



Kinetics Study on Lithium Leaching of Spent Lithium Iron Phosphate Batteries in Low Concentration of Sulfuric Acid

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Abstract

Recovery of valuable metals from spent lithium iron phosphate (LiFePO_4) batteries are quite challenging because it needs a lot of process. The recycling of these spent batteries can avoid environment contamination from the waste, meanwhile the valuable metallic components in the batteries including lithium can be treated as a resource for potential recovery of lithium. Low concentration of sulfuric acid (H_2SO_4) as a leachant and hydrogen peroxide (H_2O_2) as an oxidant, was used to leach elements from cathode materials of spent LiFePO_4 batteries that mainly contained Li, Fe and P. Li could be selectively leached into the solution and while Fe and P was assumed to remain in the residue. The significant effects of acid concentration, solid-liquid ratio, reaction temperature and reaction time on the leaching rate are determined. Under the optimum conditions of 0.1 M H_2SO_4 , 2 vol% H_2O_2 , S/L ratio of 75 g/L, 60 °C and 60 min, the leaching efficiency determined were 74.74% for Li and 0.99% for Fe. A leaching mechanism of shrinking-core model with diffusion through product layer control was proposed. It was found that the apparent activation energy was $12.69 \text{ kJ mol}^{-1}$ as calculated by the Arrhenius equation together with an enthalpy (ΔH) of 10 kJ mol^{-1} and an entropy (ΔS) of $-264.54 \text{ J mol}^{-1} \text{ K}^{-1}$.

Keywords: Leaching, Kinetics study, Spent lithium iron phosphate batteries, Sulfuric acid, Lithium

Introduction

Lithium ion battery (LIB) is a secondary type battery which rechargeable properties enable it for energy storage and conversion. The battery works by converting the chemical energy into electrical energy and distributing power to electrical and electronic equipment. Not only that, LIBs also popular and widely used in electric vehicles (EVs) production, sophisticated telecommunications tools, home and industrial applications (Zhang *et al.*, 2018).

Li *et al.*, 2019 said that the evolution and constant producing of LIBs is due to the overuse of these digital devices. 24.6 million is gained by Chinese car sales in 2015 and rising by 4.7%, making China the first in the world for car sales reputation (Wang and Wu, 2017). There are many types of lithium ion batteries, but mostly used are lithium iron phosphate (LiFePO_4) series especially in EVs production. LiFePO_4 is an excellent cathode materials because of its longer life cycle than other types of LIBs, low cost, non-toxicity, high theoretical capacity with 170 mA h g^{-1} (Yang *et al.*, 2018), high energy density and low self-discharge.

As the world grows faster, these technologies expanding and demand for power source and metals, especially on lithium, and results in an increase growth of spent LiFePO_4 batteries. China as the major LiFePO_4 producer and consumer country, ship out LiFePO_4 with an amount that reached 32 400 tonnes in 2015, taking over 65% of the worldwide market (Li *et al.*, 2017). LiFePO_4 batteries does not contain any mercury, cadmium or other toxic heavy metals making it non-toxicity battery. However, this does not mean LiFePO_4 batteries are non-polluting products as they contain toxic organic electrolytes, fairly high levels metals and plastics. These factors can lead to a serious environmental problem when the batteries are disposed improperly in the landfill area. Furthermore, lithium resources will decrease eventually because lithium is needed as the main ingredient for LiFePO_4 batteries.

Gaines, 2018 explained that demand is expected to continue, thus needing more raw materials to produce the product. One of the ways to solve this problem is to recycle the spent batteries and recover the lithium. Not only it will relieve the inadequacy of lithium resources, but also will reduce the environmental pollution.

In this research, by using selective leaching process, lithium (Li) is leached and recovered in a low concentration of sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2), while Fe and P dissolution are suppressed in the solution. The leaching kinetics of the cathode materials of spent LiFePO_4 batteries with H_2SO_4 at low concentrations and temperatures ($< 80^\circ\text{C}$) is studied for further application in hydrometallurgy processing.



