

Recovery of rare metals from spent lithium ion cells by hydrothermal treatment and its technology assessment

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Abstract

A novel cobalt recovering process from a cobalt-based cathode electrode in a lithium secondary cell was developed using a hydrothermal treatment combined with a pyrometallurgical technique. A cobalt-based cathode electrode was prepared by casting the mixture of LiCoO_2 , poly(vinylidene fluoride) and conductive carbon black onto an Al foil, and this model electrode was used as a test sample. A hydrothermal treatment of the cathode sample was carried out using pure water as a solvent in the temperature range of 423–473 K for the duration of 0–40 h. The hydrothermal treatment at 473 K for more than 15 h led the cathode sample to the disintegration into powdery particles. By the hydrothermal treatment under the optimum condition at 473 K for 20 h, more than 99.9 mass% of Co and 98 mass% of Al in the cathode sample was reclaimed as a form of spinel type $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$), and most of Li and F could be dissolved into the solution. Subsequently, metallic cobalt was successfully recovered from the spinel compound and carbon mixture by the pyrometallurgical treatment with additives for slag formation under a reducing condition at 1623 K for 5 h.

Keywords: spent lithium ion cell, hydrothermal treatment, cobalt recovery, pyrometallurgical treatment.

1 Introduction

In the past one decade, lithium ion cell has been spreading its occupation in the world cell market because of its properties superior to other conventional secondary cells [1]. Due to its incomparable advantages, the lithium ion cell has been exploited for many electric appliances or even in a medical field [2]. Furthermore, the lithium ion cell contains less toxic metals comparing to the



nickel-cadmium cell. Taking these overall advantages into consideration, it is quite explicit that the lithium ion cell will be equipped continuously in a number of new electric applications.

It has no doubt that a tremendous number of the spent lithium ion cells will be disposed when they reach the end of their practical life [3]. These wastes should be appropriately treated in order to recover cobalt in the spent cells since cobalt is classified as one of rare metals. The consumption of cobalt always leads to the market price appreciation due to little reserves of cobalt-containing ore in the earth's crust. In addition, a large amount of cobalt is demanded not only in lithium ion cells, but also in various sorts of industrial materials such as hard alloys, paints or magnets. Therefore, recovering cobalt from spent lithium ion cells is quite beneficial to solve the pressing problem on stable cobalt-supply.

Up to the present time, most of practical recycle process for the spent lithium ion cells is based on a pyrometallurgical method. This process mainly consisted of two heat-treatment stages, *i.e.*, the gasification removal of lithium and fluorine in the spent cell, and the reduction and condensation of cobalt from the residue. It is obvious that this process needs less chemical reagents, but a large amount of energy is required for the whole heat-treatment processes. Additionally, there is a serious problem in the first heat-treatment stage that a furnace wall has a severe damage by corrosive gasses.

Recently, a cobalt reclamation process has been investigated by a hydrometallurgical technique of the cathode materials in the spent lithium cell. For example, Zhang et al. [4] attempted to recover cobalt from the cathode by three steps, *i.e.*, (1) the cobalt dissolution step from the cathode using hydrochloric acid, (2) the extraction step from the leached liquid into kerosene and (3) the inverse extraction step with sulfuric acid to form cobalt sulfate. Nan et al. proposed another hydrometallurgical process, which was based on the dissolution-deposition and extraction methods [5]. These reports imply that cobalt-recovering process has an advantage from the standpoint of smaller energy consumption compared with the pyrometallurgical method; however, this process requires an appreciable amount of toxic chemicals or complex multistage-treatments.

In order to reduce the environmental loads arising from both the pyrometallurgical and hydrometallurgical treatments, we propose a novel cobalt-recovering process based on a hydrothermal technique, which is incorporated into the current pyrometallurgical treatment by replacing the heat-treatment process for the gasification of lithium and fluorine. In this paper, the disintegration process of the cobalt-based cathode electrode by hydrothermal treatment in pure water was investigated in detail and the feasibility of cobalt reclamation was also examined.

