Extraction of metals from spent lithium ion batteries– Role of acid, reductant and process intensification in recycling

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A comparison of various approaches evaluated to process spent lithium ion batteries to extract metals has been carried out. The leaching is carried out with sulphuric acid in the presence and absence of reductant, thus defining the role of reducing agent ($NaHSO_3$ and H_2O_2) in assisting dissolution of all metals, especially Co and Mn. As the direct process incurs all metals in solution and employs high concentration of acid, a two-step process (acid baking and leaching) has been attempted to lower acid consumption indicating benefits in the selective dissolution of metals viz., Co and Li (in 1st stage) over other metals (Ni and Mn in 2nd stage).

Rechargeable batteries are present in numerous waste electrical and electronics equipment (WEEEs). Because of significant use of critical metals in rechargeable batteries, their recycling is important[1]. Newer requirements for lighter and more powerful rechargeable energy storage systems have driven the development of lithium-ion based batteries rapidly over the last few years. Rechargeable lithium batteries are superior to all other secondary battery technologies with their high energy and power density, wide temperature range, long cycle and calendar life, lower self-discharge, fast charging rate and absence of the so-called memory effect[2]. The growing market for lithium-ion batteries (LIBs) raises concerns about sustainable management of these batteries at the end-of-life. Current recycling efforts of LIBs focus mainly on the cathode materials viz. cobalt and nickel, but largely neglect manganese and lithium even where sophisticated recycling systems are in place[3]. Lthium is generally not considered for recycling because it is cheap enough to dump old batteries and mine the virgin material.

The two main recycling routes available for Li-ion batteries are a combined mechanical and hydrometallurgical process, and a combined pyro-and hydrometallurgical process. In the mechanical-hydrometallurgical process, batteries dismantled to cell size enter a shredder as the shredding is dangerous due to the risk of explosion and release of hazardous volatile organic compounds (VOCs). Toxco (Canada) applies an energy-intensive cryogenic process to freeze the VOCs, while Recupyl (France) uses inert gases (CO_2 and Ar) to flush the shredder and prevent fire[4]. Shredding produces three fractions. The fluff (plastic and paper) goes for landfill, metals (Cu, Al, Fe) for sorting and re-melting, and the black mass [anode graphite and cathode (Co, Ni, Al, Mn, Li oxides) materials] for incineration to remove graphite and hydrometallurgical recovery of the metals.

Recycling of these spent batteries is important to address the stringent environmental regulations and also to ward off the adverse effect of mining/ brine extraction, and exploitation of such resources for virgin metal production, raw material transportation, energy consumption, etc. As a result, there is a great interest in secured supplies of metals such as Li, Ni, Co and Mn to be met from the spent batteries[5]. But the process flowsheets prevalent globally address the problem only partially because of emphasis of recovering mostly cobalt while ignoring associated metals such as Li, Ni, Mn, etc., besides dithering to the process economy and generation of the slag/sludge in turn lead giving rise to another source of waste[6]. In this paper, different aspects of leaching of spent LIBs are studied that covers the importance

of reductant as well as selective separation of metals from such raw material.

Experimental Section

Nearly 100 spent LIBs of various make used in laptops, weighing 20 kg were collected from a local service center as well as from a recycling plant and dismantled them using a manual procedure after discharge.

Dismantling of spent LIBs and analysis of cathode active material

The batteries (~20 kg) were first discharged before dismantling them manually while removing the plastics and steel case mechanically. Anode and cathode were uncurled manually, and cathode active material in the form of powder was separated from Al-foil and processed for leaching studies by various routes. The particle size of the cathode powder was determined by a laser particle size analyzer (Malvern®, UK); the particle size was found to be <60 µm and the average size being ~20 µm. The powder sample was analyzed for the phase identification by XRD (Bruker™ D8 Discover). All the chemicals used were analytical grade reagents. The chemical composition of the cathode active material shows the presence of 35.8% Co along with 6.5% Li, 11.6% Mn and 10.6% Ni along with trace amount of Cu, Al, and Fe.