Experimental Method

Materials and experimental procedure

The spent LiFePO_4 batteries used in this research was the similar type of batteries that used in national EVs research that are using LiFePO_4/C as active cathode materials. The batteries were discharged and dismantled to obtain the cathode materials inside the batteries. Before leaching process was carried out, the cathode active materials were treated with 0.3 M sodium hydroxide (NaOH, Merck) solution for 2 hours to separate the cathode materials from Al-foils. After filtration, the residue was dried for 4 hours at 110 °C and cathode powder was obtained. The powder was then analyzed using energy-dispersive x-ray fluorescence (EDXF) to identify the elemental composition of materials.

The leaching process was carried out by mixing 8.25 g sample with a leaching solution of varied concentration of sulfuric acid (H_2SO_4 , Merck, 95-97%) and hydrogen peroxide (H_2O_2 , Merck, 30 vol%) into 500 ml three-necked round-bottom Pyrex reactor equipped with thermometer and condenser. All the solutions used in this study were prepared with distilled water and all experiments were conducted in batch mode with a stirring speed of 300 rpm.

During the leaching experiment, the samples of 3 ml volume were taken at various time intervals for 60 min. Other leaching parameters involved in the experiments were concentration of H_2SO_4 (0.1 M, 0.3 M, 0.5 M, 1.0 M and 2.0 M), temperature (25, 60, 70 and 80 °C), and solid-liquid ratio (33, 50, 75 and 100 g/L). The H_2O_2 volume was fixed at 2 vol% as the previous research has discovered that 2 vol% H_2O_2 could yield a maximum of 106.7% for lithium, 96.7% for cobalt, and 97.9% for nickel (Aaltonen *et al.*, 2017). The chemical samples was then analyzed using inductively coupled plasma (ICP-AES) to analyze concentration of major and trace elements like Li and Fe in the samples.

Kinetics leaching study

LiFePO_4 cathode materials dissolution within acidic solution is a heterogenous process and depends on the reactant concentration and its change during the reaction. The rate equation can be formed to show the relation between the experimental data and time (Hidalgo *et al.*, 2018). Kinetics study of the reaction was carried out to determine the reaction phenomenon between H_2SO_4 and LiFePO_4 compounds. The reaction rate controller, reaction mechanism, rate constant and activation energy required to leach the LiFePO_4 cathode to recover Li is determined.

For the non-catalytic reaction of particles covered by fluid, two simple idealized models were considered, the shrinking-core models (SCM) and the progressive-conversion model (PCM). However, more data shows that most cases the SCM approaches real particles more closely than does the PCM (Levenspiel, 1998). Therefore, the shrinking-core model was selected, where the reaction occurs at the outer skin of the particle first and moves into the remaining bulk solid leaving behind completely converted material and inert solid. At given time, unreacted core of material will form, which shrinks in size during reaction.

The shrinking-core model suggests the formation, upon charge, of FePO_4 shell with migration of $\text{FePO}_4/\text{LiFePO}_4$ interface into each particle from the surface with a continuous shrinking of the LiFePO_4 core. Extraction of the Li from the unconverted LiFePO_4 at the center of the larger particles is not efficient, which leads to the capacity loss. (Yuan *et al.*, 2011)

Kinetic modelling completes when the experimental data fits to the solid-liquid reaction models (Ebrahimzade, Khayati and Schaffie, 2018). Activation energy can be calculated following Arrhenius correlation as follows (Eq. (1)). k_c is the rate constant, A the collision frequency, E_a the activation energy, R the universal gas constant and T is the absolute temperature.

$$k_c = A e^{\left(\frac{-E_a}{RT}\right)} \quad (1)$$

For plotting purposes, the Arrhenius equation is rearranged into linear equation as Eq. (2).

