

# Li Recovery via Physical-Chemical Treatment from Spent EV Lithium-Ion Battery for Circular Economy

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Lithium-ion batteries (LIBs) is the main energy storage for electromobility vehicles. As the demand for LIBs rises, a significant amount of battery waste is produced, which contains numerous valuable metals and has a potential to be a substantial metal resource. Recycling is one of the most efficient method for recovering materials from used spent LIBs and transferring the material across the critical supply chain. In accordance with the consisting of organic components (electrolyte, separator, casing, etc.), the Li recovery technologies will involve the physical processes (crushing and sieving), followed by chemical processes (leaching and precipitating). In this work, the leachability of the valuable metal (Lithium: Li) was evaluated after the recovery process via variety of acid extraction, concentration of acid, leaching temperature, reaction time and solid/liquid (S/L) ratio. The leaching solution were evaluated by inductive plasma optical emission spectrometry (ICP-OES). The optimum condition results in more than 99% of Li leaching under 2 M H<sub>2</sub>SO<sub>4</sub> at 75 °C for 1 h. Co-precipitation of Na<sub>2</sub>CO<sub>3</sub> and CO<sub>2</sub> were applied to form lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>), which was then crystallized via evaporation to a 95 % purity.

## 1. Introduction

Thailand had constantly advocated for a policy encouraging the use of electric vehicles (EVs) as a result of EVs is ability to reduce air pollution, specifically particulate matter (PM) 2.5 and greenhouse gas emission, which are the main cause of global warming. Consequently, the manufacture of EVs is influenced by increasing demands for decarbonization and carbon dioxide (CO<sub>2</sub>) emission reduction, which promotes a rapid rise in the number of Lithium-ion battery (LIB) waste with an increase in the use of electronic vehicles (Ghassa et al., 2021). LIBs play a significant role in energy storage in electronic vehicles due to their high energy density and high working voltage (Arshad et al., 2020), with the demand of LIBs for EVs expected to reach 240,000 pieces in 2023. LIBs waste from EVs will challenge the waste management solutions in end-of-life (EoL) treatment according to various battery chemistry using to create the LIBs. Unsuitable disposal of wasted LIBs can cause groundwater contamination causing serious dangers to the environment and human health. Due to the reason that spent LIBs contain hazardous organic electrolytes and heavy metal ions (Nshizirungu et al., 2020). Recycling process is the best method for the material circulation, especially the valuable metals such as lithium (Li), nickel (Ni), cobalt (Co), and manganese (Mn) being high-priced metals (Duarte et al., 2022). The recovery of specific materials with recycling techniques will contribute to higher outputs that will minimize the cost of a new battery manufactured from recirculated components. To improve the quality of recovered materials, thermal pre-treatment is typically employed to eliminate organic compounds and carbon before the leaching process. However, hydrometallurgy process for valuable metal recovery necessitates considerable energy consumption

for thermal treatment at 700 to 900 °C, which has an impact on the high cost of recirculated materials, CO<sub>2</sub> emissions and difficult for local community to operate (Costa et al., 2021).

In view of the above reasons, the physical-chemical treatment process is preferable due to low energy requirement and provides high metal recovery rates and uncomplicated operation. The suitable and sustainable route for Li recovery should be demonstrated. Physical processes include separating, crushing, sieving, etc. Chemical processes are leaching, extraction and precipitation. In order to extract the valuable metal and increase the recovered yield, some studies have been carried out using the leaching method (Shin et al., 2005). For the acid leaching process, inorganic acids including hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>) are mostly used. According to Guo et al. (2016), a leaching yield of more than 99.4 % of lithium was obtained using a 3 M HCl solution at 80 °C and a 90 min leaching time (Guo et al., 2016). Aaltonen et al. (2017) presented 100 % of recovered cobalt yield at 2 M of H<sub>2</sub>SO<sub>4</sub>, at 80 °C of leaching temperature for 6 h of leaching time (Aaltonen et al., 2017). In order to extract Li and Mn, the acid hydrolysis process was applied to extract those metal from cathode materials with nitric acid, and produced the recovery of 100 % Li and 95 % Mn (Castillo et al., 2002). Finally, the addition of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) or supercritical CO<sub>2</sub> to obtain Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) is necessary for the separation of Li products (Huang et al., 2018).

