

폐일차리튬전지로부터 유기금속을 회수하기 위한 해체공정의 최적화

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Optimum Conditions of Dismantlement for Recovery of Valuables from Spent Lithium Primary Batteries

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요 약

폐일차리튬전지는 열을 가하거나 파쇄하면 폭발할 수 있기 때문에 재활용을 위해 비폭발 폐일차리튬전지의 해체공정이 요구된다. 이 연구에서는 비폭발 해체공정을 위한 최적 방전공정을 조사하였다. 폐일차리튬전지가 0.5 kmol·m⁻³ 황산용액에서 방전되었을 때, 전지의 반응성은 35 °C에서는 4일 후, 50 °C에서는 1일 후에 감소하였다. 황산용액을 사용했을 때 유기금속이 손실되기 때문에 황산용액과 물을 순차적으로 사용하는 방전공정이 제안되었다. 0.5 kmol·m⁻³ 황산용액에서 6시간 방전 후 물에서 24시간 동안 방전했을 때, 폭발없이 배터리의 해체가 가능하였다. 새로운 공정에서 금속 손실이 감소하였기 때문에, 새롭게 제안된 2단계 방전공정에 의해 경제적인 재활용 공정이 가능하였다.

주제어 : 리튬일차전지, 재활용, 방전공정, 금속회수

Abstract

Dismantlement of lithium primary batteries without explosion is required to recycle the lithium primary batteries which could be exploded by heating too much or crushing. In the present study, the optimum discharging condition was investigated to dismantle the batteries without explosion. When the batteries were discharged with 0.5 kmol·m⁻³ sulfuric acid, the reactivity of the batteries decreased after 4 days at 35 °C and after 1 day at 50 °C, respectively. This result shows that higher temperature removed the high reactivity of the batteries. Because loss of metals recycled increases when the batteries are discharged only with the sulfuric acid, discharging process using acid solution and water was newly proposed. When the batteries were discharged with water during 24 hours after discharging with 0.5 kmol·m⁻³ sulfuric acid during 6 hours, the batteries discharged were dismantled without explosion. Because decrease in loss of metals was accomplished by new process, the recycling process of the batteries could become economic by the 2-step discharging process.

Key words : lithium primary battery, recycling, discharging process, recovery of metals

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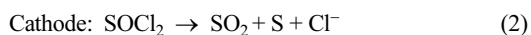
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1. Introduction

Lithium has some advantages for battery e.g. it is the lightest metals and also has the highest electrochemical potential at 3.04 V¹⁾. For over thirty years lithium primary batteries became famous for their performance in various applications such as IT, medical, and military²⁾. They gained a reputation for their long shelf life, constant voltage, wide operating temperature range, and low self-discharge characteristics³⁾. There are rapidly increasing requirement for lighter and more powerful rechargeable energy storage system and batteries⁴⁾.

The lithium primary batteries have very various sizes and components. Lithium batteries are made with lithium metal as anode active material and non-aqueous solvent as electrolyte. As cathode active material, various kinds of materials were used such as manganese dioxide (nominal voltage, 3.5 V), thionyl chloride (3.6 V), and carbon monofluoride (3.0 V). In Fig. 1, cross-sectional view of Li/SOCl₂ cell is shown¹⁾. Representative reactions were as follows³⁾.



In Korea, 50 % of the spent lithium primary batteries must be recycled because spent lithium primary batteries have been listed in EPR (Extended Producer Responsibility) of the enforcement decree of the act on the promotion of saving and recycling of resources. However, the batteries have been landfilled since there is no economic method to recycle the batteries in Korea^{1,2)}. When the batteries were heated too much, charged, pierced, over discharged, or short-circuited, the batteries explode because lithium reacts violently with water or air and because contents such as lithium, electrolyte, and sulfur become flammable by high temperature²⁾. Therefore, it is so difficult to recycle safely the spent lithium primary batteries.

