



# Targeting high value metals in lithium-ion battery recycling via shredding and size-based separation



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## ABSTRACT

Development of lithium-ion battery recycling systems is a current focus of much research; however, significant research remains to optimize the process. One key area not studied is the utilization of mechanical pre-recycling steps to improve overall yield. This work proposes a pre-recycling process, including mechanical shredding and size-based sorting steps, with the goal of potential future scale-up to the industrial level. This pre-recycling process aims to achieve material segregation with a focus on the metallic portion and provide clear targets for subsequent recycling processes. The results show that contained metallic materials can be segregated into different size fractions at different levels. For example, for lithium cobalt oxide batteries, cobalt content has been improved from 35% by weight in the metallic portion before this pre-recycling process to 82% in the ultrafine (<0.5 mm) fraction and to 68% in the fine (0.5–1 mm) fraction, and been excluded in the larger pieces (>6 mm). However, size fractions across multiple battery chemistries showed significant variability in material concentration. This finding indicates that sorting by cathode before pre-treatment could reduce the uncertainty of input materials and therefore improve the purity of output streams. Thus, battery labeling systems may be an important step towards implementation of any pre-recycling process.

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## 1. Introduction

### 1.1. Key challenges remain in LIB waste management

Lithium ion batteries (LIBs), as an emerging technology, currently dominate the power source market for portable consumer electronics. More recently, LIBs have started being used in electric vehicles (EVs) and are becoming more popular due to their high energy density, no memory effect, long cycle life, etc. In 2006, \$1.1 billion of LIBs were consumed globally (BU, 2011a); according to Research and Markets, the global market for LIBs is expected to reach \$25 billion by 2017 (Wood, 2013). After their use phase (ranging from 2 years for consumer electronics batteries to about 10 years for EV batteries), a large amount of end-of-life (EOL) LIBs will enter the waste stream (Richa et al., 2014). Even though LIBs contain less hazardous materials compared to lead acid batteries or nickel-cadmium batteries, there is still a potential for some toxic materials to leach and contaminate the ground water system when disposing of EOL LIBs into uncontrolled landfills (Majeau-Bettez et al., 2011). Additionally, many metallic materials in EOL

LIBs still have economic value (Wang et al., 2014a) and may have associated criticality or scarcity concerns regarding their supply. Particularly for LIBs, niobium, cobalt, and manganese have been deemed critical by various organizations (Commission, 2014). Although the collection rate of EOL LIBs has been improving over the years, it is still extremely low. For example, only 0.5% of EOL LIBs were collected in the EU in 2002, and this figure only improved to 2.7% by 2007 (Weyhe, 2008). Currently, a few companies (e.g., Umicore and Toxco) process EOL LIBs; however their recycling technologies were not designed specifically for LIBs, usually processing multiple types of rechargeable batteries (e.g., nickel-metal hydride batteries) and/or non-battery scraps (e.g., metallic materials) at the same time, which results in lower recycling efficiency (Umicore; Olapiriyakul and Caudill, 2009). Therefore, development of a technology that can effectively recover more types of materials contained in LIBs is important.

A growing number of studies have been performed on EOL LIB recycling, with the focus on improving the recycling efficiency of cobalt, which is the most valuable material contained in LIBs from consumer electronics (Shin et al., 2005; Dorella and Mansur, 2007; Xia et al., 2008; Li et al., 2009). However, other materials contained in LIBs also show motivation to be recovered at a higher level, when considering both economic and environmental perspectives

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(Wang et al., 2014a). Copper, nickel, and lithium make a significant contribution to the potential recoverable value of EOL LIBs together, ranging from 27% of the total material value for LiCoO<sub>2</sub> cathode LIBs to 74% of the total material value for LiFePO<sub>4</sub> cathode LIBs. While the aluminum content is relatively low (ranging from 1% to 8% of the total mass for most LIB types), its recovery presents significant energy savings, since secondary production of aluminum saves up to 88% of the energy required during its primary production (Wang and Gaustad, 2012). With the consideration of the potential economic and environmental savings from recovering these contained materials, LIB recycling technologies must have a broader target than cobalt recovery alone (Table 1).

As LIB recycling efforts expand to target a broader spectrum of metals, the recycling technology must also be optimized to achieve higher efficiencies and selectivities of desired metals. LIBs come in different sizes, form factors, and cathode chemistries, indicating a highly co-mingled, uncertain waste stream if pre-sorting by cathode type cannot be done. A typical LIB consists of a cathode, an anode, separators and electrolyte, all of which contains a variety of metallic materials (e.g., copper, nickel, cobalt, lithium, aluminum, etc.), as well as plastics, carbon black, and organic liquids. A range of chemistries has been used as cathode materials as well, introducing further compositional uncertainty for unlabeled batteries. While lithium cobalt oxide battery dominates the market currently, LIB technology is transitioning to low-cost cathode chemistries (e.g., LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and some mixed-metal cathodes). As these cathodes grow in market share, profits for recyclers will be greatly impacted (Wang et al., 2014a). Recovering cobalt alone will not make the LIB recycling process financially successful due to this transition; however, as states are already enacting landfill bans, recyclers may still need to process this mixed stream. Successful segregation of materials has the potential to enrich the constituent of targeted material(s) in a certain size fraction, which helps to improve the efficiency of subsequent recycling processes and improve the profit for recyclers. The goal of this work is to quantify the potential for material segregation via shredding and mechanical size separation for LIBs.

### 1.2. Shredding and size segregation as LIB waste management strategy

Shredding or sorting has widely been used in other products' recycling processes to increase the surface area, liberate the component materials, achieve material segregation, and improve the efficiency of subsequent recycling processes, all at relatively low cost and environmental impact (Khoo, 2009). For LIBs specifically, while a few studies have included some type of pre-recycling steps into their proposed recycling process, the possibility of scaling these steps up may be limited and is usually not considered. For example, cutting battery cases is the first step of the laboratory-scale LIB recycling process proposed in many studies (Contestabile et al., 2001; Li et al., 2010b; Chen et al., 2011). While these authors recommend cryogenic treatment on an industrial scale according to their experimental experience (i.e., heat caused by the internal short-circuit of the cell during cutting), the feasibility of manually extracting the active materials has not been addressed for process scale-up. In (Nan et al., 2006), EOL LIBs were first dismantled to separate the outer steel cans from the contained materials using a custom dismantling machine; however, specific details on this process were not clearly presented. Li et al. used ultrasonic washing to separate cathode materials from the aluminum foils and separate carbon powder from the copper foil before the leaching process. However, their sorting process is limited by the low concentration (28% by weight) of cobalt in the targeted fraction (Li et al., 2009). Yamaji et al. proposed a novel method of under-water explosion to disassemble EOL LIBs (Yamaji et al., 2011). While this method can successfully prevent fires

**Table 1**

The price of materials (USGS, 2014).

