3.64	25.60	3.45

TABLE 3 : Percentage weight analysis of different parts in V 83 type spent lithium ion battery.

SL.NO	Potential Voltage	Weight (gm)	Branding Level(gm)	External Casing(gm)	Chip of Circuit(gm)	Plastic Material(gm)	Cathode (gm)	Al-Foil (gm)	Anode (gm)	Cu-Foil (gm)
1	3.7V	23.787	0.499	3.206	0.379	3.174	7.899	0.967	5.785	0.869
2	3.7V	24.507	0.507	3.523	0.401	3.263	8.535	0.983	5.812	0.918
3	3.7V	24.610	0.493	3.363	0.385	3.463	8.853	0.967	5.892	0.927
4	3.7V	23.852	0.495	3.512	0.391	3.319	8.354	0.965	5.797	0.895
5	3.7V	24.879	0.519	3.626	0.397	3.256	8.836	1.053	5.906	0.956
Av. Wt		24.327	0.503	3.446	0.391	3.295	8.495	0.987	5.838	0.913
Wt (%)	-1.89	100	2.06	14.17	1.61	13.54	34.92	4.06	24	3.75

TABLE 4 : Comparison of weights of the different components parts of the two types of batteries.

Components	M 660	V 83
Whole battery	30.540 gram	24.327 gram
Level for Branding	0.506	0.503
External Casing	4.887	3.446
Chip of Circuit	0.395	0.391
Plastic Material	3.627	3.295
Cathode Electrode	10.910	8.495
Aluminum Foil (25μm)	1.122	0.987
Anode Electrode	7.824	5.838
Copper Foil (25μm)	1.054	0.913
Loss	0.215	0.458

Composition of the outer casing

The chemical compositions of external casing of the two types of spent lithium ion batteries selected for this investigation were determined by optical emission spectroscopy and were essentially the same (TABLE 5). The material may be classified as commercially pure Aluminium with the usual impurity elements.

TABLE 5 : Optical emission spectroscopic analysis of the casing of spent lithium ion battery.

Elements	Na	Si	P	S	Cl	Al	Cr	Mn	Fe	Ni	Cu	V	Ti
Wt% (M 660)	-	0.20	-	-	-	98.3	0.02	0.72	0.54	0.08	0.06	0.01	0.04
Wt% (V 83)	-	0.21	-	-	-	98.4	0.03	0.70	0.49	0.04	0.07	0.01	0.03

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Estimation of aluminum in aluminum foil

The thickness of the Aluminium foil in both the types of batteries under investigation was 25 μm. The amount of aluminum in the aluminum foil was determined by Atomic Absorption Spectroscopy (AAS). The amount of aluminum in the foil of M660 type battery was found to be 98.90% while the amount of Aluminium in the foil of V 83 type battery was found to be and 98.66%. Aluminum foil used as current collector is expected to be 100 percent pure. The presence of impurities in the Aluminium foil of the spent batteries may be attributed to the physical contamination during the manual dismantling process. Aluminum could also have been contaminated by oxidation when the coating material was removed.

Estimation of copper in copper foil

The thickness of copper foil in both the types of batteries was 25μm. The amount of copper in copper foil was determined by wet chemical analysis. In the M 660 type battery the amount of copper was found to be 99.06% while the amount of copper in the V83 type battery was found to be 98.86%. In good agreement with the results of wet chemical analysis, the X-ray diffraction patterns of the copper foils did not indicate the presence of impurities (Figure 2).