There are very a few researches about recycling of the batteries. Toxco, a Southern California environmental firm, developed the lithium recycling processing technique for all lithium batteries. The process was developed and

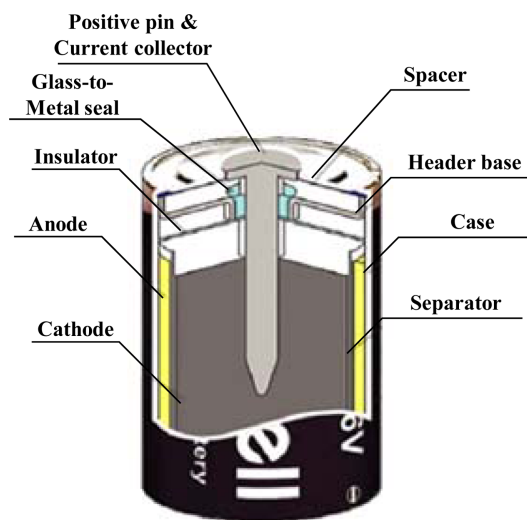


Fig. 1. The cross-sectional view of Li/SOCl₂ cell.

brought to commercial use in 1992 to meet the need for lithium battery recycling. In the process, when placing the batteries in liquid argon or liquid nitrogen, the

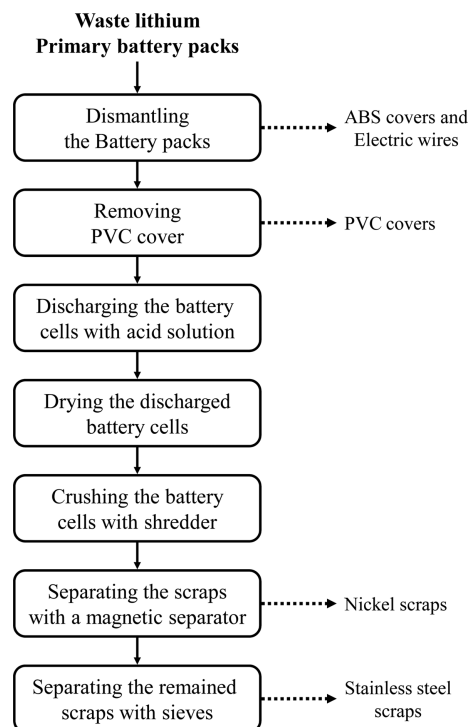


Fig. 2. The recycling process proposed in this study.

batteries are close to inert and can be safely handled regardless of their specific chemistry. Once frozen the batteries are mechanically reduced in size by shearing, cutting, or shredding¹⁾. This process is very costly because of keeping extremely low temperature.

In the previous works, several methods have been tested to dismantle the spent batteries without explosion; cutting them in water or inert solvent with a hydraulic pressure¹⁾, piercing them in nitrogen atmosphere (not published), and crushing them frozen with liquid nitrogen or liquid argon (not published), but these methods failed to dismantle the spent batteries without explosion. Finally, a recycling process for the spent batteries was proposed as can be seen in Fig. 2²⁾. Because the remained lithium in the spent batteries would be dissolved or reacted with acid solution in the process, the spent batteries do not explode by crushing. This dissolving process was operated at room temperature, and it took more than 3 weeks to stabilize the spent batteries. Therefore, in the present study, the dissolving process was investigated at 35 °C and 50 °C for stabilization of the spent batteries.

2. Experiments

2.1. Materials

Waste lithium thionyl chloride (Li/SOCl₂) bobbin type batteries, which were obtained from a domestic battery producer, were used in this study. Table 1 shows main components of Li/SOCl₂ batteries. This waste batteries have used for military radio and the waste batteries shows 0.6 V ~ 1.0 V even though discharged, which indicates that lithium metal still remains in the waste batteries. All reagents were reagent grade.

2.2. Discharging test at various temperatures

In this study, the process stabilizing the spent batteries is termed by 'discharging'. Discharging tests of the waste

batteries were performed in a shaking bath (Jeio-Tech Co., Korea). Three waste batteries were added in 1 dm³ Erlenmeyer flask with together 500 cm³ of 0.5 kmol·m⁻³ H₂SO₄. The flasks were set in the shaking bath and shaking speed and temperature were kept at 60 rpm and at 35 °C or 50 °C, respectively. Because gases were generated when the waste batteries react with the sulfuric acid, the flasks were left open during 9 hours, and then were sealed with silicon caps.