Material characterisation of cathode active material

The X-ray diffraction analysis of the cathode material shows the presence of $LiCoO_2$, $Li_2CoMn_3O_8$ and $(Li_{0.85}Ni_{0.05})(NiO_2)$ as the major constituents besides this, lithium-nickel oxide of lower Li-Ni

contents, $(Li_{0.69}Ni_{0.01})(NiO_2)$ and CoF_4 were also present as the minor phases. The morphological studies have been carried out by SEM/EDS techniques. The SEM image (Fig. 1) of the cathode active material shows the presence of $LiCoO_2$ particles with irregular morphologies and wider particle size distribution. In the untreated sample, $LiCoO_2$ particles are present in irregular morphologies along with a large number of secondary particles. The particle size of the cathodic powder was determined by a laser particle size analyzer (Malvern, UK); size of the particles was found to be < 60 µm and the average size being ~20 µm (Fig. 2).

Procedure

Leaching study was carried out in a temperature controlled three necked flat bottom borosilicate glass reactor (cap. 500 mL) on hot-plate cum magnetic stirrer (IKA®) at the desired rpm. A reflux condenser was fitted to the leaching vessel to avoid the loss due to evaporation. A known amount of the battery powder was transferred to the leach solution containing the desired concentration of the sulfuric acid maintained at a preset temperature. The slurry was stirred with a magnetic needle at 500 rpm unless specified otherwise for the entire duration of the leaching. In order to examine the progress of leaching, samples were withdrawn at different time intervals and were analyzed for the metals of interest after filtration. The redox potential during the leaching was also measured in a few cases wherever it was considered necessary, using a pH meter (Toshniwal, India, CL 46+) against a saturated calomel electrode (SCE); the redox potential values presented in the thesis are shown as E_{SCE}. At the end
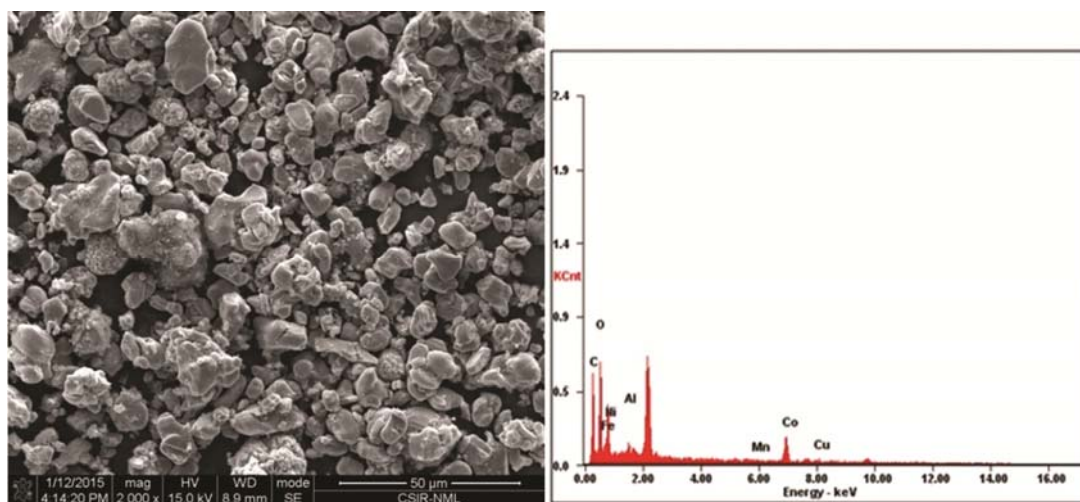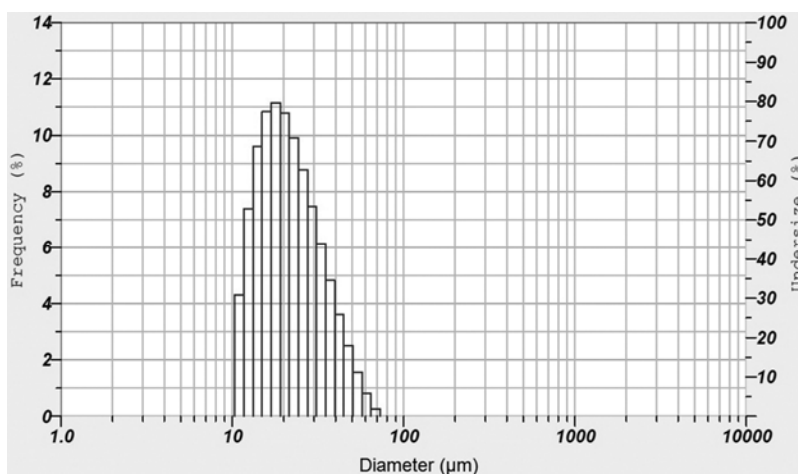

