A kinetics study of acetic acid on cobalt leaching of spent LIBs: Shrinking Core Model

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Abstract. Lithium-ion batteries (LIBs) are secondary rechargeable power sources which increasing production also leads to large amount of waste. In order to environmentally friendly reduce the waste, this work aimed to use acetic acid as a substitute leaching agent to leach Co metals which constitutes about 72.39% wt of the battery cathode. The leaching process was done in a three-necked-flask where calcined LIB cathode powder was mixed with acetic acid solution. The variables of the leaching process under investigation were solution pH, concentration of H_2O_2 in the solution, S/L ratio, temperature and reaction time. Experimental results showed that only temperature significantly influenced the leaching rate of Co. Since the process was exothermic, the maximum recovery decreased as temperature increased. Conventional shrinking core model that considers diffusion and irreversible surface reaction resistances was found not sufficient to predict the kinetics of the Co leaching with acetic acid. A more representative kinetics model that considers a reversible reaction of Co complex formation needs to be further developed.

1 Introduction

Lithium-ion batteries (LIBs) are secondary rechargeable power sources dominantly used to power portable gadgets. This kind of batteries are mostly used in laptops, toys, handsets and many others. Nowadays, the usage of LIBs are being shifted to power more complicated and power-consuming electronics such are electric car and medical equipment [1]. With its high demand, the increasing waste of LIBs presents dire harm to environment in the form of its containing heavy metals and electrolyte. On the other side, these harmful materials can be recycled into valuable materials [2].

There are many methods in the recycling of LIBs, which are pyro-metallurgy, bio-metallurgy and hydrometallurgy. Hydrometallurgy method is the most used method now because of the high concentration of recycled metal, low energy cost and low emission [3]. The most important step in the hydrometallurgy itself is the leaching process. Leaching is a process in which a desired metal is extracted into a body of solution with the use of a certain solvent such as acid. The leaching process is usually assisted by the use of reducing agent which reduces metal ions to a more soluble state. Solute metal will then be purified and precipitated using electrochemistry, multi-step precipitation or solvent extraction [4].

Though the researches in perfecting the leaching process of LIBs have been widely conducted, the main problem present is the leaching agent. Commonly used leaching agents are inorganic acids such as HCl, H_2SO_4 and HNO_3 which were although efficient, yield side

products such as Cl_2 , SO_3 and NO_x gases that can harm the environment [5]. In order to introduce a more environmentally friendly process, scientists have developed alternative process using organic acids such as citric acid [6] and oxalic acid [7]. The experimental results using organic acids showed promising recovery but the cost of recycle is still higher than that of inorganic acids.

In order to lower the cost from organic acid use, the present work proposed the use of acetic acid as a cheaper substitute. Acetic acid itself has been produced commercially for thousands of years and the synthesis process has been refined over and over in order to lower the price [8]. The potential of acetic acid as leaching agent has already been investigated. In the leaching of heavy metal contaminant from waste, acetic acid showed considerable recovery in a broader range of pH than other inorganic and organic acids. [9]. However, for LIBs there is still no research that specifically uses acetic acid.

In order to optimize the condition of the leaching process for scaling up, there is a need to study the kinetics and construct a mathematical model that can sufficiently predict those condition. Leaching process itself is a heterogeneous solid-liquid reaction which basic model has been described Yagi and Kunii as shrinking core model [10]. This model although accurate for some conditions need honing for various leaching process with different material and condition. The shrinking core model has been widely used in the scope of leaching research, for example in the leaching of gold ore with varying concentration and temperature [11], activation energy study of manganese ore leaching [12] and uranium carbonate reactor leaching [13]. In the present work, this

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model will be used for acetic acid leaching of LIBs and then evaluated for its accuracy.

2 Mathematical Model

The leaching of Co from Li-Ion battery cathode powder proceeds through reaction between Co compounds with acetic acid that is hypothesized following mechanism described in eq. (1) – (3) [14].

Solid-liquid reaction is following shrinking core model where the reaction initially occurred at the outer skin of the particle. Reaction zone then shifted deeper in the solid and left completely reacted material and inert solid (“ash”) behind. This process would continue overtime until the shrinking unreacted core is depleted. Basically, the process consists of five steps:

- Diffusion of acid reactant through film surrounding the particle to outer surface of particle.
- Diffusion of acid reactant through ash layer to the surface of unreacted core.
- Surface reaction between acid reactant and solid reactant on unreacted core in the reaction zone.
- Diffusion of product through ash layer to the surface of particle.
- Diffusion of product through film surrounding the particle to the solution.