$$\ln k_c = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A \quad (2)$$

For liquid-solid reaction system where the whole process is commonly controlled by chemical reaction at the particle surface or diffusion. By chemical reaction controls, the reaction rate will lead to equation defined as (Eq. (3)):

$$1 - (1 - X)^{\frac{1}{3}} = k_r t \quad (3)$$

If the process is diffusion through the product surface controls, the reaction rate leads to equation as (Eq. (4)):

$$1 - \left(\frac{2}{3}\right)X - (1 - X)^{\frac{2}{3}} = k_d t \quad (4)$$

X is the fraction of metal leached in the solution, k_r is the kinetic parameter for the surface reaction control, k_d is the kinetic parameter for diffusion of product control and t is the reaction time in minutes. Thermodynamics parameters (enthalpy, entropy and Gibb's free energy) were calculated by using the transition-state theory. The

relationship between reaction rate constant and reaction temperature is given by Eyring equation as (Eq. (5)) (Hidalgo *et al.*, 2018). To determine the enthalpy, ΔH^\ddagger and entropy of reaction, ΔS^\ddagger , the equation is linearized to (Eq. (6)) to calculate the ΔH^\ddagger from the slope and ΔS^\ddagger from the intercept from a plot of $\ln(k_c/T)$ versus $(1/T)$.

$$k_c = \frac{k_b T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (5)$$

$$\ln\left(\frac{k_c}{T}\right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{k_b}{h} + \frac{\Delta S^\ddagger}{R} \quad (6)$$

k_b is the Boltzmann's constant, h is Plank constant and ΔG^\ddagger is Gibb's free energy. By using optimum leaching conditions, the kinetics of reaction, thermodynamics parameters and leaching efficiency can be obtained.

Results and Discussion

Characterization of cathode materials of LiFePO₄

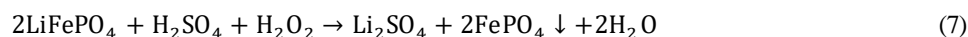
The cathode materials powder was characterized with EDXF and the chemical composition except lithium of the cathode materials powder was given in Table 1. It shows that mostly the powder contained 64.79% Fe along with 34.32% P and other metals. The lithium content in the powder was determined separately using ICP-AES after dissolution in a strong acid. Thus, lithium content in powder is found to be around 7.44% from ICP-AES analysis. The main aim of this research is to maximize the selectivity of the lithium in leaching of the cathode materials.

Table 1. Chemical Composition of Cathode Materials Powder by EDXF

Element	Fe	P	S	Ca	Cu	Zr	Nb	Sr
Composition (wt.%)	64.79	34.32	0.39	0.37	0.03	0.03	0.02	0.01

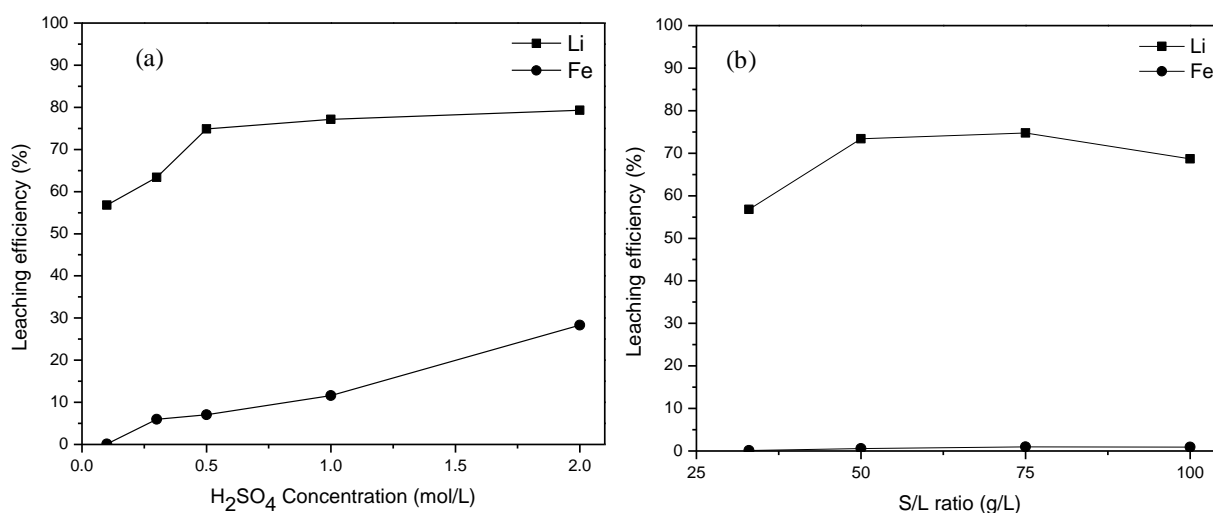
Selective leaching of cathode materials of LiFePO₄

