

Lithium Separation and Up-concentration from Battery Recycling Effluent by Synergistic Solvent Extraction

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Abstract. Exponential growth in the electric vehicle (EV) market warrants a stable supply of certain materials including lithium (Li). Due to its criticality and environmental concern, Li recycling from spent batteries is justified. Although there are several industrially established schemes for end-of-life battery recycling, major drawbacks are still encountered regarding Li recovery. In most recycling schemes, Li stands to be the last element that is recovered. This causes major loss of Li during the process and high energy is consumed to recover it from the final effluent i.e. evaporation, rendering Li recovery economically unattractive. Evaporation is generally applied to up-concentrate Li in the effluent to attain the minimum concentration required to induce precipitation and crystallization in Li salt production. In this research, solvent extraction is being proposed as a low energy alternative in Li up-concentration and separation from recycling effluent. The synergistic effect between 2-thenoyl trifluoro acetone (HTTA) and trioctylphosphine oxide (TOPO) as extractants in kerosene as diluent has been tested in batch studies to increase Li concentration in the final solution. Optimal extraction conditions reported include HTTA/TOPO mol ratio 1, shaking speed 250 rpm, extraction time 10 min, aqueous/organic volume ratio 1 and pH 10.1 (Li extraction rate 55.6 %). The maximum loading capacity of organic phase for Li was 1.2 g/L and complete stripping of Li could be achieved using 0.5 M sulfuric acid. It was demonstrated that the solvent extraction scheme can increase Li concentration in the effluent from 0.23 g/L to 10.06 g/L, which is suitable concentration for Li salt production by further precipitation or crystallization.

1 Introduction

Increasing demand for lithium (Li) occurs exponentially in recent years to supply lithium-ion battery (LIB) production as the main component in electric vehicle (EV). LIB compared to other battery type has advantages in terms of high energy density, low discharge rate and long-life cycle [1]. In 2020 it was estimated that more than 10 million EVs will hit the road and in 2030 in Europe, about 200,000 million tonnes of LIB will enter their end-of-life phase [2]. This spent LIB needs to be treated properly, otherwise it will cause major land pollution due to its heavy metal content i.e., nickel (Ni) and cobalt (Co). Aside from the pollution mitigation aspect, the treatment of spent LIBs especially recycling is justified to secure the raw material supply in LIB production since most of LIB components especially Li is considered as critical raw materials (CRM) by the European Union.

Numerous LIB recycling schemes have been proposed and developed and some are mature enough to be applied in industrial scale [3]. In general, before the recycling begins, the battery will be discharged, dismantled, shredded and milled. Among the battery components, the cathode is the most targeted in recycling process due to its value and critical element content (Li, Ni, Co). Prior to recycling, both cathode and anode components will end up as mixture called black mass (BM) and will be further processed using either

high temperature process (pyrometallurgy) [4], chemical process (hydrometallurgy) [5] or direct recycling [6]. Hydrometallurgy is in the forefront of LIB recycling technology [7]. The stages involved in hydrometallurgical Li recovery include chemical dissolution (leaching) using inorganic acids or organic acids; separation and purification either using solvent extraction, ion exchange-adsorption, precipitation or membrane and finally metal production as Li_2CO_3 and LiOH by precipitation-crystallization, which are further used as battery cathode precursors.

Although, hydrometallurgical process possesses the most advance technological readiness and commercially available for LIB recycling, several shortcomings especially for Li recovery persists. This includes significant loss of Li in the stream and sodium impurities problem in Li_2CO_3 product due to massive use of sodium carbonate as precipitant. Aside from these, Li_2CO_3 precipitation requires solution with high Li concentration (> 1.2 g/L). To reach this condition, the effluent as leaching and separation-purification product is traditionally evaporated to increase Li concentration [8].

Solvent extraction has been suggested for Li separation and purification. Extractant systems such as tributyl phosphate (TBP)- FeCl_3 -kerosene [9], and 2-thenoyltrifluoroacetone (HTTA)-TOPO-kerosene [10] have been advised for Li extraction and up-

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concentration from brine solutions or chloride media. In this research, HTTA-TOPO-kerosene system will be reviewed for its efficacy in Li recovery from leach solution produced by water leaching of BM. Water leaching was advised in previous studies for its selectivity toward Li [11-14], minimizing the impurities rendering hence facilitating direct Li salts production from the leach solution. The effect of organic to aqueous ratio, initial Li concentration, and acid stripping to Li recovery has been studied using batch process to find the optimum condition for Li up-concentration. HTTA-TOPO-kerosene system is considered more suitable for this research compared to (TBP)-FeCl₃-kerosene, whose efficiency heavily depends on chloride content in leach solution.