Metals	Prices (\$/kg)	Metals	Prices (\$/kg)
Cobalt	28.44	Aluminum	2.09
Nickel	15.02	Iron	0.73
Copper	7.50	Phosphate rock	0.09
Manganese <sup>a</sup>	2.30	Niobium	44.00

<sup>a</sup> The price on the Infomine website (<http://www.infomine.com/>) (July, 2014).

during the crushing process, its associated environmental safety issues (such as the water treatment after the explosion) need to be further analyzed. These studies lay an important foundation for understanding the feasibility and potential for several pre-recycling processes such as manual cutting, ultrasonic washing, and dismantling.

However, a key challenge still remains: development of pre-recycling process that can be easily scaled up, requires low initial and operating cost, reduces energy and materials input, and at the same time can efficiently achieve material segregation. Therefore, the aim of this paper is to determine if material segregation can be achieved via pre-processing steps, particularly through shredding and sorting technologies that are frequently already in place at waste processing centers. In addition, one of the obstacles that LIB recyclers are facing is little information on LIB composition due to non-disclosed cathode chemistries and casing materials among different battery manufacturers. The effectiveness of this proposed process is examined for current market-dominant (i.e., LiCoO<sub>2</sub> cathode LIBs) as well as three future popular cathode batteries (i.e., LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and mixed-metal cathode LIBs), from perspectives on both material distribution and economic contribution.

## 2. Materials and methodology

To evaluate the efficacy of this proposed pre-recycling process when applied to batteries of differing cathode chemistries, a mixed stream of scrap LIB cells were used in this study, including 64 battery cells removed from 10 end-of-life laptop battery packs and 49 cells purchased and cycled to end-of-life; information about laptop brand and battery manufacturer for each battery pack is shown in Table 2 using indices to preserve confidentiality. These chemistries were compared to the average material content of four popular cathode chemistry types, i.e., LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and a mixed-metal cathode (i.e., Li<sub>1.05</sub>(Ni<sub>4/9</sub>Mn<sub>4/9</sub>Co<sub>1/9</sub>)<sub>0.95</sub>O<sub>2</sub>), taken from the literature, manufacturers documentation, and previous work by the authors (composition provided in Table 3 with details in the supplemental material). All sample batteries used in this study are 18650<sup>1</sup> cells except for LiMn<sub>2</sub>O<sub>4</sub> cathodes that are only present in 26650 cells as revealed by X-ray fluorescence.

The material flow through the proposed pre-recycling process for EOL LIBs is shown in Fig. 1. LIB packs removed from laptops were disassembled to separate the digital circuit and LIB cells. Next, LIB cells were discharged and immersed in liquid nitrogen to reduce the risk of fire and then mechanically shredded by a commercial granulator (i.e., EconoGrind 180/180<sup>2</sup>) into small pieces (less than 7.5 mm). To eliminate the risk of exposure to electrolyte, the shredding process was performed under a fume hood. Shredded

<sup>1</sup> The 18650 form indicates the battery is cylindrical, having a diameter of 18 mm, and length of 65 mm. The 26650 form indicates the battery is cylindrical, having a diameter of 26 mm and length of 65 mm.

<sup>2</sup> Physical parameters of Model 180/180, Economizer, USA are as following: 200 rpm rotor speed, 13.8 in. × 13.8 in. feed opening, max. 50 kg of material throughput per hour and 3 Kw drive capacity. It is assumed shear is the dominant acting force.

**Table 2**

Sample battery packs processed in this work.

Battery Pack #	Battery OEM Indices	Cathode	# of cells	Mass per cell (g)
1	Removed from EOL laptops	Mixed-metal	6	41.0
2			6	41.1
3			6	44.5
4			6	44.6
5		LiCoO <sub>2</sub>	8	45.9
6			8	46.0
7			6	45.2
8			6	42.6
9			6	45.2
10			6	43.8
11	Purchased from OEM and cycled	LiCoO <sub>2</sub>	9	45.6
12			9	46.4
13		LiFePO <sub>4</sub>	6	39.3
14			15	45.3
15		LiMn <sub>2</sub> O <sub>4</sub> <sup>a</sup>	4	98.8
16		Mixed-metal	6	42.2

<sup>a</sup>LiMn<sub>2</sub>O<sub>4</sub> cells are in a different form factor, i.e., 26650.

LIB pieces were collected on aluminum foil and placed under the fume hood (at room temperature and 90 feet/minute air flow) for one week to allow complete evaporation of volatile chemicals. A set of custom sorting sieves was used to separate these shredded LIB pieces into five size fractions: <0.5 mm, 0.5–1 mm, 1–2.5 mm, 2.5–6 mm, and >6 mm. Size separation was performed on a Vibration Machine Test System (Model 7000-10, Lansmont, USA) using the random vibration mode (i.e., ASTM D4169 Truck profile) for 20 minutes. Material already separated into each size fraction was then analyzed for metallic composition using the XRF (Delta X Model, Innov-X, Olympus, Japan). X-ray fluorescence is able to characterize the weight percentage of the metals contained in the sample. Five random samples within each size fraction were tested and averaged; the larger size fractions had slightly more variability in compositional results compared to the finer fractions. XRF identifies the material content based on the specific wavelength of detected photons for each element. While lithium cannot be detected by this XRF analyzer even under the widest mode, the XRF analyzer is effective to characterize all of the other metallic materials of interest in LIBs (EPA, 1998). Lithium content was calculated based on the known energy capacity of each cell chemistry

**Table 3**

Average material contents of LIBs (in grams and wt%) from literature and previous work.