At designated interval, solution was sampled with a syringe, and was filtered with a membrane filter (0.45 μm). The filtrate was analyzed with 3 star series Benchtop pH meter (Thermo Fisher Scientific, Inc., USA) and AAnalyst 400 atomic adsorption spectrometer (AAS) (PerkinElmer, Inc., Germany) to measure lithium concentration. Iron, nickel, chromium concentrations were analyzed with ICP-AES.

When the experiments were terminated, precipitates were collected after removing the discharged batteries and the solution. The precipitates were examined with a Ru-200B X-ray diffractometer (Rigaku, Japan) under the following conditions; radiation, Cu Kα, 30 kV, 40 mA; step scanning method; scan speed, 8 deg/min; angle range, 5 ~ 65 degree/2θ. The precipitate dissolved with aqua regia, and then the concentrations of lithium, iron, and nickel were analyzed with AAS and ICP-AES.

The discharged batteries were dried at 60 °C during 1 day, and then were shredded to investigate if the batteries became stabilized or not.

2.3. Discharging test by 2-step method

To control temperature in 2-step discharging method, 4 dm³ beaker with 2 dm³ water was set on a hot plate. 1 dm³ beaker with 500 cm³ of 0.5 kmol·m⁻³ H₂SO₄ and 3 waste batteries were added in the 4 dm³ beaker, and then temperature was set to 50 °C. After the batteries were discharged by the sulfuric acid during 3, 6, or 9

Table 1. The main components of Lithium primary battery

	Li	SOCl ₂	Acetylene black	Nickel net	Stainless steel
Mass in cell / g cell ⁻¹	5.4	42.0	5.0	7.0	45.0
Weight / %	5.2	40.2	4.8	6.7	43.1

hours, the batteries were collected from the sulfuric acid, and then added into 500 cm³ water at room temperature. After each step, pH and concentrations of Fe, Ni, Li were measured by the method described in 2.2. The batteries were dried 60 °C during 1 day and were shredded.

3. Results and Discussion

The waste primary lithium batteries were discharged in 0.5 kmol·m⁻³ sulfuric acid solution at 35 °C and 50 °C to investigate the behaviors of metals, and the results are shown in Fig. 3 and 4 for the experiments at 50 °C and 35 °C, respectively.

As can be seen in Fig. 3, pH and Fe concentration increase rapidly at 1 day, to 2.7 and 40400 g·m⁻³, respectively, and then Fe concentration fluctuates inversely proportional to pH after 2nd day. The concentration of Cr increases to 11150 g·m⁻³ until 2nd day, and then decreases to less than 1000 g·m⁻³. The concentration of Li increases gradually to 12000 g·m⁻³ and is kept almost constant. Nickel is rarely detected through this

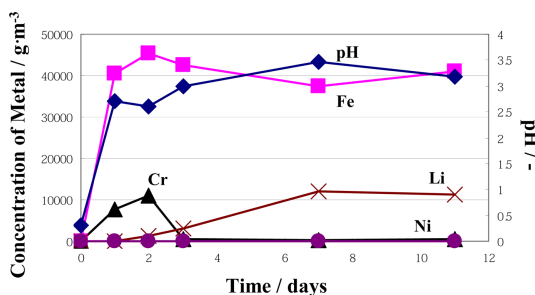


Fig. 3. pH and the concentrations of Fe, Cr, Ni, and Li in the experiment at 50 °C.

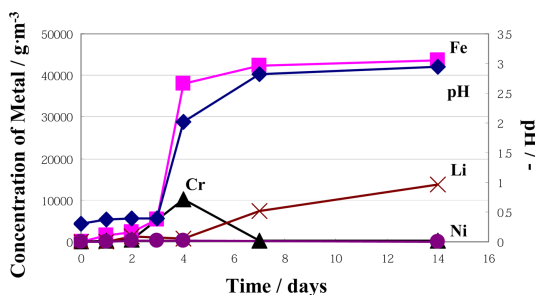


Fig. 4. pH and the concentrations of Fe, Cr, Ni, and Li in the experiment at 35 °C.

experiment. In Fig. 4 for the results at 35 °C, pH and Fe increase slowly until 3rd day, then rise rapidly after 4th day, to 2.9 and 43500 g·m⁻³, respectively. After Cr concentration increases until 4th day to 10280 g·m⁻³, it decreases sharply, and Li concentration gradually increases with time to 13700 g·m⁻³. Nickel is rarely detected in the experiment at 35 °C as well as 50 °C. As the discharging test proceeded, more precipitate was observed in the experiment at 50 °C than at 35 °C. The recovery of precipitate was tried to examine the precipitate, but only partial precipitate was recovered because it is so difficult to separate the precipitate from the battery cells or wall of the reactor and to distinguish the precipitate and the battery. The partial precipitate was analyzed with XRD, but no peak was detected. This result would suggest that the precipitate is amorphous.