The oxidation-reduction theory was used to leach and separate Li and Fe from the cathode materials of spent LiFePO₄ batteries (Li *et al.*, 2017). The reactions during the leaching process as in (Eq. (7)).



Li was expected to leach in the leaching solution from the cathode materials, and Fe would react with PO_4^{3-} to form precipitated FePO_4 . The leaching efficiency is defined as the ratio of the amount of Li^+ or Fe^{2+} in the leachate to the total amount of that species in the original cathode. The concentrations of Li^+ and Fe^{2+} were tested by ICP-AES, the effects to different parameters on the leaching efficiency of Li and Fe were recorded.

Effects of various parameters on the leaching efficiency of Li and Fe



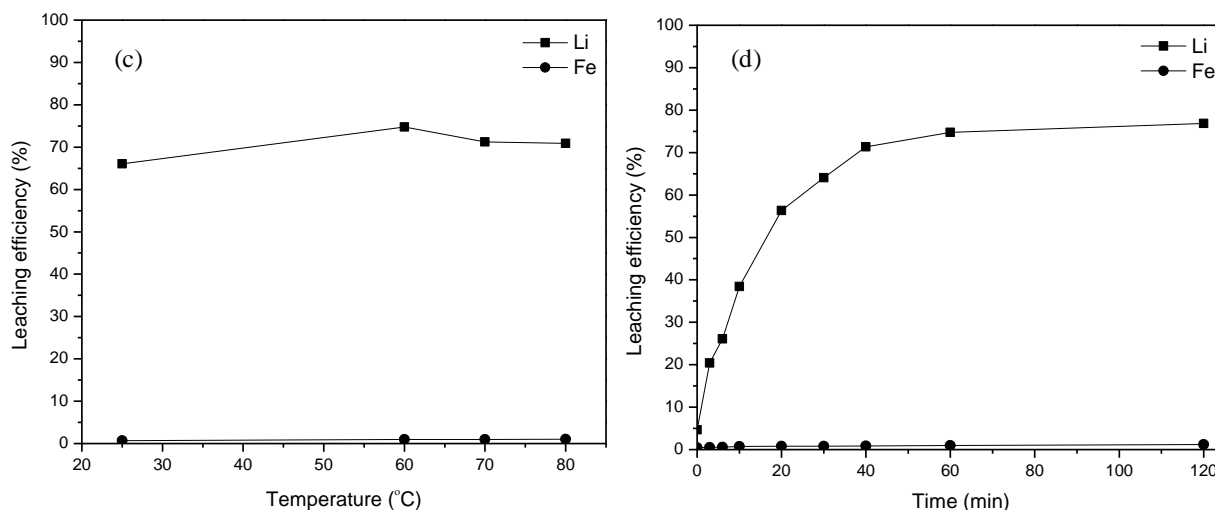


Figure 1. Effects of various parameters on leaching efficiency of Li and Fe. (a) H_2SO_4 concentration (b) Solid-liquid ratio (c) Temperature (d) Time.