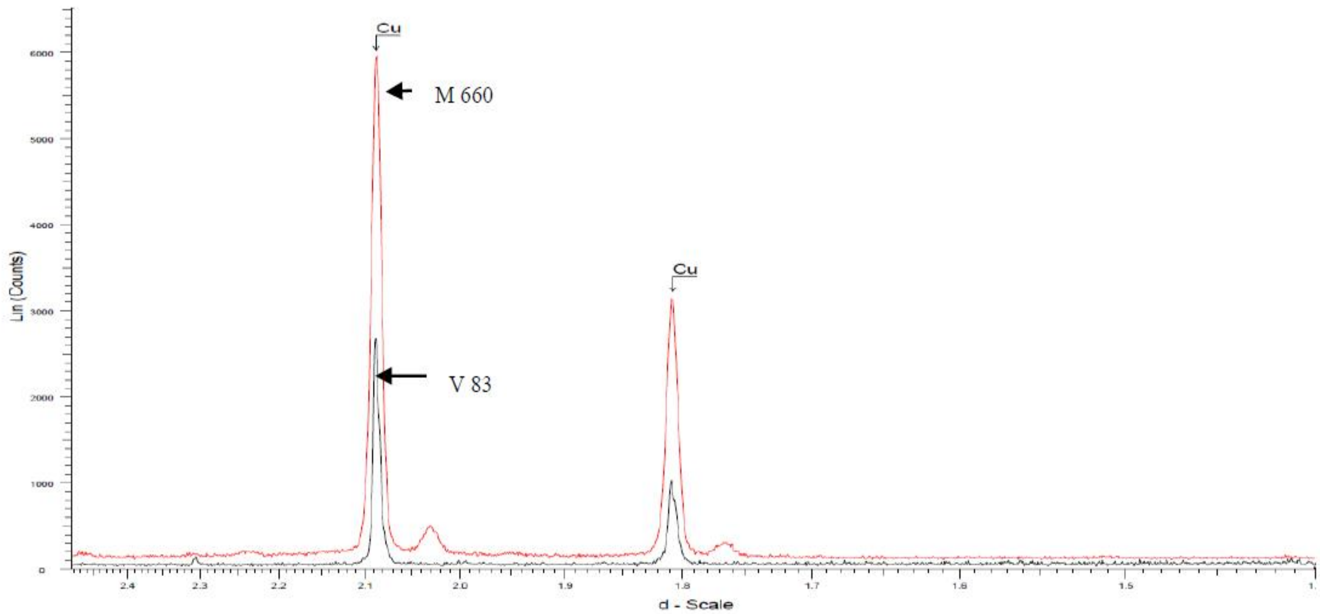

Figure 2 : X-ray diffraction analysis of copper foil of lithium ion battery.

Characterization of the cathode

The composition of the paste on the cathode could not be determined by the x-ray fluorescence analysis as lithium was present as compound. The x-ray diffraction analysis, performed to identify the phases present in the paste, showed the presence of Li and Co in the form of $LiCoO_2$ as the major constituent (Figure 3 and Figure 4). The intensity (counts) of the intense diffraction lines in the pattern of M 660 battery was much higher than those in the V83 battery. The most intense peaks in the diffraction patterns of both the batteries occurred at almost the same angle, at near 19^0 and at 46^0. These peaks correspond to $LiCoO_2$. The patterns also contained some diffraction lines that could not be identified. These diffraction lines also occurred at the same angles in the cathodic paste of both the batteries. In the figures, these lines have been marked as “U” and might be due to the binders or additives mixed with the active cathode material to facilitate its adhesion to the aluminum foil. It was thus inferred that Li and Co was present in the cathodes of lithium ion batteries in the form of lithium cobalt oxide.

Characterization of the anode

The most intense peaks in the x-ray diffraction patterns recorded the material pasted on an anode of a spent lithium ion battery (Figure 5) occurred at near 31.24^0 and at 51.56^0. These lines correspond to graphite. The diffraction lines that could not be identified has been marked as “U” and might be related to the additives or binders that were used to facilitate pasting of the active material on to the copper foil.

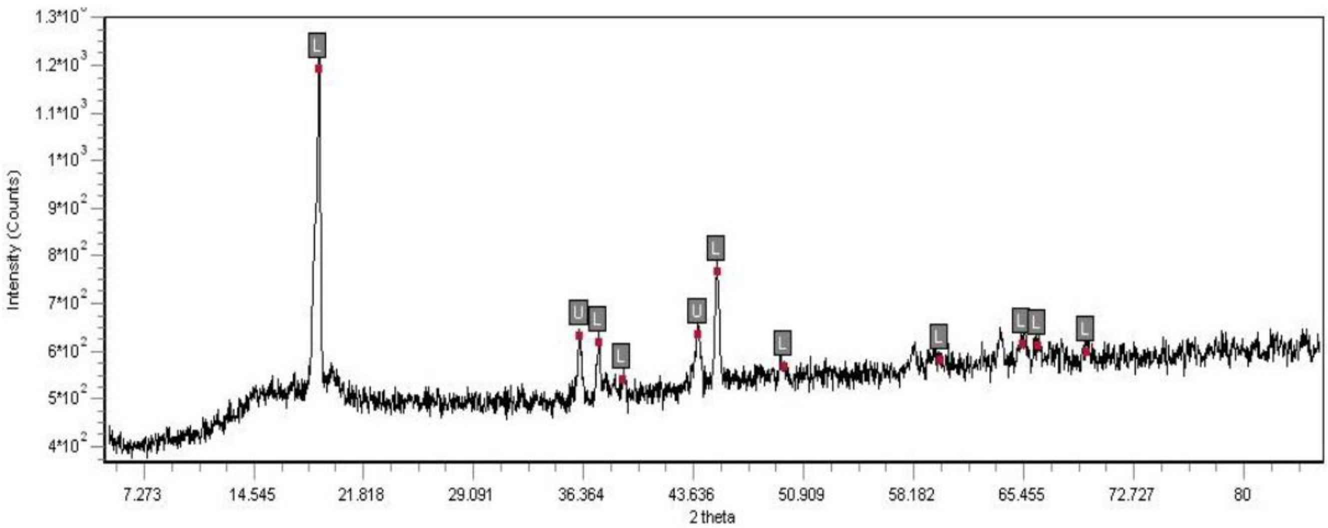

Figure 3 : X-ray diffraction analysis of cathode electrode of M 660 lithium ion battery.