Materials	LiCoO <sub>2</sub> <sup>a</sup>		LiFePO <sub>4</sub> <sup>a</sup>		LiMn <sub>2</sub> O <sub>4</sub> <sup>b</sup>		Mixed-metal <sup>c</sup>	
	g	wt.%	g	wt.%	g	wt.%	g	wt.%
Aluminum	2.4	5.2	2.7	6.5	0.5	1.1	3.6	8.5
Cobalt	8.0	17.3	0	0	0	0	0.8	2.0
Copper	3.4	7.3	3.5	8.2	0.5	1.1	6.9	16.3
Lithium	0.9	2.0	0.5	1.2	0.7	1.5	1.0	2.4
Manganese	0	0	0	0	9.1	20.4	3.2	7.5
Nickel	0.6	1.2	0	0	0	0	3.4	8.0
Steel/iron	7.6	16.5	18.3	43.2	7.4	16.5	0	0
Phosphorus	0	0	2.3	5.4	0.5	1.1	0	0
Graphite	10.6	23.1	5.5	13.0	15.0	33.6	8.7	20.6
Carbon black	2.8	6.0	1.0	2.3	0	0	0.8	2.0
LiPF <sub>6</sub>	1.7	3.7	0.5	1.2	0	0	6.2	14.7
EC/other	4.7	10.3	5.8	13.7	0.1	0.3	4.4	10.4
Binders	1.1	2.4	0.4	0.9	0	0	1.2	2.8
Plastics	2.2	4.8	1.9	4.4	9.0	20.1	2.1	4.9
Total	46.0	100	42.3	100	44.7	100	42.2	100

<sup>a</sup> The average of 2 LIB manufacturers (Table S1 in Appendix).<sup>b</sup> Adopted from Wang et al. (2014a).<sup>c</sup> Adopted from Richa et al. (2014).

type and the specific energy of Li, and validated by the calculated stoichiometric proportion of each material in the cathode as per previous work (Ganter et al., 2014; Tahil, 2010) according to Eq. (1):

Li Content per battery pack (g)

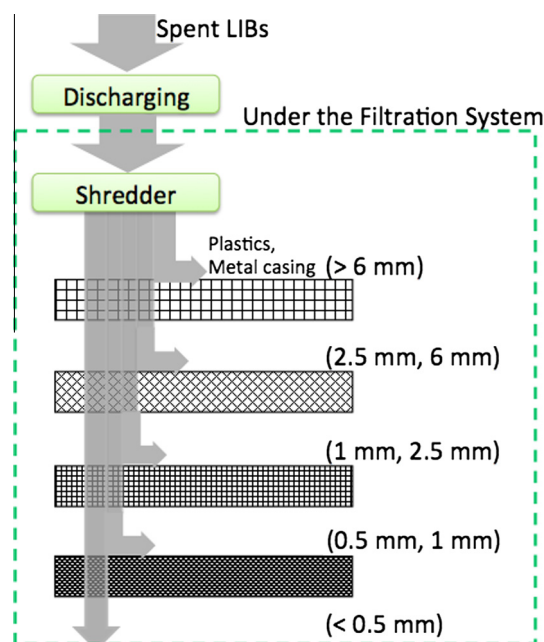
$$= \text{Ah per cell (Ah)} * X \text{ (g/Ah)} * N \quad (1)$$

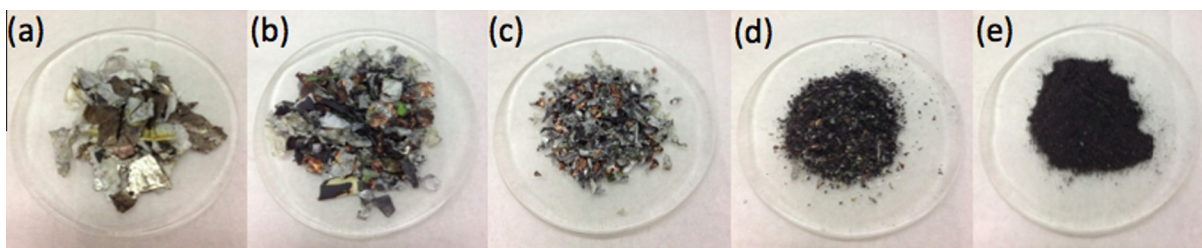
where the factor  $X$  refers to the mass of lithium metal required to produce 1 Ampere hour (Ah) of power, and  $N$  refers to the number of cells per battery pack. These results were cross-checked with published lithium content in other work.

Average primary metal as well as phosphate rock prices in 2013 from USGS (Table 1) are used to estimate the materials' maximum theoretical recoverable value (i.e., assuming 100% recovery) according to Eq. (2):

% recoverable value

$$= \frac{\text{Metal price (\$ g)} * \text{Metal in size fraction (g)}}{\sum_{\text{all metals in fraction}} (\text{Metal price} * \text{Metal amt in size fraction})} \quad (2)$$

**Fig. 1.** Flow sheet of EOL LIB pre-recycling process.



**Fig. 2.** Samples of five size fractions after the pre-recycling process for battery pack #B5 (from left to right: (>6 mm), (2.5–6 mm), (1–2.5 mm), (0.5–1 mm), and (<0.5 mm)).

Although recycling efficiencies for most of those materials are unlikely to reach 100%, the theoretical analysis provides a maximum starting point for material comparisons based on recoverable value alone.

### 3. Results and discussion

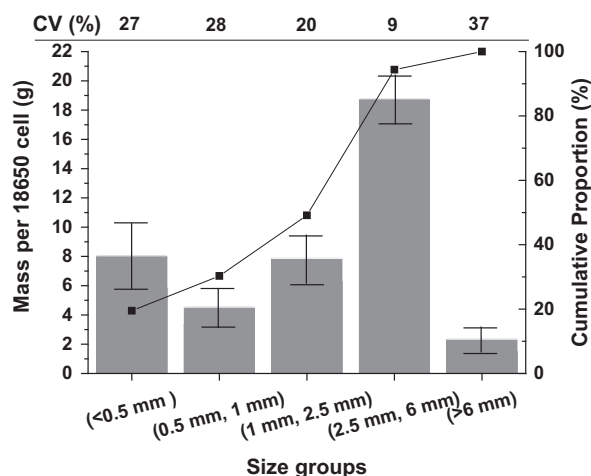
Demonstration of the pre-recycling process enabled comparisons of the separated size fractions on the basis of metal content, economic value of that content, and variability across multiple battery chemistries and manufacturers. The sorted fractions of shredded cells showed clear visible differentiation (Fig. 2a–e; for battery pack #B5), particularly in the accumulation of poorly-shredded battery housing material in the largest size fraction. The larger pieces (>6 mm) are mostly battery casings and plastic separators. Copper pieces can be visibly detected in the coarse (2.5–6 mm) and mid (1–2.5 mm) fraction. Fine black powder, likely comprised of graphite from the anode and the active materials from the cathode, dominates the ultrafine (<0.5 mm) fraction.