Effect of H_2SO_4 concentration

To determine the effect of H_2SO_4 concentration on the leaching efficiency of Li and Fe, the experiments were carried out with a concentration of H_2SO_4 varies from 0.1M to 2.0M with a constant amount of H_2O_2 at 2 vol%, a leaching temperature of 60 °C, a S/L ratio of 50 g/L and a leaching time of 60 min. Figure 1(a) shows the results of the leaching efficiency of Li and Fe, where from 0.1M to 0.5M, the leaching efficiency of Li increased significantly from 56.82% to 77.16%, while Fe increased from 0.12% to 7.05%. Unfortunately, when the H_2SO_4 concentration increased from 0.5M to 2.0M, the leaching efficiency of Fe increased to 28.32%, while Li increased slightly to 79.32%. From 0.5M to 2.0M, no significant difference on Li can be detected, so it can be concluded that 0.5M is the optimum condition. However, the highest selectivity of Li is aimed with the lowest Fe obtained, to suppress Fe in a low concentration acid solution. This means that, to achieve the maximum Fe suppression, with highest Li/Fe ratio, 0.1M of H_2SO_4 was chosen for the next experiments.

Effect of solid-liquid ratio

The effect of solid-liquid ratio on leaching of lithium was carried out in the range of 33 g/L to 100 g/L. The experiments were carried out under these conditions: H_2SO_4 concentration of 0.1M, 60 min, 60 °C and 2 vol% of H_2O_2 . As shown in Figure 1(b), from 33 g/L to 50 g/L, the leaching efficiency of Li increased from 56.82% to 73.41%. However, after increasing to 75 g/L and 100 g/L, the leaching efficiency increased to 74.74% and fall to 68.66%. For Fe, the leaching efficiency stayed below than 1%, this indicates that Fe dissolution into the solution is not significantly affected by solid-liquid ratio (Yang *et al.*, 2018). The fall from 75 g/L to 100 g/L because of insufficient of acid solution to leach or react with the $LiFePO_4$ powder, resulting in low efficiency of Li. Commonly, to increase processing throughput, high S/L ratio is needed, and to get high processing throughput without affecting the leaching efficiencies, 75 g/L S/L ratio was chosen as the optimum condition for the next experiments.

Effect of reaction temperature

Temperature is one of the important parameters that can affect the selectivity of Li in leaching solution and the leaching efficiency. The effect of temperature was examined in the experiment with the following conditions: 0.1M concentration of H_2SO_4 , 2 vol% of H_2O_2 , 60 min and 75 g/L S/L ratio. The temperature tested were 25 °C, 60 °C, 70 °C and 80 °C. Figure 1(c) shows the effect of temperature on leaching efficiency on Li and Fe. At 25 °C, the leaching efficiency of Li increased slightly from 66.04% to 74.74% at 60 °C, the efficiency then decreased slightly to 71.23% at 70 °C and remained around 70.9% at 80 °C. On the other hand, leaching efficiency of Fe ranges from 0.68% to 1.01%, which shows that high selectivity of Li with low value of Fe that can leach together in the solution. No significant difference on Li efficiency from 70°C to 80°C and slight decreased shows that H_2O_2 may decompose at temperature higher than 60 °C (Yang *et al.*, 2018). From the results, 60 °C has the highest leaching efficiency of Li, so that 60 °C was chosen as the optimum condition and used for the next experiments.

Effect of leaching duration

The effect of time was analyzed in the range from 0, 3, 6, 10, 20, 30, 40, 60 and 120 min. The experiment condition as follow: 0.1M concentration of H_2SO_4 , 2 vol% of H_2O_2 , 75 g/L and 60 °C.

Figure 1(d) shows the effect of time on leaching efficiency. The leaching efficiency L_i increases steadily from 0 to 40 min, with a level of 4.65% to 71.35%. As the leaching time going up from 40 to 60 min, leaching efficiency increased slightly to 74.74% and 76.85% at 120 min. Meanwhile, leaching efficiency of Fe stayed low from 0 to 120 min at a level less than 1.2% that shows insignificant influence of temperature. Since, there is no significant difference between 60 and 120 min, thus, the optimum leaching time is 60 min.