Fig.1 — SEM-EDS of cathode active material

Fig. 2 — Relative frequency distribution of LIB electrode powder vs diameter (in μm) for particle size analysis

of the leaching, the slurry was filtered over a Büchner funnel using Whatman filter paper (42 No), the residue was washed with distilled water and dried overnight at 353 K in an electric oven. The leaching efficiency was calculated by analyzing the metals in the filtrate after necessary dilution and acidification. In a few cases residues were also analyzed after digesting in the aqua-regia and adding additional acid (HCl). Satisfactory mass balance was obtained in such set of experiments. The parametric variations included amount of acid and its concentration required, effect of reducing agents and applications of process intensification steps to improve selective metal dissolution.

All the solutions generated in the leaching were analyzed by AAS (Atomic Absorption Spectrometer) and ICP-OES. Residue samples after drying were characterized by chemical analysis, SEM /EDAX and XRD analysis. The leach liquor obtained under the optimum conditions was subjected to precipitation studies to recover the leached metals using a suitable agent. Each experiment was performed two times, and the average of two replicates was considered for computing the final metal recovery.

Results and Discussions
Effect of acid concentration

In order to study the efficacy acid concentrations for the leaching of cathode active material, the concentration of H_2SO_4 was varied from 0.5 to 3 M at 368 K and 50 g/L pulp density (PD) for 240 min. As can be seen from Table 1 the leaching of metals viz., Li, Co, Ni, and Mn were almost constant with H_2SO_4 in the concentration range 1-3 M. Within 240 min, 93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn were

Table 1 — Effect of acid concentration on recovery of metals from spent LIBs

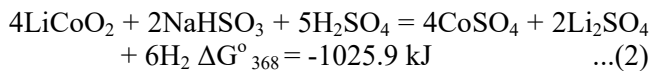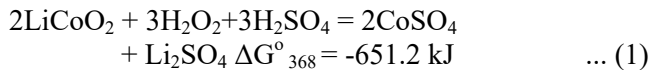| Acid conc. (M)	Li	Co	Ni	Mn
0.5	75	37.5	57.21	18.85
0.65	78.13	39.39	59.16	20.81
1	89.93	43.42	76.91	26.01
2	90.36	51.25	89.36	26.9
3	93.37	52.37	90.52	28.53

leached out with 3 M H_2SO_4 under this condition. Lower recovery of the cobalt and manganese may be attributed to the higher oxidation states such as Co^{3+} and Mn^{4+} which are not soluble in acid. The redox potential (E_{SCE}) of the solution was found to be >900 mV over the leaching period of 120 min. The leaching efficiency of cobalt and manganese depends on the concentration of reductant used. Reductant converts Co(III) or Mn(IV) to the +2 state for effective dissolution and subsequent recovery by standard methods[7,8]. Therefore, the effect of reductant is studied for leaching of cathode active powder of LIBs.