#### 3.1. Mass of fractions

The mass distribution of sorted materials in the five fractions is similar among packs. Since the number of cells per pack varies across the ten battery packs sampled (eight packs have six cells each and the other two have eight cells each), Fig. 3 reports mass for all five size fractions normalized on a per cell basis. Fig. 3 also characterizes the variability among the ten packs sampled: the height of each column shows the average mass value, and the error bars on each column refer to the maximum and minimum value. The coefficient of variation (CV) for these five size fractions ranges from 9% to 37%, which are considered to be low variance for waste streams. The coarse (2.5–6 mm) fraction and the larger pieces (>6 mm) are the largest and smallest portions in terms of the mass (45% and 6% on average respectively). Approximately 94% of the material was cumulatively less than 6 mm in size.

#### 3.2. The performance of the proposed pre-recycling process—two examples

Distribution of the metals among the various size fractions also requires the context of which metals are in the highest proportion in each size fraction, in order to determine if segregation has occurred successfully. The complete XRF results of the distribution of metals in different size fractions after the sorting process are shown in Table S2 in the Supplementary Information. In this section, one battery pack of each cathode type is selected as a representative example (i.e., #B10 for LiCoO<sub>2</sub> and #B2 for mixed-metal as shown in Table 2). Figs. 4 and 5 show the entire compositional make-up of the battery from its bill of materials in (a), the metallic portion of that bill of materials only in (b), and the metallic portion as detected via XRF analysis for each of the separated size fractions in (c). Together with Fig. 3, this allows one to determine the degree of compositional material segregation achieved via size separation.

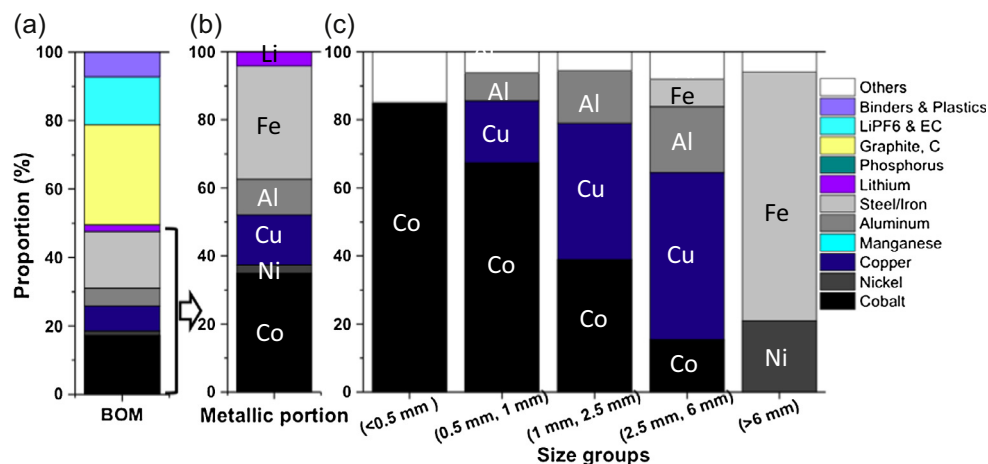


Size Groups	g/18650			Cum %	CV (%)
	LB	Avg	UB		
<0.5 mm	5.8	8.0	10.3	19.5	27
0.5 mm–1 mm	3.3	4.5	5.8	30.3	28
1 mm–2.5 mm	6.3	7.9	9.5	49.1	20
2.5 mm–6 mm	17.1	18.8	20.5	94.4	9
>6 mm	1.5	2.3	3.2	100	37

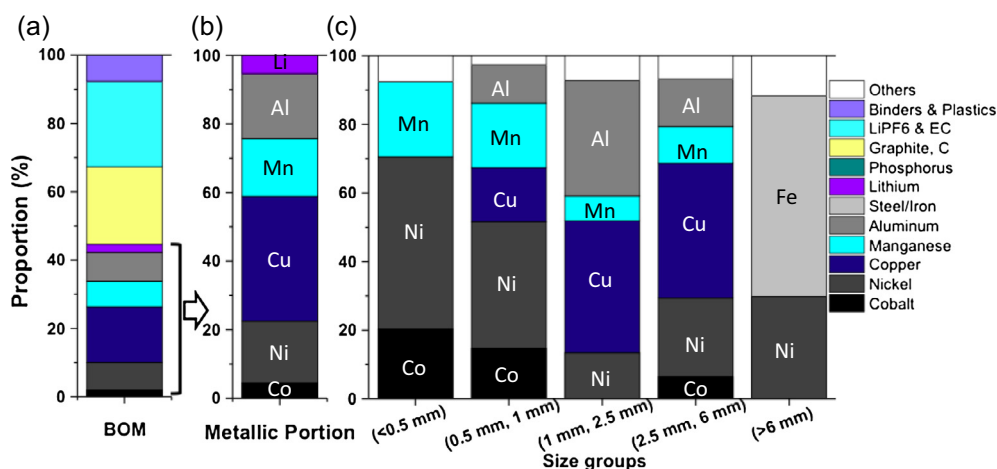
**Fig. 3 and Table 4.** Mass of each size fraction with standard deviation bar per 18650 cell along with the cumulative proportion. Coefficient of variation (CV) is also reported.

LiCoO<sub>2</sub> is the most commonly used cathode material in LIBs for electronic devices. The bill of materials (BOM) for LiCoO<sub>2</sub> cathode batteries created based on two battery manufacturers is shown in Fig. 4a (see detailed information in Table S1 in the Supplementary Information). As the compositions were measured using XRF, only the metallic content is reported in the remaining bars (b and c). In total, metals make up about 50% of total battery mass (Fig. 4a), and the metallic fraction is largely dominated by cobalt and steel (Fig. 4b). Fig. 4c shows into which size fractions the metals segregate. Cobalt dominates the size fractions less than 1 mm and steel dominates the size fraction greater than 6 mm as seen in Fig. 4c. In the case of cobalt, the most commonly recycled battery material, relative content was enriched from 35% by weight in the unsorted metallic portion to 67% in the fine (0.5–1 mm) fraction and then to 85% in the ultrafine (<0.5 mm) fraction. Cobalt is the only metallic component present in large proportion in the ultrafine fraction; all other metals made up less than 5% each of the “Other” category. Inversely, cobalt comprised less than 1% of metallic materials in the largest fraction (>6 mm). Another valuable material, copper, showed concentration in some size fractions: from 15% of metallic materials by mass before sorting to 40% in the





**Fig. 4.** (a) The mass percentage BOMs for LiCoO<sub>2</sub> cathode batteries (see Table S1); (b) the metallic portion in (a); (c) the distribution of metallic components in each size fraction of battery pack #B10; the materials having content less than 5% are combined in each fraction and labeled as “Others”, which is applicable in all figures in this study. Sample size is five for each fraction.