2 Materials and method

There were two types of leach solution (effluent) used in this study: artificial effluent (AF) and water leach effluent (WLE). AF was prepared by dissolving LiOH in MilliQ water, while WLE was obtained from water leaching of BM as advised by previous work in our research group [15], (leaching condition T = 80 °C, pH = 10, t = 30 min, agitation = 400 rpm and solid/liquid ratio = 20 g/L). BM samples was provided by research partner and chemicals such as HTTA, TOPO (90%), kerosene (reagent grade), sulfuric acid (98%), LiOH (98%) were purchased from Sigma Aldrich, and acetic acid (99.8%) was obtained from Honeywell. All chemicals were used as received and MilliQ water was used for all solution preparation.

All solvent extraction tests were done using a batch process. Organic phase consists of HTTA-TOPO as extractant and kerosene as diluent was mixed with aqueous phase (AF or WLE) in 50 ml centrifuge tube. The mixture (total volume 20 ml or otherwise stated) was homogenized using reciprocal shaker IKA® HS 501 digital (10 min, 250 rpm). After the extraction the phases were separated by centrifugation (5 min, 4000 rpm) to ensure the phase separation. The aqueous phase was then sampled, and its metal concentration was determined by Microwave Plasma Atomic Emission Spectroscopy (MP-AES, Agilent 4210). By comparing the Li concentration in aqueous phase before and after extraction or stripping, the extraction (E, %) or stripping recovery (S, %) were calculated using the mass balance (eq 1 and 2).

$$E = \frac{(C_o - C_E)}{C_o} \times 100\% \quad (1)$$

$$S = \frac{(C_{aq} \times V_{aq})}{(C_{org} \times V_{org})} \times 100\% \quad (2)$$

- C_o initial Li concentration in aqueous phase (mg/L)
- C_E Li concentration in aqueous phase after extraction (mg/L)
- C_{aq} Li concentration in strip phase after stripping (mg/L)
- V_{aq} volume of strip solution (L)
- C_{org} Li concentration in loaded organic before stripping (mg/L)

V_{org} volume loaded organic stripped (L)

In stripping test, Li-loaded organic was equilibrated with sulfuric acid or acetic acid solution using the same batch condition as the extraction test. To assess the results repeatability, all experiments were at least in duplicate.

3 Results and discussions

3.1 Effect of aqueous to organic (A/O) volume ratio

The constant parameters in this study included HTTA/TOPO molar ratio of 1 and extractant concentration 0.2 M, while the WLE was used as aqueous phase (Fig 1). From Fig 1 it is clear that Li extraction decreases when A/O increases, which is generally caused by the crowding effect (decreasing of mol ratio between extractant available to the Li). Decreasing organic volume to the aqueous volume also reduces the contact surface between organic-aqueous phases and further decrease Li transfer from aqueous to organic. During the extraction at higher A/O ratio, formation of an emulsion (third phase) was visually observed, but this problem can be prevented by adding TBP as modifier.

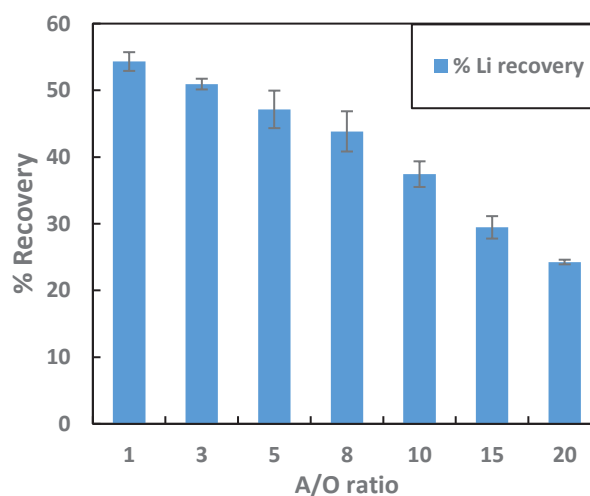


Fig. 1. Effect of A/O ratio on the % recovery of Li and Al.

Table 1. Theoretical number of stages required for ≈ 50% extraction of lithium at different A/O ratio.

A/O	Li recovered (%)	Theoretical stages
1	54.3	1 counter current
3	50.9	2 cross current
5	47.1	2 cross current
8	43.8	3 counter current
10	37.4	3 cross current
15	29.5	2 cross current and 2 counter current

The metal concentration results in aqueous and organic phase from the A/O ratio studies was further used for McCabe-Thiele plot. The plot was used to determine the

theoretical number of stages required for the extraction (Table 1). It seems that based on the plot, the total extraction of Li from could not be reached. The intersection between extraction curve and axis indicated that at least about 0.1 g/L of Li still exist in the effluent after extraction ($\approx 50\%$ extraction recovery). However, based on current studies, the maximum loading capacity of 0.2 M HTTA-TOPO obtained was 1.2 g/L (A/O 20) (Fig 2).

