Acquisition of Co metal from spent lithium-ion battery using emulsion liquid membrane technology and emulsion stability test

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Abstract. Lithium-ion batteries are the most common type to be used as energy source in mobile phone. The amount of lithium-ion battery wastes is approximated by $200 - 500$ ton/year. In one lithium-ion battery, there are $5 - 20\%$ of cobalt metal, depend on the manufacturer. One of the way to recover a valuable metal from waste is leaching process then continued with extraction, which is the aim of this study. Spent lithium-ion batteries will be characterized with EDX and AAS, the result will show the amount of cobalt metal with form of $LiCoO_2$ in the cathode. Hydrochloric acid concentration used is 4 M, temperature 80°C, and reaction time 1 hour. This study will discuss the emulsion stability test on emulsion liquid membrane. The purpose of emulsion stability test in this study was to determine optimum concentration of surfactant and extractant to produce a stable emulsion. Surfactant and extractant used were SPAN 80 and Cyanex 272 respectively with both concentrations varied. Membrane and feed phase ratios used in this experiment was 1 : 2. The optimum results of this study were SPAN 80 concentrations of 10% w/v and Cyanex 272 0.7 M.

1. Introduction

Lithium ion batteries consist of heavy metals, organic chemicals and plastics in the proportion of 5-20% cobalt, 5-10% nickel, 5-7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers [1]. Some methods to recover cobalt are liquid-liquid extraction, electrowinning, emulsion liquid membrane, vaporization, and hydroxide precipitation. In this study, leaching is used to recover cobalt, to dissolve lithium ion battery wastes with leaching agent and continued with emulsion liquid membrane to extract cobalt metal from leachtant.

Leaching is a solid-liquid extraction method where the separation of solid cobalt mixed with leaching agent so the metal inside can be dissolved into the leaching agent. Strong acids like sulfuric acid and hydrochloric acid were often used as leaching agent. There is a previous study about recovering cobalt metal from lithium ion battery, comparing three reagents as leaching agents which are sulfuric acid, hydroxylamine hydrochloride, and hydrochloric acid [2]. Between three reagents stated, hydrochloric acid is the most suitable and effective with more than 99% cobalt metal leached in a hydrochloric acid 4 M in 80°C temperature, and stirring time of 1 hour.

Emulsion liquid membrane have some attractive features, for example, simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, scope of continuous operation. By extracting and stripping in one stage, it will reduce reaction time and reagents needed unlike liquid-liquid extraction method [3]. Emulsion liquid membrane is the right choice because it has the highest degree of separation and can be applied in a large scale [4].

Separation of liquid membrane provides an interesting option for separation process. Compared with conventional process, emulsion liquid membrane (ELM) and surfactant liquid membrane (LSM) have several advantages such as easy operation, high efficiency, extraction and stripping process at the same stage, large interface area, and can run continuously. ELM technique has great potential for recovering and removing metal and hydrocarbon ions from wastes where the efficiency of conventional separation processes is lower. Liquid membrane process uses a selective liquid membrane phase during extraction/stripping process. Separation is achieved by solute permeation through liquid phase of membrane from feed phase to receiving phase. Both phases (feed and receiver phase) are usually soluble but membrane phase is not dissolved with feed phase and receiving phase [4].

Liquid membrane is divided into three types: bulk liquid membrane, liquid supported membrane, and liquid membrane with two emulsions. Of the three types, emulsion liquid membrane has the largest mass transfer area compared to other two types. Emulsion forming system can be divided into two: water-in-oil emulsions dispersed in an external aqueous phase and oil-in-water dispersed in an external organic phase. Membrane phase with type water-in-oil-in-water (W / O / W), undissolved oil phase will separate aqueous phase, whereas oil-in-water-oil (O / W / O) type, undissolved aqueous phase will separate the two organic phases that play role as a membrane. Liquid membrane has two functions which are to move one or more components selectively from external phase to internal and vice versa, and to prevent mixing of external and internal phases. Figure 1 shows configuration in emulsion liquid membrane system with the letter F showing feed phase, E is liquid membrane, and R is receiving phase.
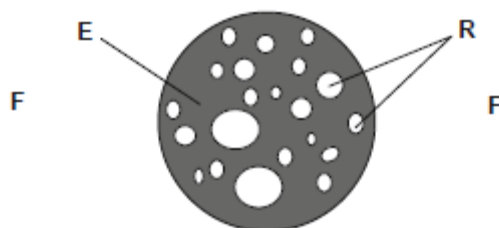