Effect of reductant concentration on the leaching of metals

Reducing agents enhance the solubility of metals which hitherto were solubilized to a lesser extent using the only acid as lixiviant. As shown in Table 2, the addition of reductant significantly improved the leaching efficiency of metals. Thus, the sulphuric acid leaching in the presence of $NaHSO_3$ comparing its efficiency with H_2O_2 has been investigated. The $NaHSO_3$ concentration slightly affects the Li and Ni recovery but recovery of Co and Mn increased from 77.1% to 92.3% and 85.3% to 88.1%, respectively, by increasing the $NaHSO_3$ concentration from 0.5% to 1.5% in 240 min. The effect of H_2O_2 amount on the

leaching of metals with 2 M H_2SO_4 indicates that the leaching efficiency increased from 55.6% to 80.2% for cobalt and 53.2% to 85.9% in 120 min for manganese as the H_2O_2 amount increased from 0.25% to 5% (Table 2). A comparison of $\Delta G^o{}_{368}$ values of - 651.2 kJ for Eq. 1 and -1025.9 kJ for Eq. 2 in the presence of H_2O_2 and $NaHSO_3$, respectively shows that $NaHSO_3$ is thermodynamically a better reductant to dissolve the major constituent ($LiCoO_2$) of the cathodic material in sulfuric acid at 368 K. This behaviour is also reflected by the lower E_{SCE} value (~400 mV) recorded experimentally with the reductant (0.075M) $NaHSO_3$ when compared with 5% H_2O_2 recording 580 mV at 368 K.

During the sulfuric acid leaching in absence or presence of a reductant, solubilization of almost all the metals takes place simultaneously without any selectivity. For selective recovery of metals, an innovative approach such as process intensification by sulfatization through the sulfuric acid baking has been explored to transform prominent metals to their sulfates, thereby resulting in selective leaching of some metals (in transformed matrix) to the bulk solution phases[9].

$$2LiCoO_2 + 3H_2O_2 + 3H_2SO_4 = 2CoSO_4$$
$$+ Li_2SO_4 \; \Delta G^o{}_{368} = \text{-651.2 kJ} \qquad ... (1)$$

$$4LiCoO_2 + 2NaHSO_3 + 5H_2SO_4 = 4CoSO_4 + 2Li_2SO_4$$
$$+ 6H_2 \; \Delta G^o{}_{368} = \text{-1025.9 kJ} \qquad ...(2)$$

SEM evaluation of the residues obtained in leaching at 368 K in 240 min using no additives (Fig. 3a) reflects the wide spread corrosion with lower levels of the metal constituents analyzed by EDAX, indicating clear possibility of surface diffusion of the lixiviant on the particles of cathode material. Fig. 3b depicts the SEM of the residue obtained in 240 min at 368 K in presence of sodium bisulfite, wherein $LiCoO_2$ particles are present in irregular morphologies yielding high Co, Li, Ni and Mn by decrease in particle size with corroded surface. For the acid leaching in presence of H_2O_2 after 120 min (Fig. 3c), minimum degree of corrosion of particles with large number of secondary particles showing higher metal content can be observed.

Process intensification by acid baking and leaching to extract metals from cathode material

Selective dissolution of metals has the merit of the lesser metal contamination at each stage resulting in ease of separation. Accordingly, a two-step process involved sulfuric acid baking to convert major components of spent battery material to water soluble phases (Eqn.3) yielding selective recovery of a set of metals like Li and Co (Eqn. 4) over other metals (Ni and Mn) in water leach stage. The dissolution of remaining metals is attempted in the second stage of leaching.

$$2LiCoO_2 + 3H_2SO_4 = Li_2SO_4 + 2CoSO_4 + \qquad ... (3)$$

$$Li_2Co(SO_4)_2 + 2H^+ = 2Li^+ + Co^{+2} + 2HSO_4 \qquad ...(4)$$
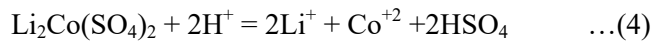
The baked cathode material is leached with distilled water at 75 °C and 25% PD for different time periods (5-120 min), and results are shown in Table 3. It is observed that the extraction of Li and Co increases apparently by leaching time up to 60 min. Further increasing the duration of leaching has a marginal effect on the dissolution of Li and Co. The selective dissolution of Li (78.6%) and Co (80.4%) over Ni (15.8%) and Mn (12.9%) is clearly noticed in 60 min of leaching.