2 Experimental

2.1 Preparation of LiCoO_2 powder

Commercially available Li_2CO_3 and Co_3O_4 powders were used as starting materials for the preparation of LiCoO_2 powder. LiCoO_2 was synthesized



through the solid-state reaction technique reported by R. Gupta and A. Manthiram [6]. The Li_2CO_3 and Co_3O_4 were first mixed by rotary ball-milling with ethanol, and then dried at 333 K for 1 h. An excess amount of about 3 mol% Li was added to the mixture to compensate for any loss of lithium that may occur during the firing. Then, the powder was precalcined in an $\text{O}_2\text{-N}_2$ stream (mole ratio of 20: 80) of for 5 h at 773 K. After the pulverization by ball-milling, the mixture was calcined again in the stream of $\text{O}_2\text{-N}_2$ for 24 h at 1123 K to form LiCoO_2 . Finally, the agglomerated LiCoO_2 was further pulverized by ball-milling to obtain powdery LiCoO_2 for subsequent cathode preparation.

2.2 Preparation of cathode electrode sample

Commercially available conductive carbon black, poly(vinylidene fluoride) (abbreviated as PVDF) for a supporting binder, an aluminum foil for a current collector (purity 99.5%, thickness: 10 μm) and the synthesized LiCoO_2 powder were used for the components of a model cathode electrode sample.

The conductive carbon black, PVDF and LiCoO_2 powders were, respectively mixed at the ratio of 10: 5: 85 mass% by ball-milling. Then, N, N-dimethylformamide was added to the mixture to form viscous slurry, and the resulting slurry was cast onto one side of the aluminum foil (size: 2 \times 2 cm). The sample was cold-isostatically pressed at 200 MPa for 1 min, and then vacuum-dried at 393 K. About 450 mg of the mixture was cast onto the Al foil to ensure an enough amount of the treated sample for subsequent analyses.

2.3 Hydrothermal treatment

Hydrothermal treatment was conducted using a stainless steel vessel lined with poly(tetrafluoroethylene) (PTFE) in an inner volume of 60 mL. A cathode electrode sample was placed into the vessel and then immersed with 30 mL of deionized and distilled water. The experiment was performed in the subcritical temperature range of 423–473 K for duration up to 40 h. At any experiment, the heating and isothermal step was regulated by applying an external heating, but the cooling process was spontaneously done in ambience. After the hydrothermal treatment, the solid component was collected by filtration using a membrane filter (pore size: 0.45 μm) under reduced pressure.

2.4 Pyrometallurgical treatment

Cobalt aluminates ($\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$, $x=0$) were prepared from $\gamma\text{-Al}_2\text{O}_3$ (particle size < 20 nm) and Co_3O_4 by referring to the paper reported by Casasdo and Rasines [7]. The synthesized CoAl_2O_4 was mixed with additives, such as SiO_2 , CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$ and carbon black. The mixing molar ratio of CaCO_3 : SiO_2 : $\alpha\text{-Al}_2\text{O}_3$: CoAl_2O_4 = 1: 0.8: 0.2: 0.02 was applied for slag formation. The powders were mixed by ball-milling, uniaxially pressed into a pellet with diameter of 15 mm, and then cold-isostatically pressed at 200 MPa for 1 min. The green compact was charged into a graphite crucible, muffled with carbon in mass quantities, and thermally treated in an electric furnace in Ar flow at 1623 K for



5 h. This temperature was determined so as not only to reduce the CoAl_2O_4 but also to generate the liquid slag phase in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system by referring to the phase diagram in the ternary system of CaO , SiO_2 and Al_2O_3 [8], and the Richardson-Jeffes diagram for the each oxide [9].

3 Results and discussion

3.1 Hydrothermal treatment of the cathode electrode

Figure 1 shows the photographs of (a) as-prepared cathode and the hydrothermally treated specimens in H_2O at 473 K for (b) 5 (c) 15 and (d) 40 h. As-prepared cathode was collapsed depending on the treatment time; the cast mixture of LiCoO_2 , carbon black and PVDF was peeled off from the Al foil, and then was disintegrated into powdery particles; the Al foil became thinner and was broken apart with duration of the treatment. The fractured Al foil can be seen in the disintegrated mixture at the treatment time of 5 h (see Fig. 1(b); bright gray fragments are Al foil), but the foil disappeared completely when the treatment time was more than 15 h (see Figs. 1(c), (d)).