The waste lithium primary battery cells used in this study are covered with stainless steel 304L, which contains 18 ~ 20% Cr and 8 ~ 12% Ni. The iron, chromium and nickel detected in the solution would be dissolved from the stainless steel cover. When metal dissolves in acid solution, the reaction can be expressed like following equation.



where M and M²⁺ represent metal and metal divalent ion, respectively. The increase of pH in Fig. 3 and 4 would be resulted from hydrogen ion consuming by the dissolution of the stainless steel.

It would be expected that the fluctuation of metal concentration results from variation of pH^{5,6)}, so the effect of pH on metal precipitation was investigated as below. It was assumed that Fe, Cr, Ni, and Li would precipitate as Fe(OH)₂, Fe(OH)₃, Cr₂O₃, NiSO₄, Li₂CO₃, respectively. These precipitates are formed as following equations.



Therefore, equilibrium constants of Eq. (4) ~ (8) are

given by

$$K_{\text{Fe(OH)}_2} = \frac{[\text{H}^+]^2}{[\text{Fe}^{2+}]}, \log K_{\text{Fe(OH)}_2} = -2\text{pH} - \log[\text{Fe}^{2+}] \quad (9)$$

$$K_{\text{Fe(OH)}_3} = \frac{[\text{H}^+]^3}{[\text{Fe}^{3+}]}, \log K_{\text{Fe(OH)}_3} = -3\text{pH} - \log[\text{Fe}^{3+}] \quad (10)$$

$$K_{\text{Cr}_2\text{O}_3} = \frac{[\text{H}^+]^6}{[\text{Cr}^{3+}]^2}, \log K_{\text{Cr}_2\text{O}_3} = -6\text{pH} - 2\log[\text{Cr}^{3+}] \quad (11)$$

$$K_{\text{NiSO}_4} = \frac{[\text{H}^+]^2}{[\text{Ni}^{2+}][\text{H}_2\text{SO}_4]}, \log K_{\text{NiSO}_4} = -2\text{pH} - \log[\text{Ni}^{2+}] - \log[\text{H}_2\text{SO}_4] \quad (12)$$

$$K_{\text{Li}_2\text{CO}_3} = \frac{[\text{H}^+]^2}{[\text{Li}^+]^2[\text{H}_2\text{CO}_3]}, \log K_{\text{Li}_2\text{CO}_3} = -2\text{pH} - 2\log[\text{Li}^+] - \log[\text{H}_2\text{CO}_3] \quad (13)$$

where K_i represents the equilibrium constant of species i , and $[i]$ concentration of species i . The activity constant is assumed to be 1 in this study. The equilibrium constants were calculated from Gibb's free energies shown in Table 2⁷⁾, and the calculated data were shown in Table 3. Using Eq. (9)~(13) and the equilibrium constants in Table 3, the behaviors of Fe, Cr, Ni, and Li were shown in Fig. 5. This shows that Ni^{2+} , Fe^{3+} , and Cr^{3+} could

Table 2. Gibb's free energies for the species in Eq. (4) ~ (8)⁷⁾

Species	Gibb's free energy (kJ·mol ⁻¹)	Species	Gibb's free energy (kJ·mol ⁻¹)
Fe ²⁺	-91.2	Li ⁺	-293.8
Fe ³⁺	-16.7	Li ₂ CO ₃	-1132.4
Fe(OH) ₂	-486.6	Ni ²⁺	-46.4
Fe(OH) ₃	-696.6	NiSO ₄	-773.9
Cr ³⁺	-215.0	H ₂ O	-237.18
Cr ₂ O ₃	-1058	H ₂ SO ₄	-744.63
H ⁺	0	H ₂ CO ₃	-623.4