Figure 1. Emulsion liquid membrane system configuration
(Source: Kislik, 2010 [4])

2. Experimental

2.1 Materials
Lithium ion batteries that are used are from cell phone batteries various brand sold at the market (Samsung, iPhone, Xiaomi, and LG). Hydrochloric acid used as leaching agent, Cyanex 272 as extractant. Commercial kerosene, with density of 830 kg/m^3 used as diluent. SPAN 80 used as surfactant, and H_2SO_4 as stripping agent. All the materials were immediately used without reprocessing to purify the materials.

2.2 Experimental procedure
Initial step is preparation of materials. One of the preparation that needed to be done is soaking lithium ion batteries into sodium chloride solution to emptied the remaining electrical charge inside the batteries which may still be inside. Next step is leaching process with varying leaching agent which has been specified before, and will not be discussed further in this study. Solution after leaching (called leachant) then filtered to get rid of solid components which can't dissolve. After filtered, leachant then analysed of cobalt metal content with AAS (Atomic Absorption Spectroscopy). Next step is emulsion stability test using kerosene, Cyanex 272, SPAN 80, and H_2SO_4 with concentration of Cyanex 272 as extractant and SPAN 80 as surfactant being varied.

3. Results and discussion

3.1 Characterization lithium-ion battery waste

To characterize lithium ion battery waste with EDX and AAS analysis, cathode sheet scraped and crushed, after that filtered with 100 mesh filter so the result is cathode powder with size as small as possible so leaching process will be more effective, to make leaching efficiency high, it needs a particle with the size 100 mesh [5]. Figure 2 shows EDX analysis result of battery cathode powder. There is cobalt metal in the powder. EDX analysis is quantitative so AAS analysis is needed to determine how much cobalt metal is in the battery precisely. AAS analysis result with the amount of cobalt metal in cathode battery powder is 11.09%w/w. This goes with previous study by [5], in general range of cobalt metal content in lithium ion battery is 5 – 20% weight, depends on the battery's manufacturer.
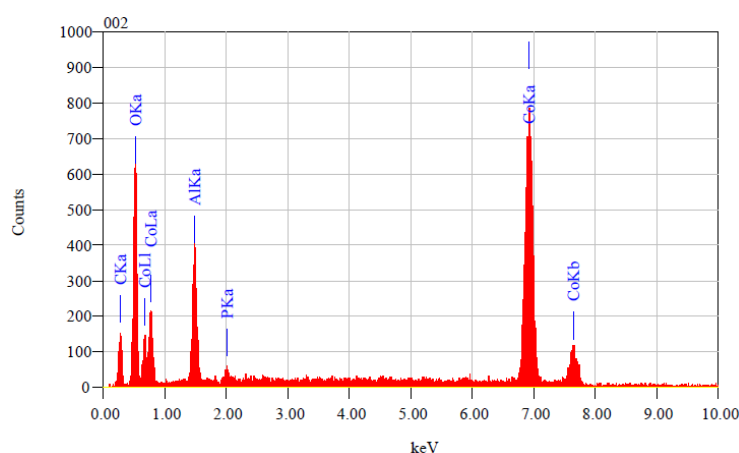

Figure 2. EDX analysis result graph

3.2 Emulsion stability test

Emulsion stability test is done based on eyes visual and percentage of stability based on how the emulsion volume decreases.

3.2.1 Effect of surfactant concentration. Surfactants are usually organic compounds that are amphipathic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water [6]. Surfactants plays a very important role in the emulsion formation and in the extraction process. It reduces the interfacial tension between oil and water by adsorbing at the liquid-liquid interface [6], maintains the emulsion stability and influences the transport rate of metal ions [7,8]. Wan and Zhang [9] revealed that the selection of a surfactant is the key measure to reduce emulsion swelling and membrane breakage. Therefore, the choice and development of a suitable surfactant [10-12] and establishment of surfactant concentration correctly will determine the success of ELM process.