**Fig. 5.** (a) The BOM for mixed-metal cathode batteries (see Table 3); (b) the metallic portion in (a); (c) the distribution of metallic components in each size fraction of battery pack #B2, all in mass percentage.

mid (1–2.5 mm) fraction and to 49% in the coarse (2.5–6 mm) fraction. These results need to be viewed in the context of Fig. 3, however, as more total material ends up in the 2.5–6 mm fraction. Beyond these high-value materials, the content of other metals have also been enriched in certain fractions by this sorting process. For example, steel only shows up in two fractions: (1) 8% of metallic materials in the coarse (2.5–6 mm) fraction, which is unlikely being targeted at recycling facilities due to its low content and low unit value; and (2) 73% in the larger pieces (>6 mm). Other materials detected by the XRF but present in very low proportions (less than 5%) are combined in the “Other” category and assumed to not be economically recoverable in such small proportions; an example of this would include niobium which is detected because it is used as an alloying element in some of the steel casings but would not be individually recoverable.

Interpreted together, the results of Fig. 3, which indicates the mass per size fraction, and Fig. 4, the percent of metals per specific size fraction, determine the degree to which valuable metals, like cobalt and copper would be recoverable by this method. Given that most individual cells of the same chemistry have relatively consistent makeup of major metallic elements, the results presented in Figs. 3 and 4 are likely scalable for a waste stream, provided it contains a single chemistry as is discussed later in the manuscript.

Besides LiCoO<sub>2</sub> cathode batteries, three out of ten selected battery packs removed from laptops were found to be mixed-metal cathode batteries (Table 2), which have also become popular in EVs, for example the Chevy Volt (Fletcher, 2011). The BOM for Li<sub>1.05</sub>(Ni<sub>4/9</sub>Mn<sub>4/9</sub>Co<sub>1/9</sub>)<sub>0.95</sub>O<sub>2</sub> cathode batteries made by a representative manufacturer was adopted as a base case (see Fig. 5a and b). The XRF results show that contained battery materials were segregated by the sorting process (comparing Fig. 5c with Fig. 5b); but to a smaller degree than separation observed for the LiCoO<sub>2</sub> cathode batteries (comparing Fig. 5c with Fig. 4c). The cobalt content was slightly enriched in the two smallest size fractions and excluded from the larger pieces (Fig. 5c). However, it should be noted that mixed-metal cathode batteries have much lower cobalt content (4.5% of the metallic fraction) as compared to LiCoO<sub>2</sub> cathode batteries (where cobalt is 35% of metallic fraction), indicating that this chemistry will be less economically favorable to recycle (Wang et al., 2014a). For mixed-metal cathode batteries, nickel contributes significantly in both ultrafine and fine fractions, i.e., 50% and 37% of the metallic portion respectively, and has the potential to be recovered at a higher level. In addition, copper, having the highest content (40%) among metallic materials in both mid and coarse fractions, is a candidate to target in the subsequent recycling process. Common to both chemistries is the strong segregation

of iron and steel, originating from the battery casing, in the largest size fraction, suggesting potential opportunity for automated separation and recycling of ferrous content after the pre-recycling process. “Ferrous content” here means metallic materials that contain iron. In general, there are two groups of metals, ferrous and non-ferrous. Ferrous metals include carbon steel, stainless steel (both alloys and mixtures of metals) and wrought iron. Although not considered in this study, iron and steel could potentially be separated via magnetic methods, which could leave a nickel-rich portion in the larger pieces (>6 mm), however this will depend on the degree of liberation possible. For example, austenitic stainless steel can contain large amounts of nickel in solid solution, which would not be able to be separated.

These examples demonstrate that the proposed pre-recycling process has the potential to effectively improve materials’ concentration in certain size fractions, particularly for several high value materials, i.e., cobalt, nickel, and copper. Because the relative enrichment of targeted metals varied between the two case study cathode types, the pre-recycling process may be further improved at an industrial scale by first sorting incoming battery waste into different chemistries. Processing single chemistries at a time would be expected to result in greater purity of output streams. Manufacturer labeling of LIBs to indicate chemistry would be a strong enabler for the success of this technology. However, current policies related to spent battery management either do not have specifications regarding the labeling system or only require basic information (e.g., the crossed-out dustbin symbol and chemical symbols for above-threshold chemicals) on the package (NYS 2010; EU, 2006). To provide a policy-directed assessment of benefits from labeling systems, the next section will compare the performances of this proposed pre-recycling process when applied to another two emerging cathode types.

### 3.3. Comparison among LIBs with alternate cathode chemistries

The average distributions of metallic materials in five fractions for  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  cathode batteries are shown in Fig. 6a and b, respectively. The distribution of metallic materials in each size fraction varies significantly from the two types of batteries analyzed here and from the results shown previously for cobalt-based cathodes (Section 3.2). Of particular note, the ultrafine fraction in both cases is dominated by metallic elements contained in the respective cathodes (i.e., iron for  $\text{LiFePO}_4$  cathode cells and manganese for  $\text{LiMn}_2\text{O}_4$  cathode cells). The changing economics of LIB recycling will have a large impact on the recovery routes, for example, if cobalt is the focus of recovery, then metals like iron and manganese would be removed as impurities from the cobalt recovery process. However, if the process is moving towards enhanced material recovery, then the iron and manganese would need to be further separated, removed, and purified to be reused.

While a clear difference was observed among different cathode types, several key findings can be concluded from the sorting results. First, the dominant material in the ultrafine fraction highly depends on the cathode type, largely because cathode materials originate as fine powders, which are double side coated on the aluminum foil cathode substrate, and therefore remain in this size fraction through the shredding and separation processes. This may indicate that these results are generalizable i.e. materials produced this way will typically segregate into the fine fraction. Secondly, copper, mainly from the copper foil anode substrate (typically coated with graphite), is likely segregated into mid and coarse fraction. Finally, the battery casings make up the majority of the larger pieces.