For irreversible reaction, step d and step e usually do not contribute to the resistance of reaction and thus would not be the rate-controlling step. Therefore, the proposed model would only need to emulate step a to step c in the model as follows:

- Diffusion of acid reactant (A) through film surrounding the particle

$$-\frac{dN_A}{dt} = k_L 4\pi R^2 (C_{AL} - C_{ALS}) \quad (4)$$

- Diffusion of reactant through ash layer

$$-\frac{dN_A}{dt} = \frac{4\pi D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} (C_{ALS} - C_{AS}) \quad (5)$$

- Surface reaction

$$-\frac{dN_A}{dt} = k_r 4\pi r_c^2 C_{AS} \quad (6)$$

From the equation above, the rate of leaching of B (Co) could be derived as follow:

$$-\frac{dN_B}{dt} = \frac{C_{AL}/2}{\frac{1}{k_L 4\pi R^2} + \frac{1/r_c - 1/R}{4\pi D_e} + \frac{1}{k_r 4\pi r_c^2}} \quad (7)$$

where $-\frac{dN_B}{dt}$ = Total rate of decrease of Co (B) (mole s⁻¹)

C_{AL} = Concentration of acetic acid (A) in liquid body (mole A/m³ of liquid)

C_{ALS} = Concentration of acetic acid (A) in ash layer (mole A/m³ of liquid)

C_{AS} = Concentration of acetic acid (A) on unreacted core surface (mole A/m³ of liquid)

k_L = Mass transfer coefficient through liquid film (m s⁻¹)

D_e = Effective diffusion coefficient (m² s⁻¹)

k_r = Reaction rate coefficient (s⁻¹)

R = Outer radius of particle (m)

r_c = Radius of unreacted core (m)

In this process of leaching of LIBs using acetic acid, the effect of diffusion of acid reactant and products through film surrounding the particle (step a) were negligible. The usual particle size of cathode powder from LIBs are about 0.5-2.0 micron [15], this combined with adequate agitation would result in the resistance caused by film to become negligible.

The pre-treatment of the cathode of LIBs have already eliminate any inert materials that has the potential of forming an ash “layer” surrounding the particle. Thus the resistance that is caused by diffusion through ash layer is negligible. The radius of unreacted core can be expressed in term of conversion (X_B) as follows:

$$r_c = R(1 - X_B)^{1/3} \quad (8)$$

Thus, the equation in favor of conversion (X_B) is:

$$\frac{dX_B}{dt} = \frac{C_{AL}}{C_{B0}} 2\pi R^2 k_r (1 - X_B)^{2/3} \quad (9)$$

Where $\frac{dX_B}{dt}$ is the total conversion rate of Co (B) and X_B is the conversion of Co (B).

3 Material and method

3.1. Materials and reagents

Spent laptop LIBs were collected from local vendors and treated with saline solution for 2 hours to remove the residual charge. They were then dismantled from its plastic and steel shell using plier. Anode and the cathode of the batteries were then separated after the batteries coil was cut using knife. Metal-rich material from the cathode was scratched from the aluminium foil, powdered using spatula and calcined at 700°C for 4 hours at a heating rate of 5°C/ minute to remove the residual carbon. The powder was then analyzed for its metal content.

3.2. Metal Leaching

The leaching process used 0.5 gram of calcined cathode powder in 50 ml of 2.8 M acetic acid solution 2% v/v

H₂O₂ (pH=2). Experiments were done in a flask equipped with magnetic stirrer that runs at 400 rpm. Samples were taken after 5, 10, 15, 30, 60, and 120 minutes of experiment. The pH of acid solution, temperature, H₂O₂ concentration and S/L ratio of the leaching process were varied.

3.2. Elemental analysis

For analysis, 0.25 ml of the leachates were taken and diluted to 25 ml using distilled water. The resulting solution were then filtered using 0.22 μ m membrane filter to separate possible suspended solid. The filtrate was then analyzed using ICP-AES (Optima 8300, Perkin Elmer, USA).