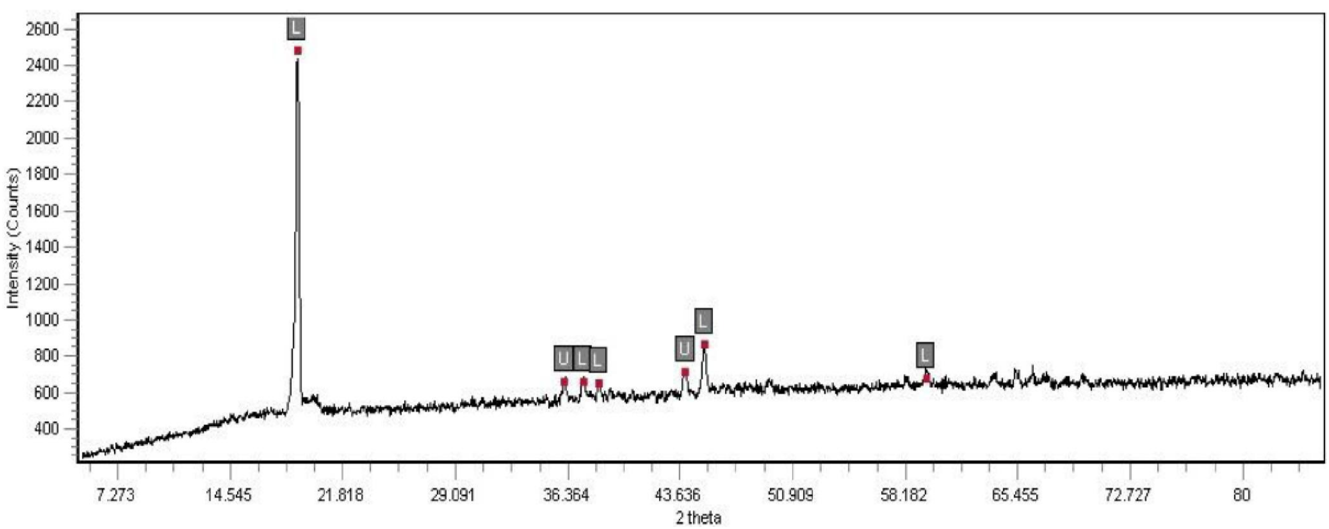

Figure 4 : X-ray diffraction analysis of cathode electrode of V 83 lithium ion battery.