In this work, the process and equipment for recovering precious metals from deteriorated batteries is conceptualized and designed for local community in Thailand. A physical-chemical process for recovering valuable metals from spent LIBs using inorganic acid extraction without thermal treatment was investigated. The developed process will achieve efficient recovery of spent LIBs. The recovery procedure included the following steps: (1) physical disassembly; (2) acid leaching of black powder; and (3) precipitation. The major objective was to determine how different factors affected on acid extraction: the type of acid, size of crushing LIBs, acid concentration, solid and liquid ratio (S/L), time and temperature.

## 2. Experimental methods

### 2.1 Materials and chemicals

The chemical composition of the spent LIBs was determined to be a combination of lithium iron phosphate (LiFePO<sub>4</sub>) and Lithium cobalt oxide (LiCoO<sub>2</sub>) which are commonly utilized for EVs in Thailand. Spent LIBs were crushed into to smaller pieces using a shredding machine and sieved to separate the black powder into three different particle sizes (small (< 1 mm.), medium (1 – 5 mm.) and large (> 5 mm.)). An inductively coupled plasma technique (ICP-OES) was used to characterize the black powder, and determined the concentration of valuable metals. For the leachability study, black powder was leached with 1 M of Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and nitric acid (HNO<sub>3</sub>) for 1 h reaction time, 75 °C for leaching temperature and 1:100 of S/L ratio to minimize the effect of experiment which the equipment was shown in Figure 1.

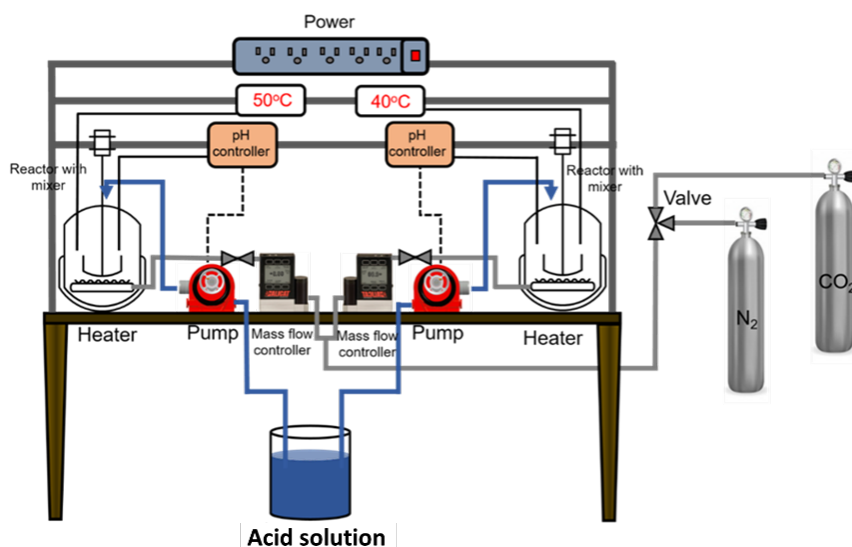


Figure 1: Equipment for the recovery processing of spent LIBs using acid extraction

## 2.2 Acid leaching of black powder and recovery of Li from leaching solution

1,000 mL of acid was added to 100 g of black powder, then the mixture was continuously stirred for 1 h at 75 °C with adding 5 v/v of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The solid was removed using filtration, and the solution was collected for the precipitation process. After adding NaOH to the solution to adjust pH to be 4, it was filtered to remove the solid residue. The pH of the solution was adjusted to 8 – 10, the solid residue occurred this process was filtered out, and the final solution was heated to 95 °C. In this experiment, two precipitation techniques were employed: (1) Na<sub>2</sub>CO<sub>3</sub> was added in the solution until the amount of precipitate remained constant (2) Co-precipitation: 3 g of Na<sub>2</sub>CO<sub>3</sub> with 50 mL/min of CO<sub>2</sub> for 1 h.

## 3. Results and discussion

The influence of different factors on the acid extraction was examined: acid type, particle size of crushing LIBs, acid concentration, solid and liquid ratio (S/L), time and temperature.