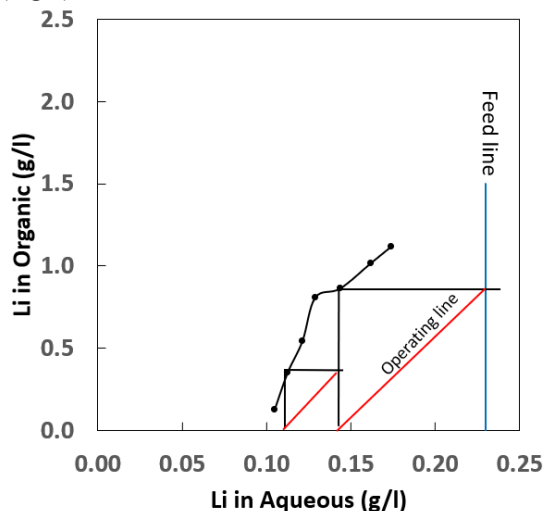


Fig. 2. Extraction isotherm of Li using HTTA-TOPO 0.2 M. McCabe-Thiele plot is shown for A/O 10.

3.2 Effect of initial Li concentration

The objective of this study was to determine and confirm the maximum loading capacity of HTTA-TOPO obtained in the previous section using artificial leachate (AF), of which Li concentration varied between 0.14 and 2.93 g/L. This typical Li concentration mimics the pregnant leach solution obtained in water leaching of BM in previous studies [15]. The control variable in this test includes A/O 1 and the results are shown in Table 2. It can be seen that increasing Li in aqueous phase enhanced the loading capacity of the organic phase. Hypothetically, HTTA-TOPO complexation with Li occurs with mol ratio 1, therefore the maximum loading capacity of Li in the organic phase would be 0.2 M or about 1.39 g/L. The maximum loading capacity obtained with this study (1.26 g/L) confirmed this hypothesis.

Table 2. Effect of initial lithium concentration on loading capacity of HTTA-TOPO 0.2 M (A/O 1)

Initial Li in aqueous (g/l)	Final Li in aqueous (g/l)	Li recovered %	Li in organic (g/l)
2.93	1.67	42.9	1.26
1.41	0.27	81.1	1.14
0.66	0.091	86.2	0.57
0.28	0.039	86.2	0.24
0.14	0.023	83.9	0.12

There is a discrepancy in the results shown Table 2 and the results in previous section. In Table 2, with

initial concentration of Li 0.28 g/L resulted in 86% extraction recovery, while and the results in the previous section using Li initial concentration 0.23 g/L only resulted in 54% extraction rate. This discrepancy was caused by different pH between two solutions. The AF used in Table 2 has higher pH (12.6) compared to real solution (WLE) used in previous section (pH 10). pH has significant effect on HTTA-TOPO extraction system, which is favoured in alkaline pH. In alkaline condition enolic hydrogen atom of HTTA is released and replaced with metal ion to form chelate ring (35). pH adjustment was not done in this study since the pH adjustment required the addition of alkalis especially potassium and sodium, while the competitive effect of potassium and sodium on Li extraction is not yet well understood.

3.3 Effect of acid and its concentration on stripping studies

Two kinds of acids (sulfuric acid and acetic acid) were used to strip Li from loaded organic. Loaded organic was prepared according to extraction condition outlined in section 3.2 (Li synthetic solution 2.93 g/L, A/O 1, HTTA-TOPO 0.2 M), resulted in Li concentration in organic phase 1.45 g/L. The control variable used in stripping test includes organic to aqueous volume ratio (O/A) 1, total vol 20 ml, rpm reciprocal shaker 250, 10 min), (Fig 3). The figure shows that increasing acid concentration has positive effect on stripping rate of Li, while in control condition (stripping using water) the rate was negligible. The figure also shows that the increase of stripping recovery occurred until acid concentration 0.5 M (sulfuric acid). Higher acid concentration decreased the Li stripping recovery. It is postulated that the viscosity factor of sulfuric acid at higher concentration affect the Li mass transfer from organic to aqueous phase (stripping efficiency). However, further study is required to confirm this hypothesis. In the case of acetic acid, the maximum stripping rate happened at acid concentration 0.8 M (91.4% recovery), while the stripping rate slightly declined at higher concentration (1 M, 86% recovery).

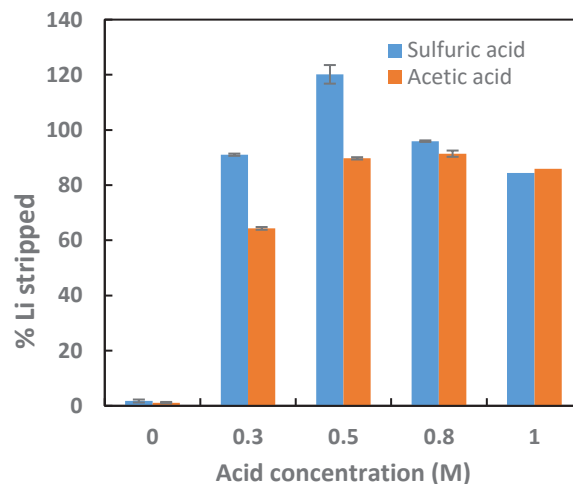


Fig 3. Effect of Type of acid and its concentration on Li stripping rate.