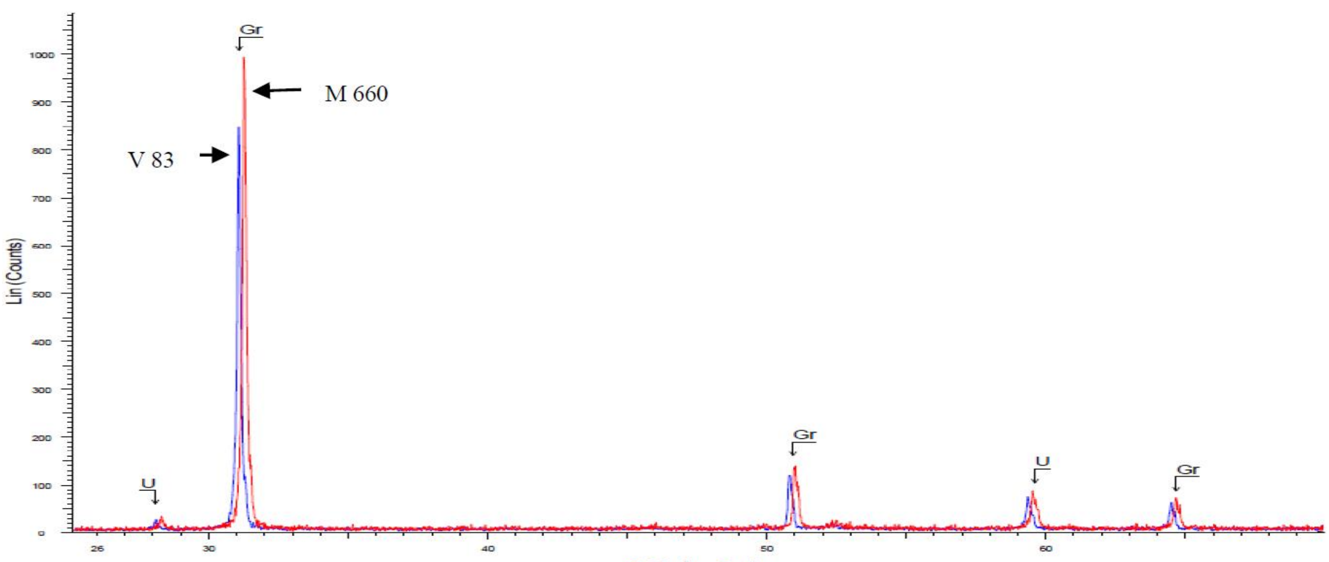

Figure 5 : X-ray diffraction analysis of anode electrode of lithium ion battery.

TABLE 6 : Average metal proportions in the spent M 660 & V 83 lithium ion batteries*.

Types	Spent Lithium ion Battery							Total value metals			
	Total Weight (gm)	Al casing (gm)	Al Foil (gm)	Amount of Al (gm)	Cu Foil (gm)	Amount of Li in Cathode(gm)	Amount of Co in Cathode(gm)	Total Al %	Total Li%	Total Cu %	Total Co %
M 660	30.540	4.804	1.09	5.786	1.04	0.774	6.57	19.29	2.53	3.41	21.51
V 83	24.327	3.390	0.97	4.282	0.90	0.602	5.12	17.92	2.47	3.69	21.05
Weighted Average								18.64	2.51	3.53	21.31

Total value metal percentage

The average values of the metal contents of the whole battery in lithium ion spent types are given in TABLE 6. Lithium was found to be around 2.5 percent and cobalt around 21.3 percent of the total weight of the battery in spent types. LIBs constituted aluminum around 18.64 percent and copper around 3.53 percent of the total weight. The remaining part is occupied by the carbon, PCB, plastics, adhesive and other minor elements.

CONCLUSIONS

This study on the characterization of spent lithium ion batteries yielded the following results:

1. Pure aluminum and copper in the form of thin foils act as current collector in cathode and anode respectively.
2. $LiCoO_2$ was found to be the prominent component of the active material of the cathode of lithium ion batteries, while graphite was the active material of the anode.
3. Lithium and cobalt content was 23.82 percent of the total weight of the battery. Aluminum and copper constituted about 18.64 percent and 3.53 percent of the total weight of the battery.

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REFERENCES

[1] A.Lundblad, B.Bergman; Synthesis of $LiCoO_2$ starting from carbonate precursors. Solid State Ionics, **96**, 183-193 **(1997)**.

[2] E.Plichta, M.Salomon; Rechargeable Li/$LixCoO_2$ cell. J.Power Sources, **21**, 25-31 **(1987)**.

[3] A.M.Bernardes, D.C.R.Espinosa, J.A.S.Teniorio; J.Power Sources, **130**, 291-298 **(2004)**.

[4] Q.Wu, W.Lu, J.Prakash; J.Power Sources, **88(2)**, 237-242 **(2002)**.

[5] J.Chen, C.Yao, S.Sheu, Y.G.Chiou, H.C.Shih; J.Power Sources, **68(2)**, 242-244 **(1997)**.

[6] S.M.Shin, N.H.Kim, J.S.Sohn, D.H.Yang, Y.H.Kim; Hydrometallurgy, **79**, 172-181 **(2005)**.

[7] C.K.Lee, Kang-In Rhee; Reductive leaching of cathodic active materials from lithium ion battery wastes, Hydrometallurgy, **68**, 5 -10 **(2003)**.

[8] B.R.Conard; Hydrometallurgy, **30**, 1-28 **(1992)**.

[9] H.Zhong, J.Li, L.Chai; Rare Earth Metal Hard Alloy, **144**, 1-3 **(2001)**.

[10] C.Lupi, M.Pasquali; Minerals Engineering, **16**, 537-542 **(2003)**.

[11] M.Contestabile, S.Panero, B.Scrosati; J.Power Sources, **83**, 75-78 **(1999)**.

[12] J.Kondas, J.Jandova, M.Nemekova; Hydrometallurgy, **84**, 247-249 **(2006)**.

[13] P.Zhang, T.Yokoyama, O.Itabashi, T.M.Suzuki, K.Inoue; Hydrometallurgy, **47**, 259–271 **(1998)**.