### 3.1 Battery characterization

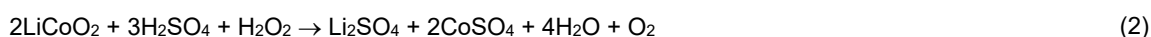
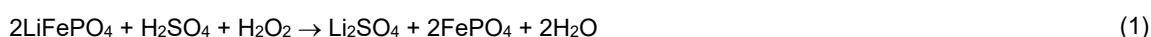
The cathode, anode, separator, and electrolyte are the four main parts of the spent LIBs, the amount of composition was presented in Table 1. Commonly, a plastic film covering a metal shell wrapped in another plastic is used to separate the electrodes. Anode made of graphite is attached to an aluminium (Al) sheet and cathode material made of LiCoO<sub>2</sub> or LiFePO<sub>4</sub> is adhered to a copper (Cu) sheet. The electrodes are soaked in an electrolyte. From element analysis using ICP-OES, the result of metal composition of the spent LIBs in table 1 showed the determination of the contents of cathode in spent LIBs. It can be supposed that the detected concentrations of Ni and Cu represent the impurities remained after the pre-treatment of the black powder. The great portion of the analyzed materials consisted of LiCoO<sub>2</sub> and LiFePO<sub>4</sub> is Li about 0.69 – 2.81 %.

Table 1: The material and metal of the spent LIBs

	Weight percent (%)	LiFePO <sub>4</sub>	LiCoO <sub>2</sub>
Material composition	Plastic	11.29 – 25.72	1.09
	Al	0.28 – 0.85	-
	Cu	1.80 – 5.80	-
	Cathode and Anode	65.06 – 80.32	76.42
	Electrolyte	2.10 – 8.40	-
	Steel casing	-	22.49
Metal composition	Li	0.69 – 1.87	1.18 – 2.81
	Fe	0.006 – 17.45	0.066 – 0.176
	Cu	12.61 – 29.47	7.73 – 16.68
	Mn	0.001 – 0.18	0.0002 – 0.0007
	Cd	N/A	N/A
	Ni	0.003 – 0.12	14.13 – 32.99
	Co	0.003 – 0.007	0.34 – 1.78

### 3.2 Effect of acid extraction

For the leachability study, 1 M of H<sub>3</sub>PO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> were used to investigate the performance of Li recovery. After a leaching time of 1 h leaching operation at a leaching temperature of 75 °C with 1:100 of S/L ratio, the leaching yield of Li in H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> was approximately 78 – 82 %, while HCl produced a Li leaching yield of 65 %. When considering the price of acid, H<sub>2</sub>SO<sub>4</sub> costs less than other acids. Moreover, H<sub>2</sub>SO<sub>4</sub> is a strong mineral acid resulting more dissolve ability of lithium in a typical cathode material by lithium to be Lithium sulfate (Li<sub>2</sub>SO<sub>4</sub>) up to 96 – 99 % (He et al., 2017). Thus, H<sub>2</sub>SO<sub>4</sub> was selected to examine the other factors. The leaching reactions could be described as Eq(1) and Eq(2) (Petranikova et al., 2022).



### 3.3 Effect of LIBs crushing size and acid concentration

Following physical processing, black powder was sieved into three particle sizes, as indicated in Figure 2: small (1 mm), medium (1 – 5 mm), and large (> 5 mm). The 1 M H<sub>2</sub>SO<sub>4</sub> leaching efficiency of Li was evaluated at 75

°C and 1:100 of S/L ratio. It was shown in table 2 that LIBs crushing size had no influence on the leaching efficiency of Li. Then, 1 M and 2 M H<sub>2</sub>SO<sub>4</sub> were used to investigate the impact of acid concentration. Leaching efficiency of Li was improved to a range of 97 – 99 % as a result of the enhance in acid concentration from 1 M to 2 M H<sub>2</sub>SO<sub>4</sub>. In order to achieve the maximum separation of Li, 2 M H<sub>2</sub>SO<sub>4</sub> was chose in subsequent experiments.

Table 2: Effect of LIBs crushing size and H<sub>2</sub>SO<sub>4</sub> concentration

	Weight of Li (g)					
	Small (< 1 millimeter)		Medium (1 – 5 millimeter)		Large (> 5 millimeter)	
Acid concentration	1 M	2 M	1 M	2 M	1 M	2 M
Leaching yield (%)	96.99	97.67	95.81	97.33	97.15	99.89