Since the potential recoverable value is the key decision factor from a recycler’s standpoint, the unit economic value of each type of material needs to be taken into consideration. The contribution of each material to the total theoretical value of each size fraction for the four battery types are plotted in Fig. 7a–d. Cobalt has the highest economic incentive for recovery from  $\text{LiCoO}_2$  cathode batteries, and this value further enhanced through size separation (close to 100% for the smaller fractions, Fig. 7a).

For mixed-metal cathode batteries, while nickel only accounts for 18% by weight in the metallic portion initially (three times more than cobalt, see Table 3), nickel has the highest priority to be recovered from an economic perspective. The potential recoverable value of nickel (ranging from 35% in the mid fraction to 84% in the larger pieces) exceeds the value of cobalt in all fractions (Fig. 7b). Thus, cobalt cannot be viewed as the only economic driver for recycling, at least for mixed-metal cathode batteries. It must also be noted that although manganese makes a contribution in all but the largest fractions of mixed-metal cathode batteries (Fig. 5c), it is unlikely to be targeted at recycling firms due to its low potential recoverable value (Fig. 7b). In fact, recovering manganese specifically is very rare in general (USGS, 2013).

$\text{LiFePO}_4$  cathode batteries have become more popular recently due to low cost (25% less expensive compared to  $\text{LiCoO}_2$  cathode batteries), low environmental impacts (less hazardous materials contained), and longer cycle life (up to 2000 cycles) (Gaines, 2012; Electropaedia). Several automotive manufacturers have already used  $\text{LiFePO}_4$  cathode batteries in their EVs, such as the Coda Sedan and the Tata Nano (Hernandez, 2011; Lucas, 2012). On an economic basis, copper makes major contributions in all but the ultrafine fractions due to its high unit value. While steel is the main material by weight in three size fractions (ultrafine, fine and larger pieces), its comparatively low value decreases its proportional contribution to the potential recoverable value. Only in the case of low-cost cathode  $\text{LiFePO}_4$  (Fig. 7c) does it provide economic incentive for recycling. It should be noted that niobium counts about 2% by weight in both ultrafine and fine fractions. In fact,  $\text{LiFePO}_4$  cathode battery samples selected in this study have used niobium elements in the cathode to improve the compound’s

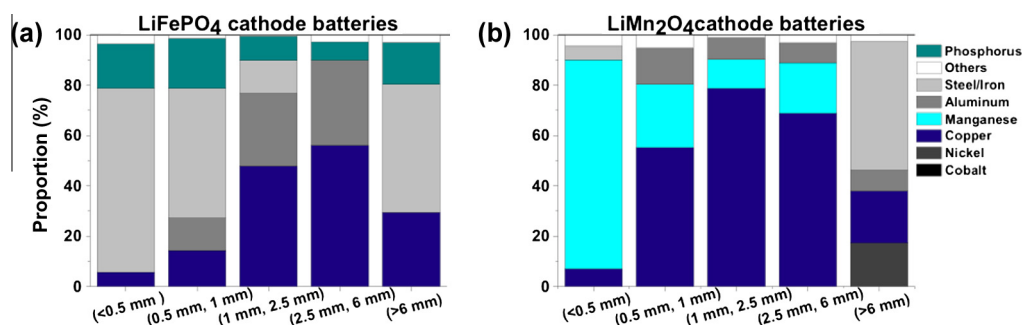
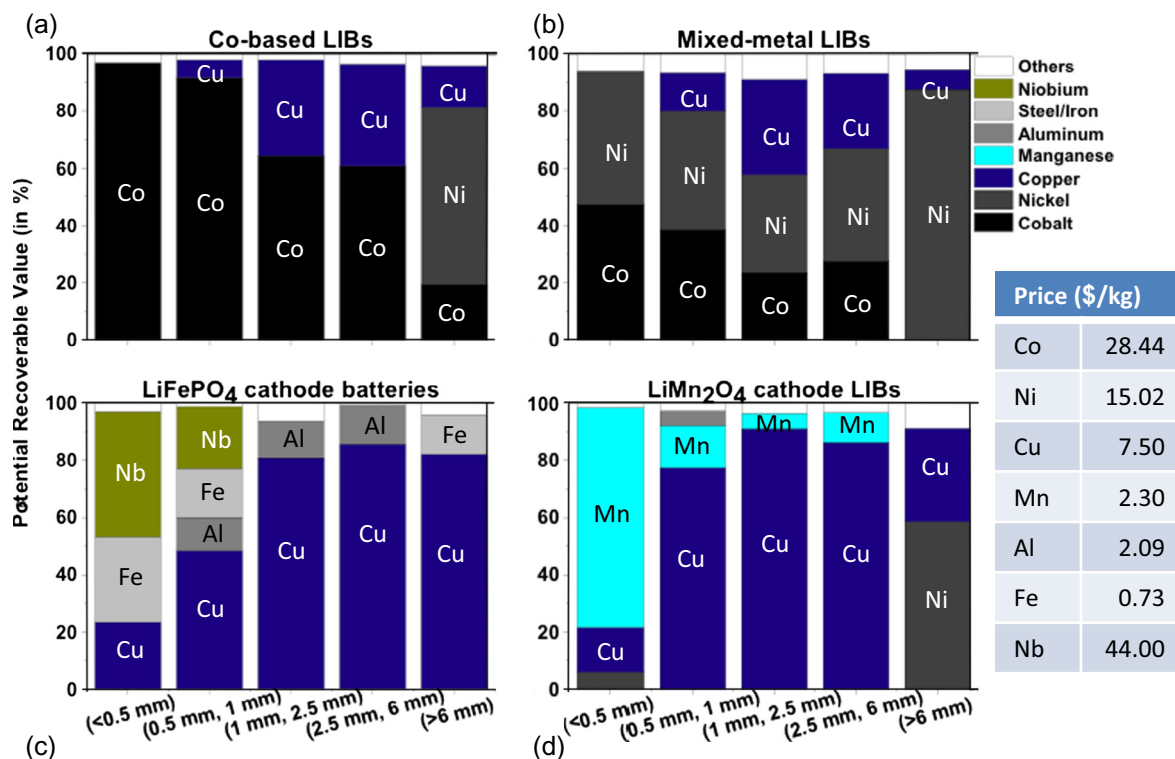
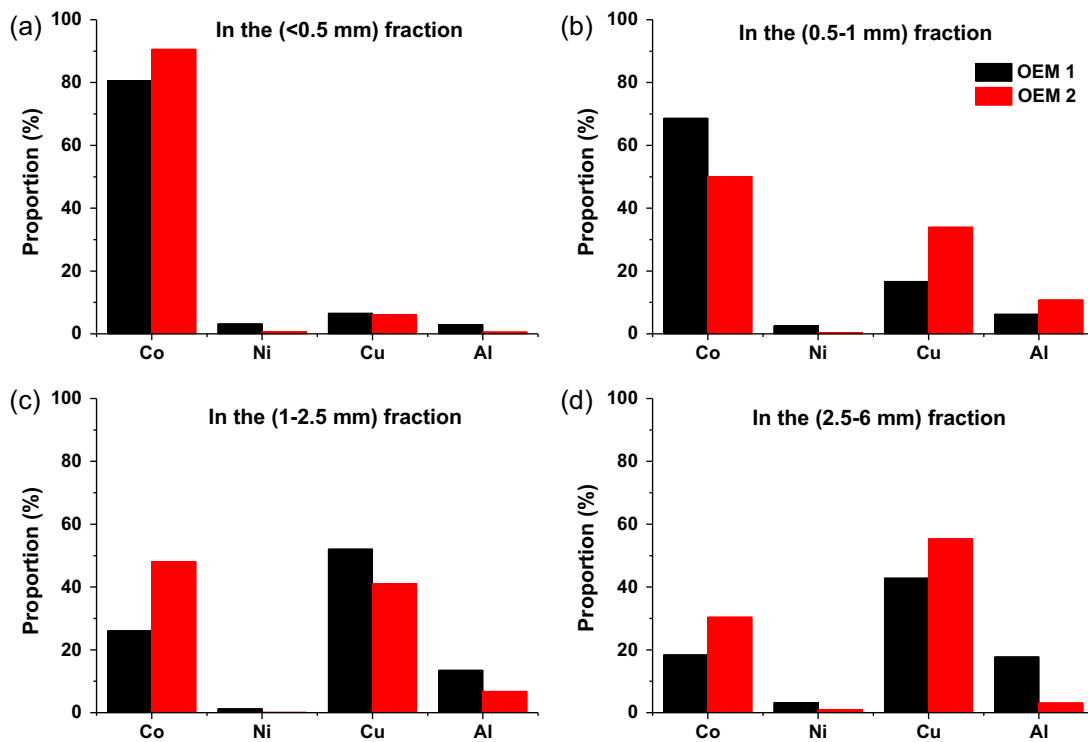