Kinetics study of leaching

To determine the nature of reaction between the particles of cathode materials of spent LiFePO_4 batteries and the H_2SO_4 leaching solution, a trial was made to fit the kinetic data gained from the leaching experiments at varying temperatures against both Eq. (3) and (4) of SCM. By plotting $1-(1-X)^{1/3}$ versus time and $1-(2/3)X-(1-X)^{2/3}$ versus time at different temperature, Figure 2(a) and 2(b) shows kinetic data tabulated in straight line. The reaction control is determined from the linearity of the line, which is the value of correlation coefficient, R^2 . R^2 value of kinetic models obtained from the graph was tabulated on Table 2. The higher the value of R^2 , the higher the linearity of the line. By comparing the R^2 values of both model, diffusion model has higher R^2 value, thus it is predicted the kinetic model for this reaction is diffusion reaction model.

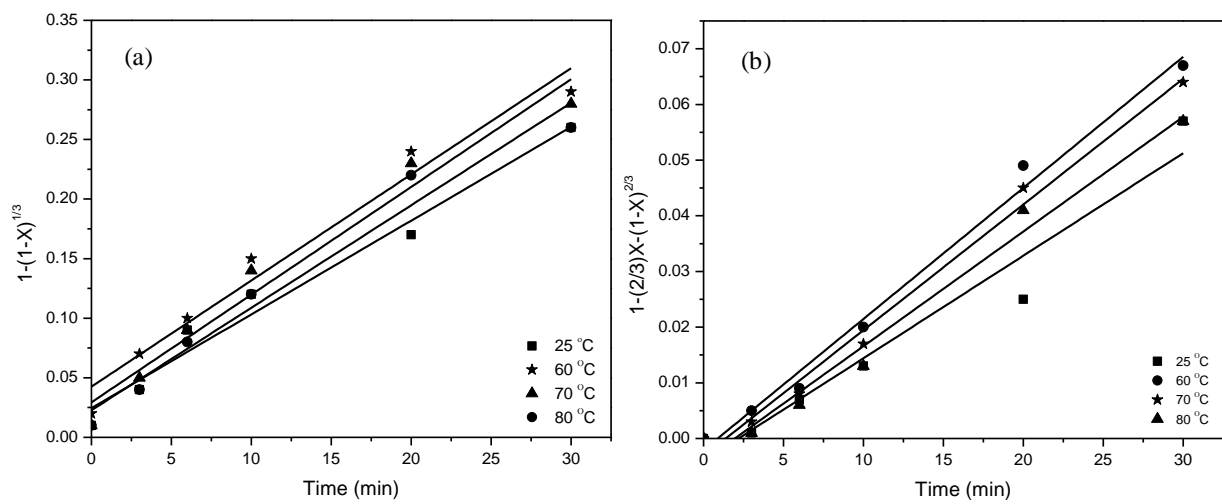


Figure 2. Shrinking core model for kinetics of leaching of Li (a) Chemical reaction control (b) Diffusion control

Table 2. R^2 Value of Kinetic Models

Temperature (°C)	R^2 value	
	Chemical reaction	Diffusion
25	0.9742	0.9485
60	0.9651	0.9904
70	0.9685	0.9903
80	0.9744	0.9813