The dissolution of Li and Co from the acid baked material is selective in the water leaching (leach-I) while the Ni and Mn dissolution are much lower. Keeping the optimized conditions of baking and using 2 mL H_2SO_4 (per 5 g cathodic material sample) at 300 °C for 30 min, leaching parameters like type of lixiviants, time, temperature and pulp density were optimized and it is found that at 75 °C in 60 min and 25% (w/v) PD, the leaching efficiencies of Li and Co were found to be 78.6 and 80.4%, respectively, besides the low dissolution of Ni(15.8%) and Mn (12.9%). The composition of the residue obtained from the leach-I under the above conditions was analyzed to be: 1.4% Li, 7% Co, 8.4% Ni and 9.7% Mn. In order to prevent the loss of residual metals- Li and Co in the leach-I residue while achieving the maximum recovery of major un-leached components viz., Ni and Mn, a second-stage leaching can be adopted.

Table 2 — Metal recoveries from spent LIBs vis-à-vis reductant(s) concentration**s**

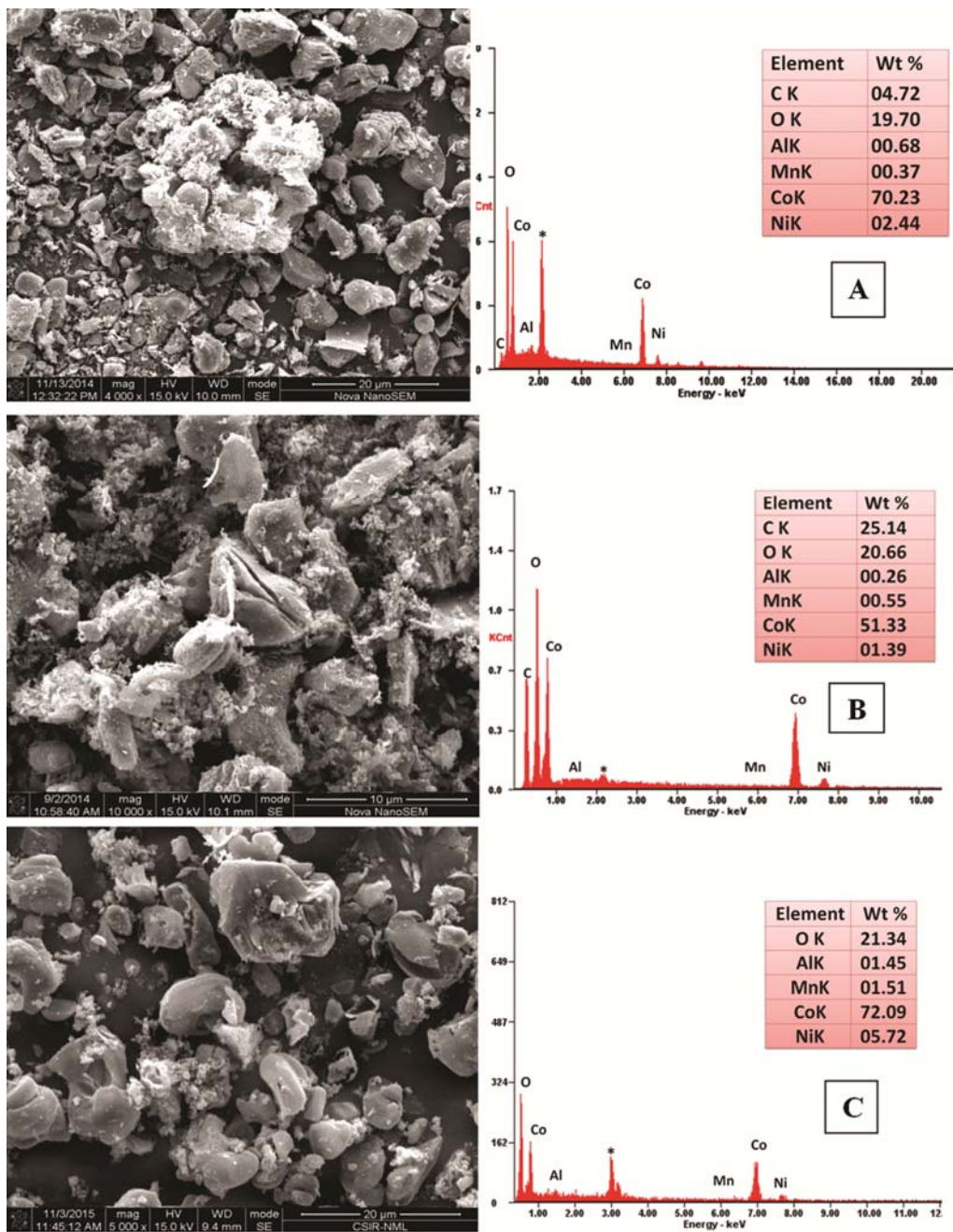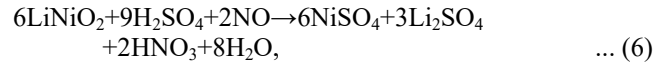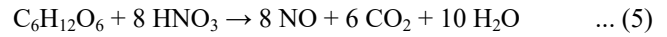| $NaHSO_3$ (%)	Li	Co	Ni	Mn	H_2O_2(%)	Li	Co	Ni	Mn
0.5	92.1	77.1	90.2	85.3	0.25	90.1	55.6	94.7	53.2
0.78 (0.075 M)	96.7	91.6	96.4	87.9	0.5	90.3	67.3	94.7	60.3
1.5	96.8	92.3	95.5	88.1	1	90.6	73.5	94.8	71.2
2.6 (0.25 M)	97.1	91.8	97.4	90.1	5	95.8	80.2	96.6	85.9
--	--	--	--	--	10	95.6	81.6	97.8	86.2