Fig. 6. The metallic material distribution in each size fraction for (a)  $\text{LiFePO}_4$ , and (b)  $\text{LiMn}_2\text{O}_4$  cathode batteries, in mass percentage.



**Fig. 7.** The contribution of each type of material to the total recoverable value of each size fraction for (a)  $\text{LiCoO}_2$ , (b) mixed-metal, (c)  $\text{LiFePO}_4$ , and (d)  $\text{LiMn}_2\text{O}_4$  cathode types; it should be noted that this total is highest for  $\text{LiCoO}_2$  and mixed-metal LIBs, with both  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  having substantially less total value.



**Fig. 8.** The mass percentage sorting results of  $\text{LiCoO}_2$  cathode batteries made by two manufacturers (a) (<0.5 mm), (b) (0.5–1 mm), (c) (1–2.5 mm), and (d) (2.5–6 mm).

electrical conductivity. While niobium has a high economic value (\$44 per kg), it might not be worth the cost of recycling due to its extremely low mass content compared to other more concentrated materials, such as steel and copper. However, this sorting

process successfully segregated niobium into two certain fractions, providing recyclers an opportunity to recover it.

Lithium manganese spinel is another promising LIB cathode type, having a three-dimensional spinel structure, which can

**Table 5**

The measure of variability calculated using the range-divided-by-mean.

Size fractions	LiCoO <sub>2</sub> cathode LIBs			Mixed-metal cathode LIBs				
	Co	Cu	Al	Co	Ni	Cu	Al	Mn
(<0.5 mm)	0.12	0.70	Na	0.55	0.35	0.70	Na	0.11
(0.5–1 mm)	0.31	0.68	0.54	0.45	0.35	0.13	0.40	0.20
(1–2.5 mm)	0.59	0.24	0.66	0.76	0.20	0.30	<b>1.75</b>	0.38
(2.5–6 mm)	0.49	0.25	<b>1.40</b>	0.69	0.20	0.10	<b>1.12</b>	0.34

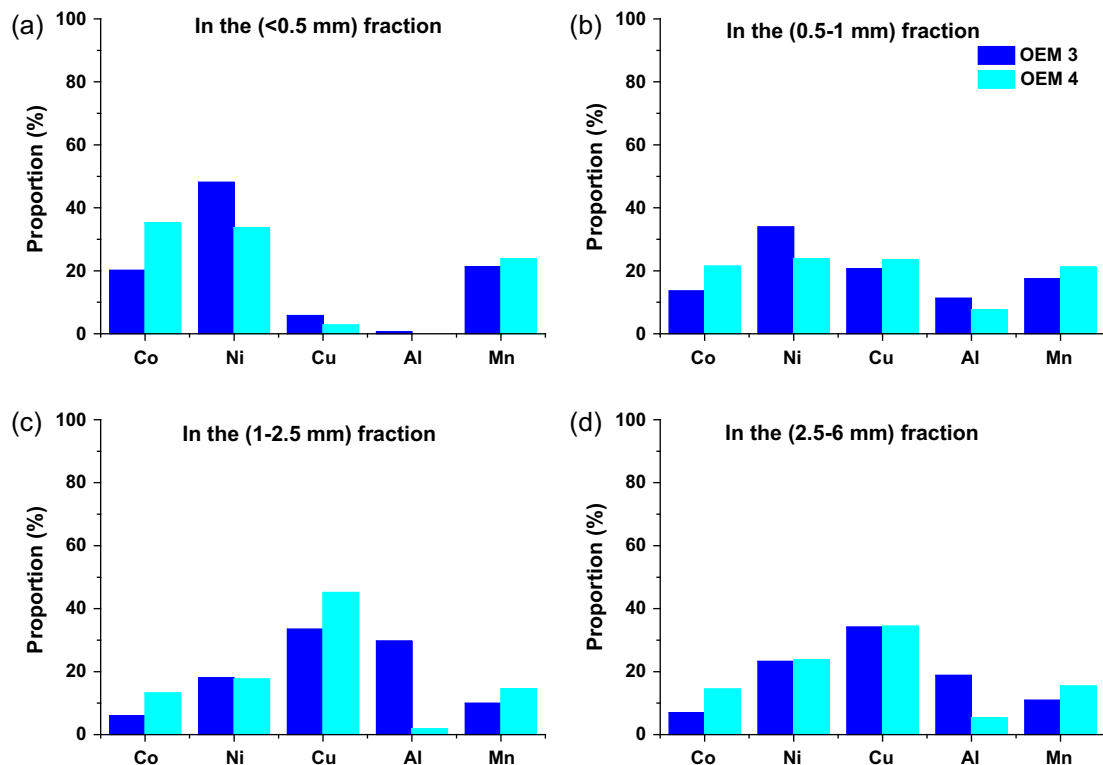
improve the ion flow between the electrodes and therefore lower the internal resistance and increase loading capability (BU, 2011b). They have already been successfully used in Nissan Leafs (Hernandez, 2011). For this case, taking economic values into consideration does not change the materials' recovery priority significantly except for the larger pieces. Manganese has the highest recovery priority in the ultrafine fraction in terms of both mass content and potential recoverable value; as does copper in the fine, mid, and coarse fractions. It should be noted that selected LiMn<sub>2</sub>O<sub>4</sub> cathode batteries are in a different form factor (i.e., 26650) from the rest of battery samples used in this study. LIBs labeled as "IMR" purchased from three manufacturers were found to be mixed-metal cathode batteries. As can be compared between Fig. 7b and d, these two cathode types have different recovery targets due to their distinct material compositions (see Figs. 5c and 6b). Misinformation about battery content may present economic or safety barriers to recycling at EOL, further supporting the need for appropriate labeling systems to include identification of battery cathode. For example, one labeling method would be to use color code casings for LIB cells, which provides an opportunity to adopt an optical sorting technologies at recycling facilities.