3.4 Effect of organic to aqueous (O/A) ratio in stripping

The effect of O/A to stripping rate was studied at control variable acid concentration 0.5 M and 0.8 M for sulfuric acid and acetic acid, respectively. The main goal is to determine the stripping capacity of each acid, (Table 3). The table shows that some stripping rates are higher than 100%. This might be caused by random error in regard to Li concentration in loaded organics. Loaded organic for stripping test was prepared by equilibrating LiOH solution with organic phase (HTTA-TOPO in kerosene). The concentration of Li in loaded organic was not directly measured but rather then calculated using mass balance based on the difference of Li concentration in aqueous phase before and after extraction.

The results show that sulfuric acid has more stripping capacity than acetic acid. This is because acetic acid as weak acid did not completely release its H⁺ during stripping for exchange for Li⁺. McCabe-Thiele plot (Fig 4) for stripping using Li concentration in both organic and strip phase after stripping was done to determine theoretical stage for Li stripping (Table 4). Maximum Li concentration obtained in stripping studies using sulfuric acid 0.5 M was 10.06 g/L (Fig 4), which corresponded to up-concentration factor about 45 times from the initial effluent (0.23 g/L). Final concentration of Li in strip solution is suitable for Li precipitation as carbonate (minimum concentration 1.2 g/L Li).

Table 3. Effect of O/A ratio on Li stripping rate using sulfuric acid 0.5 M and acetic acid 0.8 M.

Stripping agent	O/A	Initial Li conc. in org. (g/L)	Li in strip phase (g/L)	Li stripped (%)
H ₂ SO ₄ 0.5 M	10	1.19	10.06	84.5
	8		8.43	88.5
	5		7.52	126.0
	3		4.66	130.0
	1		1.29	108.9
CH ₃ COOH 0.8 M	10	1.46	3.61	24.7
	8		3.65	31.2
	5		2.86	39.1
	3		2.38	54.2
	1		1.36	92.7

Table 4. Li stripping rate and theoretical stage for complete Li stripping using 0.5 M sulfuric acid.

O/A	Li stripped (%)	Theoretical Stage
1	108.9	1 counter current
3	130.0	1 counter current
5	126.0	1 counter current
8	88.5	2 counter current
10	84.5	2 cross current

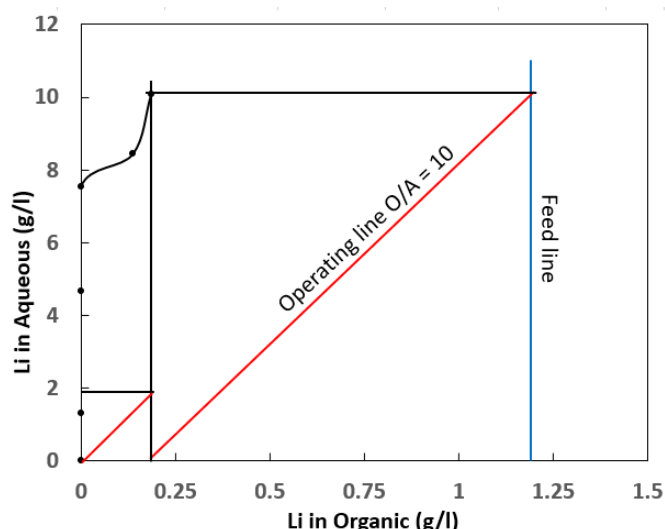


Fig 4. Stripping isotherm of Li using sulfuric acid 0.5 M. McCabe-Thiele plot is shown for O/A ratio 10.

4 Conclusions

Li up-concentration from effluent was achieved using solvent extraction. Synergistic effect between HTTA and TOPO effectively and selectively extract Li from water effluent and release it during stripping using both acetic acid and sulfuric acid. Extractant concentration 0.2 M gave the maximum extraction rate (55.79%), while minimum Li concentration for effective extraction was 0.1 g/L. Based on effect of A/O ratio and initial Li concentration studies, maximum loading capacity of 0.2 M extractant was 1.2 g/L Li, which is stoichiometrically confirmed by H⁺ exchange from the extractant. Stripping of Li was quantitative using sulfuric acid 0.5 M. In this case Li concentration in strip solution can reach about 10.06 g/L, which is suitable concentration for Li precipitation as carbonate.

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