Fig.3 — SEM-EDAX analysis of residues on leaching with 1 M H_2SO_4 at 368 K and 50% PD with (A) no additive in 4h; (B) 0.075M $NaHSO_3$ in 4h; and (C) 5% H_2O_2 in 2h [*- Ag coating]

Table 3 — Recovery of metals during two stage leaching of baked cathode active material

Time (min)	First stage leaching (with distilled water at 75 °C, 25% PD)				Second stage leaching (with 1 M H_2SO_4 + 0.5 M HNO_3 at 50 °C and 10% PD)			
	Li	Co	Ni	Mn	Li	Co	Ni	Mn
15	60.67	55.6	6.12	6.98	8.53	6.62	60	30
30	65.93	58.89	8.18	9.21	10.2	7.66	59.6	31
45	70.47	76.42	12.98	9.72	14.6	10.12	67	64.8
60	78.63	80.39	15.8	12.85	14.6	10.66	67	65
120	79.84	82.3	16.98	14.4	14.6	10.32	68	66.21

Leach recovery of metals with time in the optimized acid mixture (1 M H_2SO_4 and 0.5 M HNO_3) in presence of glucose at 50 °C and 10% PD is also presented in Table 3. The increase in leaching time improved the dissolution of all metals. With the increase in duration of leaching from 15 to 45 min, the recovery of metal increased from 8.5% to 14.6% for Li, 6.6 to 10.1% for Co, 60 to 67% for Ni and 30 to 64.8% for Mn. With no increase in the metal recovery beyond 45 min of leaching, the optimum duration of 45 min was used in further experiments. Increased recovery of Ni is attributed to the formation of NO by the reaction of HNO_3 with glucose[10,11] as shown in Eq. (5). The resulting NO species helped in

the dissolution of lithium nickelate as per reaction (6) in the presence of H_2SO_4.

$$C_6H_{12}O_6 + 8\ HNO_3 \rightarrow 8\ NO + 6\ CO_2 + 10\ H_2O \qquad ...(5)$$

$$6LiNiO_2 + 9H_2SO_4 + 2NO \rightarrow 6NiSO_4 + 3Li_2SO_4 \\ + 2HNO_3 + 8H_2O, \qquad ...(6)$$