Subsequent recycling technologies targeting multiple types of materials (e.g., cobalt, nickel, and copper) must be developed to maximize the profit from recycling different cathode types

(Wang et al., 2014b). Wang et al. (2009) proposed a hydrometallurgical process, designed to recover cobalt, manganese, nickel, and lithium from LIBs; however, before scaling up, associated environmental impacts need to be analyzed since this process requires strong acid and a significant energy input (Wang et al., 2009). In fact, some undergoing research is focused on substituting strong acids with organic acids to recover metallic materials from LIBs (Li et al., 2010a, 2013).

### 3.4. Comparison among different battery OEMs

Previous studies point out that LIBs having the same cathode chemistry but made by different manufacturers are likely to show variations in their material content (Wang et al., 2014a). To understand whether this variation would bring uncertainties to this pre-recycling process, Fig. 8a–d shows the average XRF results of four size fractions of LiCoO<sub>2</sub> cathode batteries made by two battery manufacturers, i.e., #BM5 and #BM6. Material distribution in each size fraction varies slightly between these two manufacturers (Table 5), as determined by the range of values (mass percentages) divided by the mean value (Karpati et al., 2002). Usually if this measure of variability is less than one, it is considered low-variance; otherwise, it is considered high-variance. In this case, only three results are greater than one (bolded), indicating that the variation of material distribution in each size fraction between these two manufacturers is relatively low. Similar results have been found for mixed-metal cathode batteries (Fig. 9a–d, Table 5), suggesting that inter-cathode variability due to manufacturing is unlikely to be a barrier to implementing the pre-recycling process. Findings from these comparisons indicate that detailed manufacturing information is likely unnecessary when enhancing the labeling systems since significant compositional difference in the same size fraction exists among different cathode types but not among manufacturers.



**Fig. 9.** The mass percentage sorting results of mixed-metal cathode batteries made by two manufacturers (a) (<0.5 mm), (b) (0.5–1 mm), (c) (1–2.5 mm), and (d) (2.5–6 mm).



#### 4. Conclusion

Facing a large volume of EOL LIBs entering the waste stream in the near future, it is essential that feasible, automated, low-cost recycling processes be developed. The pre-recycling process proposed in this study, including mechanical shredding and size-based sorting, requires only a few pieces of equipment (i.e., shredder, vibration source, and sorting sieves) and low energy consumption, which has potential for scale-up at recycling firms with some adjustment (e.g., a continuous inclined vibrating screening system). Our methods used liquid nitrogen to freeze batteries before processing to reduce the risk of fire that might be caused by short-circuiting or overheating during the mechanical shredding, an approach consistent with existing recycling facilities, such as Toxco (Thompson, 2011). When scaling up, processing materials at very low temperatures could present other challenges and is certainly an additional cost; this is an area that would benefit greatly from further research. Another key challenge to be addressed in scale-up is the emission of organic electrolyte. In this paper, it was evaporated under a fume hood, however, in an industrial shredding setting, it could produce hazardous air pollutants (HAPs) that need additional treatment. Many industrial shredding centers are beginning to make use of emission controls such as enhanced air handling and suction systems like cyclones, scrubbers and baghouse filters (McGlothlin, 2011; Al-Salem et al., 2009).

Given the results for the four most common battery cathode types, this proposed pre-recycling process can effectively segregate target LIB materials into size fractions, which would enable recyclers to select upgrading technologies and material recovery hierarchies that maximize mass or value to be recovered. Instead of processing the entire portion of EOL LIBs using a single technology, multiple recycling processes (such as physical treatment, pyrometallurgical technology, acid leaching and electrochemical processing) could be integrated to target specific materials enriched in each size fraction (e.g., copper from the mid and coarse fractions, and steel from the larger pieces). In particular, as battery recyclers are strongly driven by economic incentives, this paper takes the potential recoverable value of battery materials into consideration, resulting in a more clear recovery priority.

The results suggest that pre-sorting by cathode type has the potential to further improve the segregation efficiency of battery waste streams. While this might be expensive to perform in certain locales, emerging economies might be an ideal place for labor intensive pre-processing (Wang et al., 2012). Particularly, while lithium cobalt oxide is the most common cathode type at present, cobalt is not even contained in several projected next-generation LIBs (e.g., lithium iron phosphate, lithium manganese spinel, and lithium polymer). If LIB recycling is carried out without any pre-sorting by cathode chemistry, a significant uncertainty would be involved, and recycling yields will likely be diminished. Lower yields erode the positive environmental impact of recycling; a full life-cycle assessment of a scaled-up industrial process could validate the environmental savings realized through this pre-recycling process. Implementing a battery labeling system that specifies recycling-relevant information (electrode chemistry, casing materials, manufacturer, etc.) would increase the effectiveness of the pre-recycling system.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2015.10.026>.

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