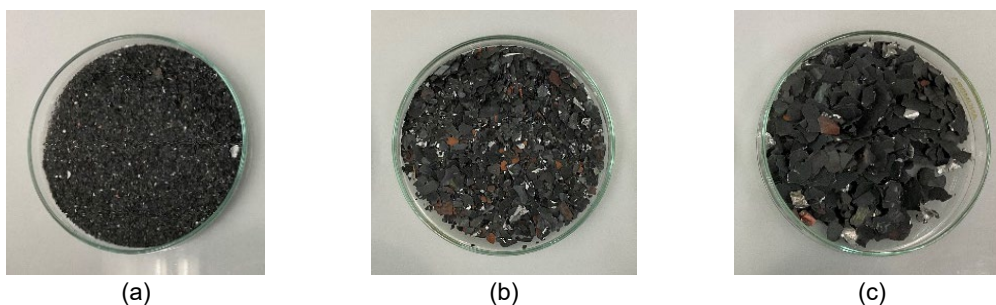


Figure 2: Black powder particle sizes and characteristics (a) small (< 1 mm), (b) Medium (1 – 5 mm) and (c) large (> 5 mm)

### 3.4 Effect of acid leaching time and temperature

In order to investigate the effect of acid leaching time and temperature on the leaching efficiency of Li. Leaching efficiency of Li using 1 M H<sub>2</sub>SO<sub>4</sub> was tested under 1:100 of S/L ratio for 1 h. With an increase in the temperature, the leaching efficiency of Li increased from 90 to 94 % for 30 °C to 96 to 97 % for 75 °C as shown in Table 3. Furthermore, the Li leaching efficiency always remained higher than 99 % for 2 M H<sub>2</sub>SO<sub>4</sub>, indicating the complete reduction of Li. When considering the increment of time, the maximum leaching yield was 96.8% at 1 h and 97.65 % at 2 h. The reaction time of acid extraction showed less significant different changes to Li leaching efficiency. Therefore, 2 M H<sub>2</sub>SO<sub>4</sub> at 75 °C for 1 h can be used the optimal condition.

Table 3: Effect of H<sub>2</sub>SO<sub>4</sub> leaching time and temperature

H <sub>2</sub> SO <sub>4</sub> concentration	Weight of Li (g)					
	1 M		2 M		2 M	
Leaching time	1 h		2 h		1 h	
Leaching temperature (°C)	30	75	30 °C	75	30	75
Leaching yield (%)	90.78	96.80	93.89	9.65	92.67	99.11

### 3.5 Effect of solid-liquid (S/L) ratio

The influence of S/L ratio on the leaching efficiency of Li was examined under the constant condition of 2 M H<sub>2</sub>SO<sub>4</sub> at 75 °C for 1 h. The influent of the S/L ratio on the performance of Li leaching was investigated at varied ratios of 1:5, 1:10, and 1:20. With an increase in S/L ratio, leaching efficiency of Li was improved from 92.69 % for 1:5 to 99.11 % for 1:10. However, the improvement of Li leachability was not caused from a higher S/L ratio. As a result, it was found that a S/L ratio of 1:10 was best suited.

### 3.6 Recovery of Li from the leaching solution via precipitation

To control the solubility of Li<sub>2</sub>CO<sub>3</sub>, which decrease with rising temperature, the Li precipitation process was examined at high temperatures. The Li<sub>2</sub>CO<sub>3</sub> precipitate was generated using two different techniques: (1) Na<sub>2</sub>CO<sub>3</sub> (2) Na<sub>2</sub>CO<sub>3</sub> with CO<sub>2</sub>. Li<sub>2</sub>CO<sub>3</sub> was precipitated more than 94 % efficiency using 100 to 130 g of Na<sub>2</sub>CO<sub>3</sub> at 100 °C after acid extraction with 2 M H<sub>2</sub>SO<sub>4</sub> at 75 °C for 1 h with S/L ratio of 1:10. While, more than 96 % of Li<sub>2</sub>CO<sub>3</sub> was crystallized after adding 3 g of Na<sub>2</sub>CO<sub>3</sub> with 50 mL/min of CO<sub>2</sub> for 1 h. Figure 3 illustrated the

precipitated powder of  $\text{Li}_2\text{CO}_3$  via  $\text{Na}_2\text{CO}_3$  (yellow) and  $\text{Na}_2\text{CO}_3$  with  $\text{CO}_2$  (white) for precipitation process. The leaching reactions could be described as Eq(3) and Eq(4) (Li et al., 2017).