There are some considerations of choosing surfactant for ELM separations. The hydrophile-lipophile balance (HLB) of surfactant determines the type of emulsion produced. Surfactants with a low HLB, typically ranging from 1 to 10, are more soluble in oil than water and tend to make a water-in-oil emulsion while those with a high HLB, typically ranging from 10 to 20, are more soluble in water than oil and tend to make an oil-in-water emulsion [6]. While to get stable emulsion, surfactant with least hydration capacity and low diffusivity due to its high molecular weight is preferable [9]. However, for overall ELM process, too stable emulsions are unfavorable for the difficulty in demulsification process.

According Figure 3, it is seen that the extractant concentration of 0.7 M and SPAN 80 10% w/v surfactant mixture makes the most stable emulsion and SPAN 80 4% w/v surfactant mixture makes the most unstable emulsion among all variations of surfactant concentration. This is because the emulsion stability depends on the concentration of the surfactant. An excessively high concentration of surfactant will increase resistance to interphase surfaces and this may contribute to the increase in viscosity of emulsion liquid membrane. Using too high surfactant concentrations but not importantly needed will decrease the efficiency of metal extraction due to the formation of high interphase resistances. Conversely, when the surfactant concentration is too low, emulsion leakage may result in a decrease in the volume of the emulsion in this experiment [13]. Beside of surfactant concentration, the emulsion stability is also significantly affected by the types of surfactant. Hasan et al. [14] reported that Span 80 with 12% concentration gave the least breakage compared to Span 85 and Arlacel A.
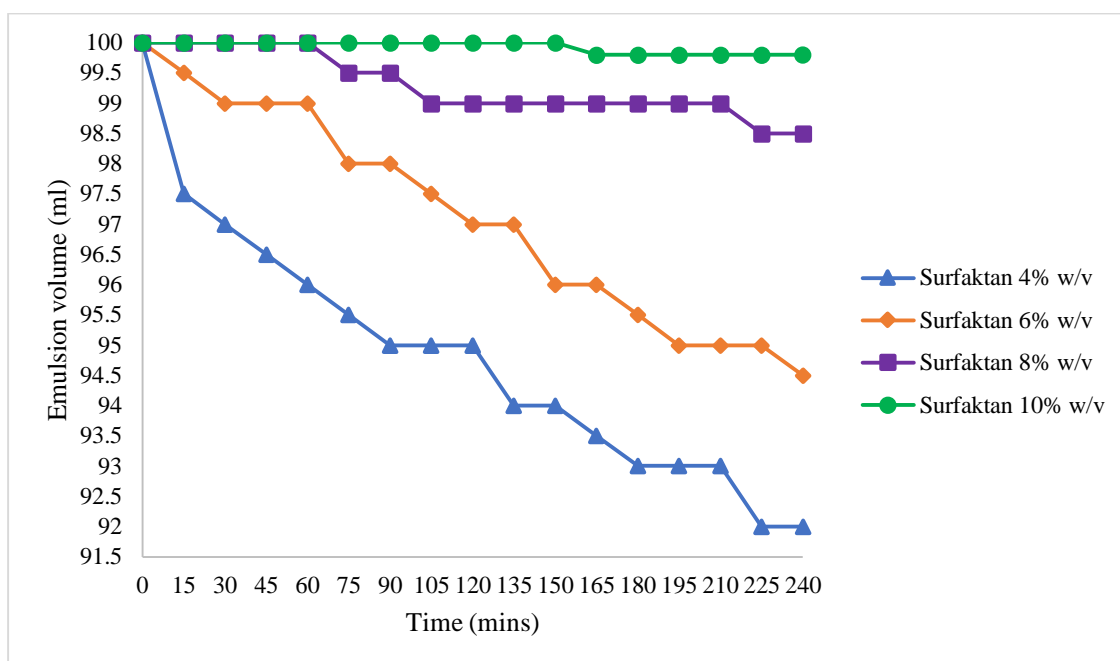