Table 3. The equilibrium constants calculated in this study

Equations	(4), (9)	(5), (10)	(6), (11)	(7), (12)	(8), (13)
Equilibrium constants	1.32×10 ⁻¹⁴	2.75×10 ⁻⁶	2.09×10 ⁻¹⁵	9.75×10 ⁻⁴	1.51×10 ⁻¹⁴

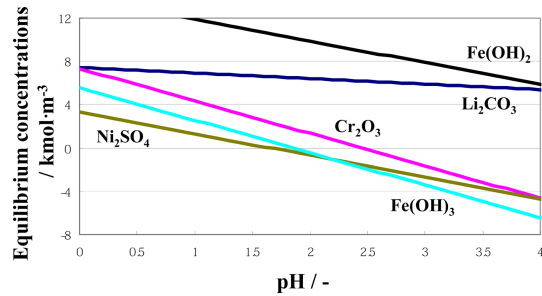
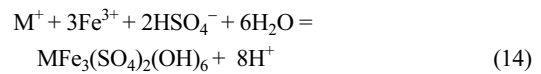


Fig. 5. Equilibrium concentrations of precipitates with pH.

be easily precipitated as NiSO₄, Fe(OH)₃, and Cr₂O₃ with increasing pH, respectively, whereas Fe²⁺ and Li⁺ would not precipitate in the pH zone. When considering electrolytes, SOCl₂, and minor components in the lithium primary battery, it is difficult to compare directly the experimental results and the calculated data, but both show a good agreement in precipitating order of metals. In the case of Fe, jarosite could be also considered as Fe precipitate²⁾. Jarosite precipitates as following equation²⁾.



where M⁺ represents monovalent ion. Jarosite could be formed and precipitate even in low pH.

Figure 6 and 7 show the comparisons of pH and Fe concentration at 35 °C and 50 °C. As discussed above,

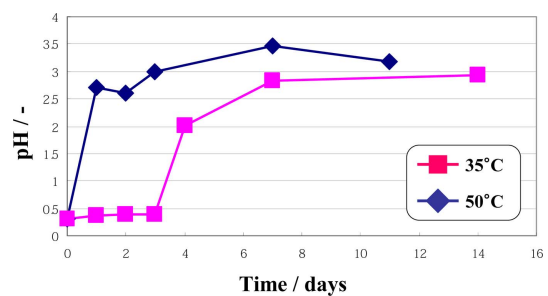


Fig. 6. The comparison of pHs in experiments performed at 35 °C and 50 °C.

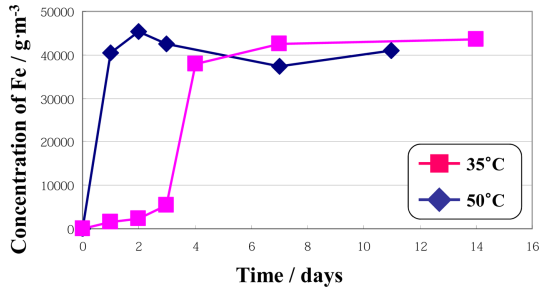


Fig. 7. The comparison of Fe concentration in experiments performed at 35 °C and 50 °C.

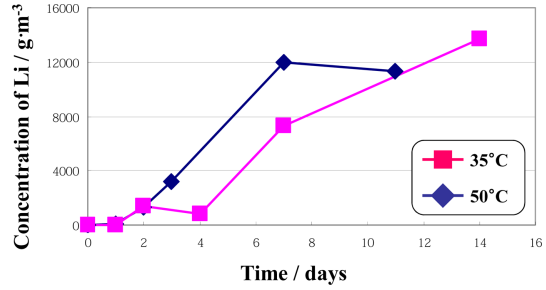


Fig. 9. The comparison of Li concentration in experiments performed at 35 °C and 50 °C.

pH and Fe concentration increase as metal like Fe become dissolved by acid solution, but Fe concentration is kept almost constant around at 40000 g·m⁻³ when pH increases to about 3. As can be seen in Fig. 5, because ferric ion could precipitate more easily than ferrous ion, Fe ion detected in the solution would be considered to be ferrous ions. The concentration of Fe and pH increase more rapidly at 50 °C than at 35 °C, and this result which be due to temperature increase.