(a)

(b)

Figure 3:  $\text{Li}_2\text{CO}_3$  powder from Li precipitation process (a)  $\text{Li}_2\text{CO}_3$  precipitate from  $\text{Na}_2\text{CO}_3$  and (b)  $\text{Li}_2\text{CO}_3$  precipitate from  $\text{Na}_2\text{CO}_3$  with  $\text{CO}_2$

According to sulfuric acid leaching presented the best performance, was most preferable because of a cheaper and less-toxic (Mantuano et al., 2006). The comparison of leaching efficiency was summarized by other work in Table 4).

Table 4: Summary of leaching efficiency

Material	Acid extraction and Leaching efficiency	Precipitation efficiency	Reference
$\text{LiFePO}_4$	96.85% for Li, 0.3 M $\text{H}_2\text{SO}_4$ , $\text{H}_2\text{O}_2$	96.85% for Li was recovered by $\text{Na}_3\text{PO}_4$	Li et al., 2017
	97.23% for Li, 1 M $\text{H}_2\text{SO}_4$ , $\text{NaClO}_3$	-	Tang et al., 2020
	94.29% for Li, 0.6 $\text{H}_3\text{PO}_4$ , EDTA-2Na	82.55% for Li was recovered by $\text{Na}_3\text{PO}_4$	Yang et al., 2017
$\text{LiCoO}_2$	99.00% for Li, 2 M $\text{H}_2\text{SO}_4$ , 5 v/v $\text{H}_2\text{O}_2$	-	Jha et al., 2013
	87.00% for Li, 2 M $\text{H}_2\text{SO}_4$ , 2 v/v $\text{H}_2\text{O}_2$	71.00% for Li was recovered by $\text{Na}_2\text{CO}_3$	Zhu et al., 2012
Mix $\text{LiFePO}_4$ and $\text{LiCoO}_2$	95.00% for Li, 2 M $\text{H}_2\text{SO}_4$ , 5 v/v $\text{H}_2\text{O}_2$	96.00% for Li was recovered by $\text{Na}_2\text{CO}_3$ with $\text{CO}_2$	This work

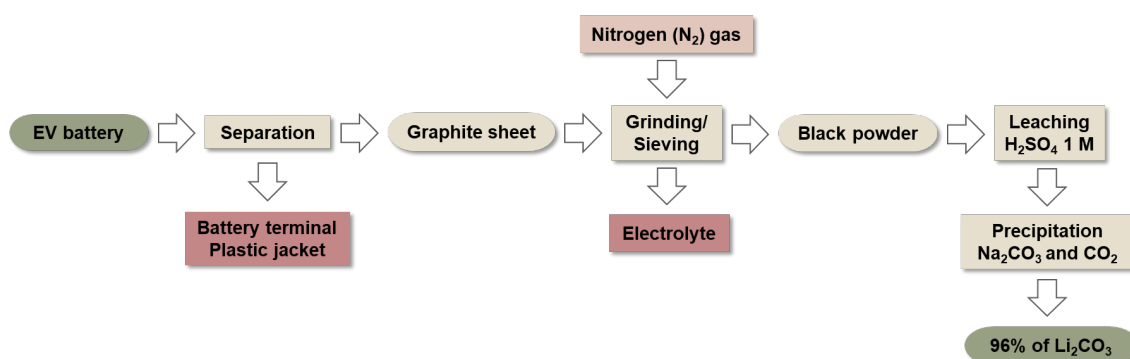


Figure 4: the process for recovering precious metals from deteriorated batteries

#### 4. Conclusions

It was determined that the  $\text{Li}_2\text{CO}_3$  products from acid extraction at various influences presented impacts to the Li recovery efficiency. When the acid concentration, leaching temperature, and S/L ratio were increased, the leaching yield was also increased. The temperature of acid leaching was raised from 30 to 75 °C, a steady

improvement in the leaching yield was presented. While, the increase of time and particle size did not promote any positive impact on Li leaching samples which longer reaction time related to high energy consumption. Thus, the optimal conditions are 2 M  $\text{H}_2\text{SO}_4$  at 75 °C for 1 h with S/L ratio of 1:10. Under these conditions, high recovery efficiency of Li precipitation via  $\text{Na}_2\text{CO}_3$  and  $\text{CO}_2$  is 95% of  $\text{Li}_2\text{CO}_3$  precipitation. The process for recovering precious metals from deteriorated batteries was presented in Figure 4. However, method in this work for recovering valuable metals from deteriorated batteries is an illustration of a small trial before a larger power amplification in actual application.

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