The overall recovery in the two-stage leaching of the baked cathode powder could be worked out as 93.2% Li, 90.5% Co, 82.8% Ni and 77.7% Mn. The leaching of metals with time was further examined by comparing the morphological changes through the SEM studies. Fig. 4a reflects the SEM image of the material baked at the 300°C depicting a porous
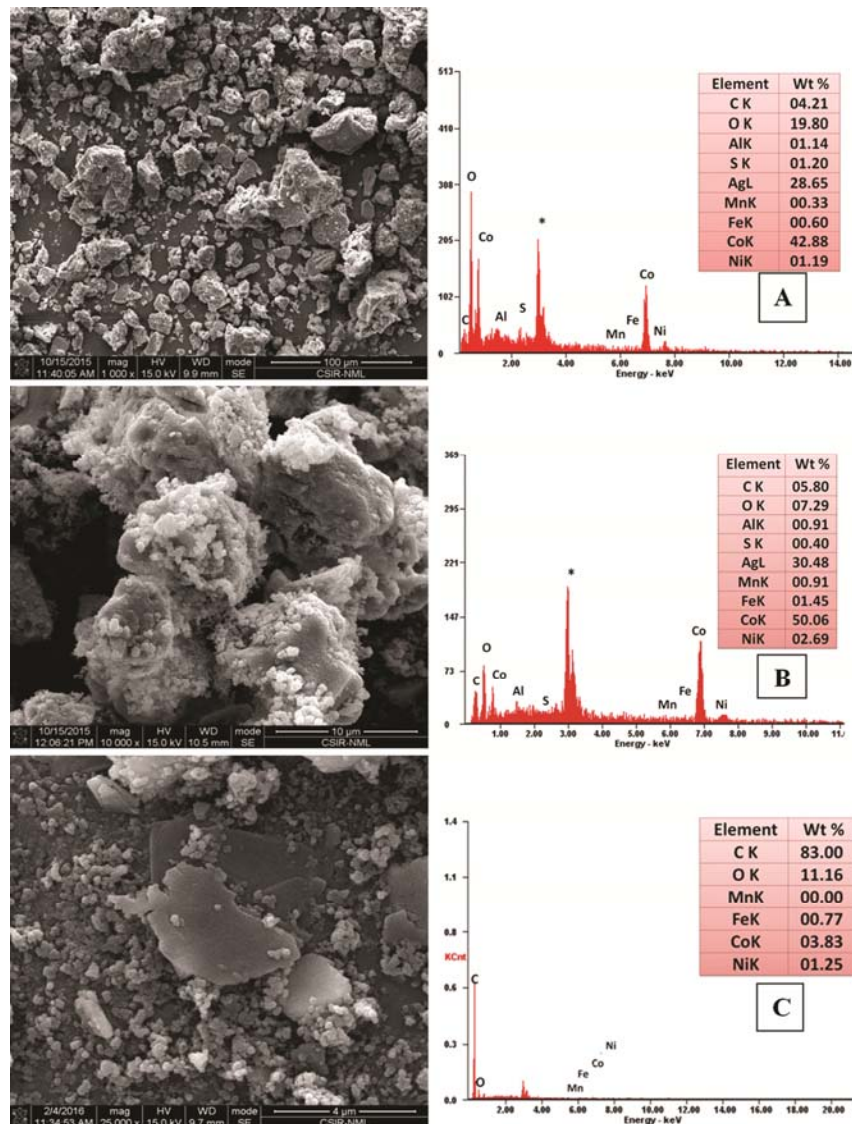