Figure 3. Emulsion stability, surfactant concentration being varied (extractant concentration 0.7 M, stirring speed 1500 rpm, stirring time 60 mins)

3.2.2 Effect of extractant concentration. Extractant acts as a 'shuttle' to carry the metal element through the liquid membrane [15]. However, its presence in membrane phase can decrease the emulsion stability. This is caused by the competitive adsorption with the surfactant as they have opposite behaviour. Interfacial tensions increased with an increase in carrier concentration in the membrane phase leading to formation of larger sized emulsion globules in the dispersed emulsion [16], conversely, interfacial tensions decreased by increasing the surfactant concentration up to a specific value. Gu et al. [17] revealed that the key criterion in selecting a carrier is that it and the complex formed must be soluble in the membrane phase, but not soluble in both the internal and feed phase. Further precipitation within the membrane or at the interfaces must also be prevented [18].

A great number of studies gave evidence that not only the type but also the concentration of extractant affects the emulsion stability. Emulsion breakdown can occur at high concentration of carrier, since the carrier and its complex with the metal present interfacial characteristics that provoke loss of internal aqueous solution [19]. Besides, a very high content of carrier in the membrane does not result in a benefit due to the increase in viscosity, which leads to larger globules.

In Figure 4, it is seen that extractant concentration of 0.7 M is the most stable among the other variations. This shows that the addition of extractant concentration affects emulsion stability.

Interphase tension decreases as the concentration of extractant in organic phase increases, but too high concentration can cause saturation in the phase and will form molecular aggregates called micelles. In non-polar fluids such as kerosene, the solvent used in this study, SPAN 80 alters the micelles, in which the polar head is directed to the center and the nonpolar portion is directed to the dispersed fluid. The extractant used has internal activity in emulsion liquid membrane system so that no surfactant concentration is too high in the organic phase to maintain the emulsion stability. Kerosene solvents also help reduce interphase voltages with feed solutions containing metal ions. This is the most important property of organic solvents for use in emulsion liquid membranes, in addition to having low volatility and insoluble in aqueous solutions [20].
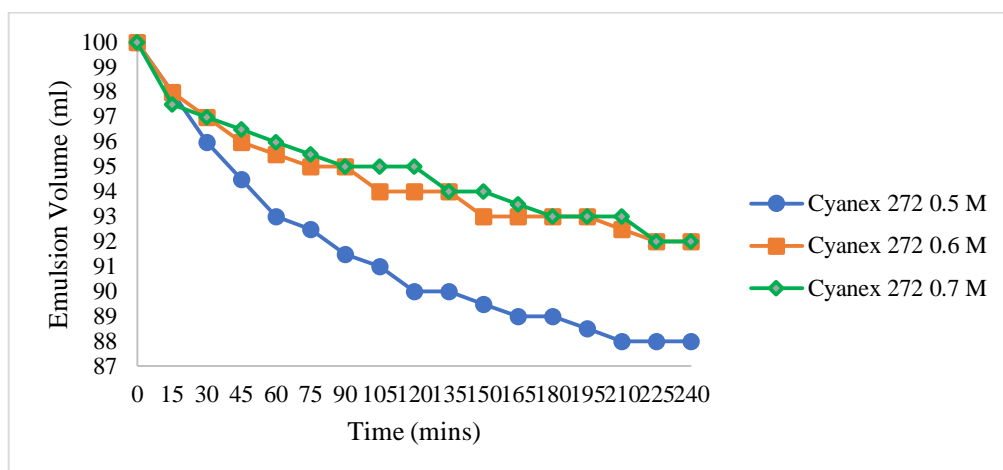

Figure 4. Emulsion stability, extractant concentration being varied (surfactant concentration 4%w/v, stirring speed 1500 rpm, stirring time 1 hour)

Membrane breakage in ELM system includes the rupture of the emulsion and the leakage of the internal reagent and extracted solute through the membrane phase to the external phase, both resulting in the decrease in the volume of the internal phase. As a result, the membrane breakage causes a decrease of driving force for mass transfer and an increase of the raffinate concentration, thereby lowering the extraction efficiency.