4 Result and discussion

4.1. Characterization of Cathode of LIB

Characterization of metal content in the cathode of LIBs was done using XRF analysis. The result of the analysis is shown in Table 1. It is shown that Co is dominating the cathode of LIB's elements used in the present work. This result is in line with characterization done by Xu et.al. [16] whose analysis showed that Co content was about 50

percent. This result also shows that the Co recovery is vital for LIB recycling process.

Table 1. Analysis Result of LIB's Cathode Content

Metal	Content, ppm	Content, % wt
Co	70.1920	72.39
Li	9.3957	8.59
Mn	6.9090	6.32
Al	5.2350	4.79
Ni	8.6630	7.92

4.2. Leaching Result

Experiment results showed that the rate of leaching is only affected by temperature. Acidity of solution (pH), concentration of H₂O₂ and S/L ratio of reactant mainly affect the resulting maximum recovery of Co. The result of Co recovery at varied variables is shown in Fig. 1.

Fig. 1 shows that with increasing temperature, the rate of which Co was recovered increases from 30 minutes at 50°C, 15 minutes at 70°C to 5 minutes at 90°C. The maximum recovery of Co was shown to be decreasing with increasing temperature from 37.5% at 50°C to 35.2 at 70°C and 33.8% at 90°C. This phenomenon shows that the leaching reaction of Co is an exothermic reaction.

Fig. 1. Recovery Rate of Co at Various Factor of: (a) pH; (b) Concentration of H₂O₂; (c) S/L ratio and (d) Temperature

4.2. Calculation Result

The experimental results were used to evaluate the shrinking core model proposed in the present work as written in eq. (9). Calculation results were compared with experimental data by means of minimizing the sum of squares of errors between the data and results from calculation. As temperature was the only variable that affected the rate of recovery, the calculation was done for every temperature that was varied. The calculation results were shown in Fig. 2. Meanwhile, parameters of the proposed model are shown in Table 2.

Table 2. Calculation Result of Leaching Rate Parameter

Temp. (°C)	A	E _A (J/mole)	k _r (1/m ² .minute)
50			9,8151x10 ⁷
70	4,7026x10 ⁷	-2,0257x10 ³	9,8984x10 ⁷
90			9,0510x10 ⁷

Calculation result shows that the shrinking core model proposed in the present work failed to approach the experimental results. The calculation results are significantly far-off from the experimental data. As shown in Fig. 2(a), 2(b) and 2(c), with increasing temperature, the degree of inaccuracy seems to increase.

As depicted in Fig. 2, experimental data shows that there is a maximum limit of recovery at each temperature. This indicates that the leaching process might reach an equilibrium condition. However, this phenomenon would not be able to simulate with the use of the conventional shrinking core model. As shown in Fig. 2, the calculation results shows that the calculated recovery continuously increases with time and the value seems able to reach unity at prolong time. The leaching process of Co in this work seems to involve a reversible reaction that would limit the maximum recovery which value is depending on process condition such as temperature. A conventional shrinking model which considers diffusion resistance and irreversible surface reaction would be unable to predict the kinetics of leaching process studied in the present work.

Further proof that the leaching process of Co is possibly an equilibrium reaction is given by van Niekerk [17] and Donaldson [14] who stated that the reaction of Co and acetic acid is not a simple ionic salt formation but rather a complexation reaction which has an equilibrium limit. This results conclude that in order to more accurately model the kinetics of leaching process of Co there is a need to construct a model based on reversible reaction of Co as rate-controlling step. The conclusion that conventional shrinking core model need to be modified for different type of ore was also achieved in the previous research such as for the leaching of gold [11], manganese [12] and nickel [18], [19].

Fig. 2. Shrinking Core Model Calculation Result of Leaching Rate of Co for: (a) 50°C; (b) 70°C; (c) 90°C and (d) k_r vs T

5 Conclusion

The experimental result showed that the leaching process of Co with acetic acid is possibly exothermic as the maximum recovery of Co decreases with increasing temperature. To maximize the recovery of Co further research with lower temperature is needed but keeping in mind that lowering the temperature will also results in a lower reaction rate.

Conventional shrinking core model is unable to sufficiently approach the experimental data of the Co leaching which calculation result showed an increasing error as temperature increased. This is due to the model was developed based on the assumption of an irreversible surface reaction. In order to more accurately simulate Co leaching with acetic acid, there is a need to develop a kinetics model based on the possible equilibrium reaction that occurs in the complexation reaction of Co.

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