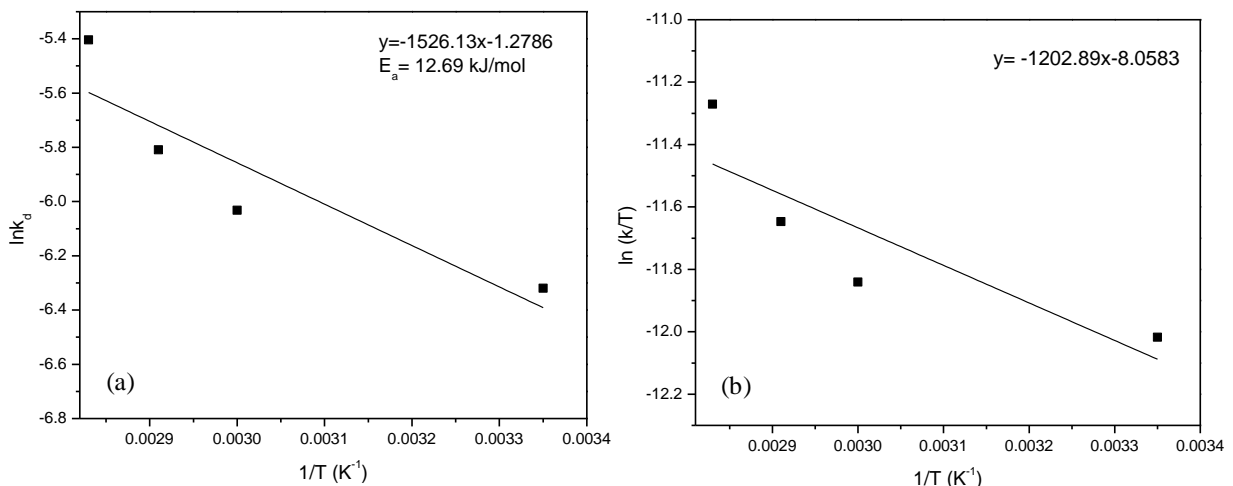


Figure 3. Kinetics analysis (a) Arrhenius equation plot (b) Eyring equation plot

To verify whether the model prediction is appropriate, the analysis on activation energy is carried out using Eq. (1). By plotting $\ln k_d$ versus $1/T$ from Eq. (2), Figure 3(a) shows the value of activation energy, E_a can be obtained from the slope of the line equation. From the calculation, the value of activation energy for lithium leaching is 12.69 kJ/mol. The prediction appeared to be true where reaction is controlled by diffusion model because diffusion model commonly has a low activation energy value (<20 kJ/mol) (Han *et al.*, 2017). Moreover, the R^2 value for diffusion controlled model for most metals must exceeds 0.87 (Meshram, Pandey and Mankhand, 2015).

For thermodynamics parameters, enthalpy and entropy values were calculated from Eq. (5) and plotting $\ln(k_c/T)$ versus $1/T$ from Eq. (6) in Figure 3(b). The value calculated from the line equation are $\Delta H^\ddagger = 10$ kJ/mol and $\Delta S^\ddagger = -264.54$ J/mol.K. From the results obtained, the positive value of enthalpy and negative value of entropy shows that the value for Gibb's free energy must be positive. When $\Delta G^\ddagger > 0$, the reaction will never be spontaneous and the formation of a transition-state complex (Hidalgo *et al.*, 2018).

Conclusions

The selective leaching of Li from spent LiFePO_4 batteries reached the maximum efficiency at 0.1 M H_2SO_4 concentration, 2 vol% H_2O_2 , 60 °C, 60 min and 75 g/L. The kinetic study showed that the leaching process is controlled by diffusion in solid particles with activation energy value, E_a of 12.69 kJ/mol. Meanwhile, thermodynamics parameters including enthalpy, ΔH^\ddagger of 10 kJ/mol and entropy, ΔS^\ddagger of -264.54 J/mol.K were obtained from the leaching process.

Acknowledgements

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Lembar Tanya Jawab

Moderator : Putri Restu Dewati (UPN "Veteran" Yogyakarta)

Notulen : Indriana Lestari (UPN "Veteran" Yogyakarta)

1. Penanya : Putri Restu Dewati (UPN "Veteran" Yogyakarta)

Pertanyaan : Mengapa digunakan Asam sulfat untuk *leaching* Li dan apakah ada senyawa lain yang dapat digunakan untuk *leaching* Li ini?

Jawaban : Banyak senyawa lain yang dapat digunakan, misalnya asam organik, namun harganya mahal. Dari sisi ekonomi Asam sulfat lebih murah dan konsentrasi asam sulfat yang digunakan pada penelitian ini cukup rendah, sehingga meminimalisir limbah. Setelah digunakan, larutan asam diencerkan dengan air dan dinetralisasi menggunakan Natrium hidroksida, kemudian dibuang ke lingkungan.