3.3 Extraction

Extraction process begins by making an optimum emulsion phase (10% w/v SPAN 80 and 0.7 M Cyanex 272). This extraction process goes in one stage with the stripping process because the extracting technology used is the emulsion liquid membrane. Then the emulsion phases that have been formed are mixed with the optimum leachant that is the result of leaching using 4 M hydrochloric acid which varied the pH of the solution, ie 5 and 6. The pH variation is done because Cyanex 272 is a slightly acidic extractant so the pH of the stripping solution should be less than the pH of leachant metal during the extraction process with the emulsion liquid membrane. NaOH solids added gradually to change feed phase pH until the pH reaches 5 and 6. The ratio of the mixing volume between the emulsion phase and the feed phase is 1 : 2. After that, the solution is stirred at 250 rpm for 15 minutes. After stirring, the mixture is both transferred to the separatory funnel for extraction and held for 15 - 30 minutes and there is a separation between the feed phase and the emulsion phase. The calculation of the efficiency of the cobalt extraction process is shown in Figure 5.
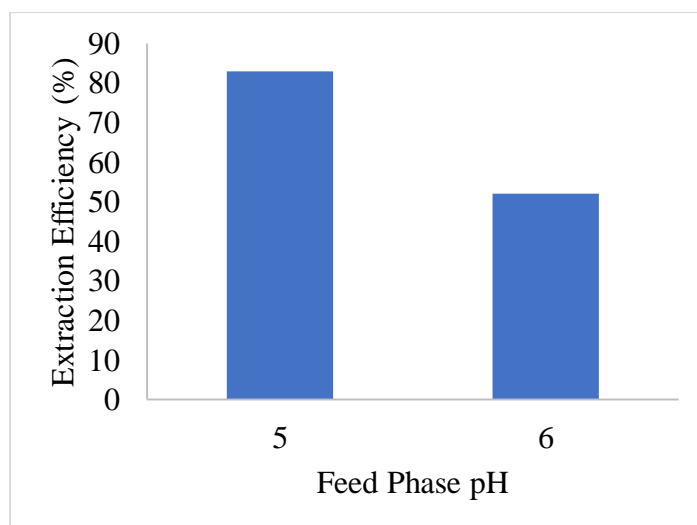
Figure 5. Extraction efficiency with pH 5 and 6 (stripping speed 250 rpm, stirring time 15 mins, room temperature)

Based on Figure 5 shows that extraction efficiency at pH 5 was 83.03% which is higher than pH 6 of 52.1%. This may occur due to emulsion instability. Because of when the pH is high, emulsion stability changes with the emulsion, whereas at too low pH can be explained by competing H^+ ions with the solute due to the release of H^+ ions from extractant to leachant [21]. Extraction rate will decrease when the pH is greater than 5 due to emulsion instability because H^+ ions transfer phenomenon from acidic feed solution to membrane phase so that the membrane can swell and decompose. pH value between stripping solution and feed solution should be different to make a difference of chemical potential for H^+ ions. Physical properties of the extractant will cause a reduction of the ion activity difference on both phases. Cobalt extraction process increases with increasing amount of proton concentration up to a certain concentration [13]. According Figure 5, at pH 6, the emulsion has swelled so the extraction efficiency is lower than that of pH 5.

Type and concentration selection of stripping solution appropriately is one of the determinants of extraction process efficiency with emulsion liquid membrane technology. Reaction by the stripping solution plays an important role in the extraction of solute from feed solution to stripping solution in emulsion liquid membrane process. Based on prior study by [21], performance of Na_2CO_3, H_2SO_4, and HCl as stripping solution was compared. In the first ten minutes, the best stripping solution sequence is $Na_2CO_3 > H_2SO_4 > HCl$. However, after the first ten minutes, emulsion stability while using Na_2CO_3 is changed so that its extraction efficiency is reduced so that the sequence of extraction efficiency at the end of process from highest to lowest is $H_2SO_4 > Na_2CO_3 > HCl$.

4. Conclusion
The amount of cobalt metal in cathode Li-ion battery powder is 11.09%w/w. The most stable emulsion is reached when extractant concentration is 0.7 M and surfactant concentration is 10%w/v. The highest extraction efficiency is reached when feed phase's pH is 5.

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