Fig. 4 — SEM-EDAX analysis of (A) baked cathode active material (temp: 300°C, time: 30 min, acid: 2 mL H_2SO_4/5 g material); (B) 1st stage leach residue (75°C, 25 % PD, 60 min); (C) 2nd stage leach residue (acid mix & glucose, 50°C, 10% PD, 60min) [*Ag coating, Li not detected]
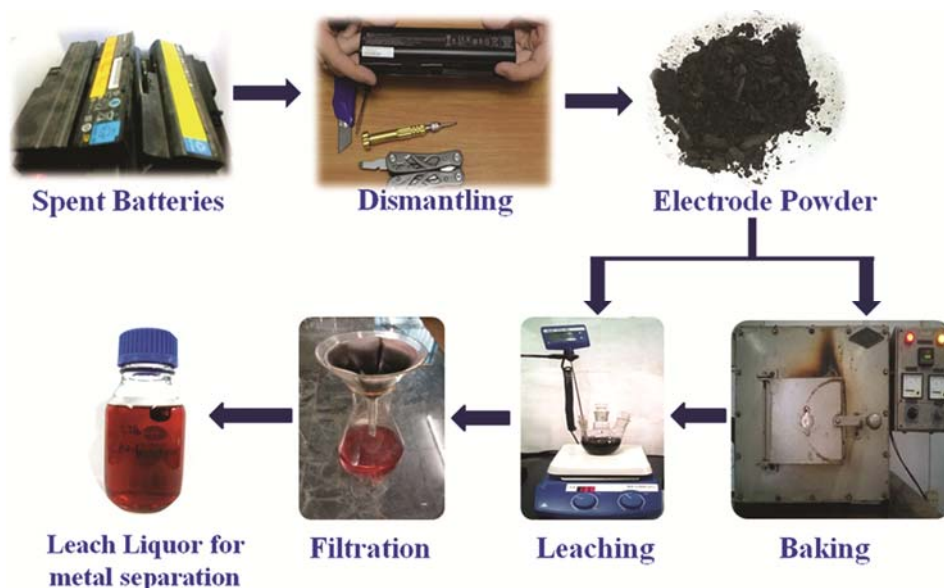
Fig. 5 — Schematic representation of various processing options used for spent LIBs

structure with the formation of new phases. The leach-I residue after water leaching performed at 75°C for 120 min shows a porous residue with corroded surface and formation of secondary precipitates on the surface (Fig. 4b). Subjecting the leach-I residue to acid mixture in the presence of glucose, a very high recovery of Ni and Mn by a decrease in the particle size (Fig. 4c), and low metal content in EDS.

A general pictorial representation of the various processing options to recover all metallic values from the batteries is shown in Fig. 5. The extracted metals, if separated into individual salts by combination of precipitation and other separation techniques, can open new avenues in synthesis of high value materials from wastes.

Conclusion

- The cathode active material of spent LIBs can be treated to recover the valuable metals by leaching in sulfuric acid in absence and presence of a reducing agent.
- Leaching efficiency of ~90% Li, 49% Co, 94.6% Ni and 48.5% Mn can be achieved when the cathodic material is leached only in 1 M H_2SO_4 at 368 K and 20 g/L pulp density for 240 min.
- Leaching efficiency with H_2SO_4 (1 M) in the presence of sodium bisulfite (0.075 M) as a reductant at 368 K and 20 g/L pulp density is found to be ~96.7% Li, 91.6% Co, 96.4% Ni and 87.9% Mn in 240 min. Use of H_2O_2 (5% v/v) as a reductant in H_2SO_4 (1M) however, yields the leaching of 94.5% Li, 79.2% Co, 96.4% Ni and

84.6% Mn at 50 g/L pulp density and 368 K in 240 min. The leaching efficiency has been justified with free energy change values.

- Process intensification by baking of cathodic material (300°C, 2 mL H_2SO_4 /5 g powder, 30 min) followed by water leaching (leach-I) selectively recovers 78.6% Li and 80.4% Co over Ni and Mn with low (<15%) dissolution in 60 min at 25% PD and 348 K. With 67% Ni and 64.8% Mn recovery using 1M H_2SO_4 and 0.5M HNO_3 plus glucose (2% w/v) at 323 K in 45 min (leach-II), the overall leaching efficiency is found to be 93.2% Li, 90.52% Co, 82.8% Ni and 77.7% Mn.
- This paper highlights the various possible options to recover Li, Ni, Co and Mn from spent lithium ion batteries aiming higher metal dissolution, improved selectivity and lower consumption of lixiviants.

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