Figure 8 shows the variation of Cr concentration in the experiments at 35 °C and 50 °C. The concentrations of Cr increase to 11150 g·m⁻³ at 2nd day in the experiment at 50 °C and to 10280 g·m⁻³ at 4th day in that at 35 °C. At the same time, Fe concentrations show 45400 g·m⁻³

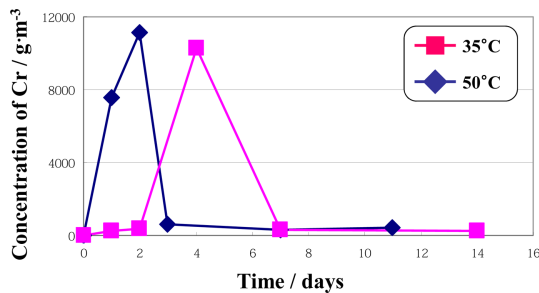


Fig. 8. The comparison of Cr concentration in experiments performed at 35 °C and 50 °C.

at 50 °C and 38200 g·m⁻³ at 35 °C. The ratios of Fe and Cr dissolved are 4 to 1 at 50 °C and 3.7 to 1 at 35 °C. This result would be closed to the ratio of Fe and Cr in the stainless steel. The concentration of Cr increases with that of Fe, but it decreases to 200 ~ 300 g·m⁻³ when pH reaches to about 3. As can be seen in Fig. 9, Li concentrations increase gradually in the experiments at 35 °C and 50 °C. This behavior would result from the fact that Li inside the battery starts to dissolve after dissolution of stainless steel.

The discharged batteries were shredded after drying to confirm if the batteries are stabilized or not. As shown in Table 4, no batteries discharged at 50 °C were exploded but even battery discharged during 3 days at 35 °C was exploded. Although the discharged batteries are stabilized during 1 day at 50 °C and 3 days at 35 °C, lithium concentrations are still low at the same time. This result would suggest that the batteries are stabilized independent of Li dissolution. It was expected that the batteries were stabilized by two ways; one is that lithium in the batteries reacts with sulfuric acid during discharging and the other is that the lithium reacts with air during drying.

Based on the above results, a pilot plant, which can treat 2 ton waste lithium primary batteries at once, had been run at 50 °C. However a few batteries were exploded

Table 4. Explosion during shredding the lithium primary batteries discharged

Day	1st	2nd	3rd	7th	11th
at 50 °C	none	none	none	none	none
Day	1st	2nd	3rd	4th	7th
at 35 °C	explosion	explosion	weak explosion	none	none

during the processes of drying or shredding even though the batteries had been discharged more than 3 days at 50 °C. If the discharging time is extended, the safety of the recycling process would be guaranteed but the loss of valuable metal would increase. Therefore, the recycling process was revised as follows; the batteries were discharged with water after dissolving the batteries with sulfuric acid,

Reaction between the batteries and air during drying induces the batteries to be exploded, and when the batteries were too discharged, loss of metal would increase. Therefore, in this study, 2-step discharging process was proposed to obtain safe and economic recycling process. The new method consists of discharging steps by sulfuric acid and water, respectively.

Figure 7 shows pHs discharged with 0.5 kmol·m⁻³ sulfuric acid during 3, 6, 9 hours and with water during 24 hours after acid solution, respectively. pH didn't increase during 3 hours and increased to 2.5~3.0 after 6 hours or 9 hours. Concentrations of Fe (Fig. 8), Ni, and Li were higher in discharging test during 6 hours and 9 hours than that during 3 hours. After the sulfuric acid was replaced with water, pHs show 2~3 after discharging with water. pH decreased because of acid remained on surface of the batteries and SOCl₂ in the batteries.

The batteries discharged during 3 hours by sulfuric acid were exploded, but no explosion was observed when the batteries discharged during 6 hours or 9 hours were shredded. Because this new method decreases loss of metal and decreases the high reactivity of the batteries efficiently, an economic and safe method was achieved.

4. Conclusions

Optimum discharging conditions of the waste primary lithium batteries were investigated to develop an economic and safe recycling method.

The high reactivity of waste batteries was decreased within 1 day at 50 °C and 4 days at 35 °C. Decrease

in the high reactivity of the waste batteries would be achieved by dissolving stainless steel which is cover jacket of the waste batteries. Because two step discharging method with sulfuric acid and water decreased loss of metal during discharging the batteries, this new method would increase economic efficiency of the recycling process of primary lithium battery.

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