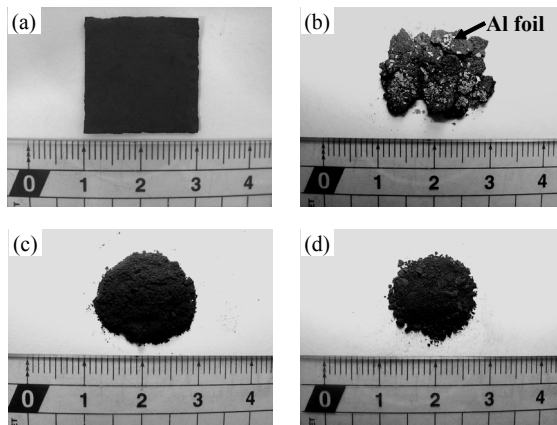
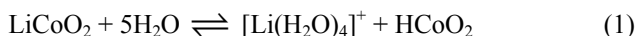


Figure 1: The appearance variation of the cathode electrodes through the hydrothermal treatments; (a) an untreated cathode and hydrothermally treated cathode for (b) 5, (c) 15 and (d) 40 h at 473 K in H_2O .

3.1.1 Analyses of the solution after hydrothermal treatment

Relationship between the pH values of (■) calculated and (▲) measured of the solution after the hydrothermal treatment at 473 K for various times is shown in Figure 2. When the sample was immersed in water, the pH value of the solution increased immediately. Subsequently, the pH value increased gradually with increasing hydrothermal treatment time, and reached about 12. The measured pH value almost corresponded to that of the calculated one according to the Li^+ dissolution reaction [10]:



Thus, the increasing behavior of pH value was mainly caused by the ion-exchange and hydration reaction between LiCoO_2 and H_2O accompanying Li^+ dissolution. Figure 3 shows the dissolution of lithium (Li^+), fluorine (F^-), aluminum (Al^{3+}) and cobalt (Co^{2+} and Co^{3+}) ions into the solution during the hydrothermal treatment. Fluorine ion was detected by the anionic chromatography, indicating that the cleavage of C-F bond in PVDF progressed on time and led to the formation of F^- . A similar dissolution behavior between Li^+ and F^- was observed; *i.e.*, both dissolution amounts gradually increased, and then reached over 97 mass% at the treatment time of 20 h. This trend resulted from Li^+ dissolution accompanied by the increase in pH value, because the hydrolytic cleavage of PVDF became more susceptible in higher concentrated alkali solution. The dissolution of cobalt ion was less than the detection limit by ICP-AES under the whole treatment conditions. The increase of pH value is also expected to have an effect on the Al foil corrosion because metal Al can dissolve into a high pH solution. As mentioned previously, the Al foil was fractured with increasing treatment time, and finally disappeared when the treatment time reached 15 h (see Fig. 1). However, the dissolution of Al^{3+} initially increased up to approximately 40 mass% until the treatment time of 10 h, but successively decreased to approximately 2 mass% at the treatment time more than 20 h. The reason for decreasing Al^{3+} dissolution will be deduced to the formation of $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$.

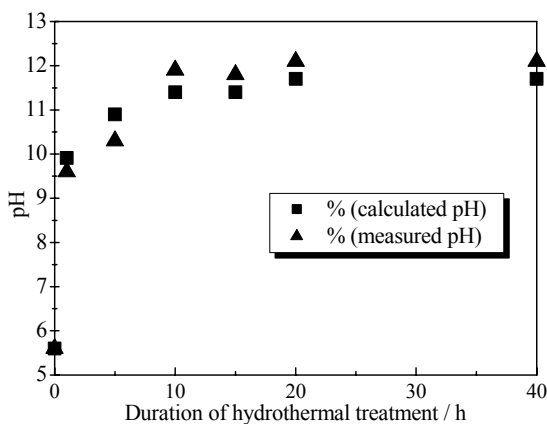


Figure 2: Relation between (■) the calculated and (▲) the measured pH value of the solution after the hydrothermal treatments in H_2O at 473 K for various treatment times.

With regard to the Al^{3+} dissolution, an electrolysis effect was considered to play an important role as another effect except for the pH factor. In order to examine this effect, the Al foil coated with or without PVDF was treated in

various solutions at 473 K for 40 h. The Al^{3+} dissolution result analyzed by ICP-AES is listed in Table 1. NaCl was chosen as an electrolyte instead of LiOH to avoid the Al^{3+} dissolution by the pH effect. These data showed that the Al foil was able to dissolve only when the foil with PVDF was treated in NaCl electrolytic solution (sample No. 1; the dissolution was nearly 76 mass%). On the contrary, the Al foil without PVDF could not dissolve both in H_2O and NaCl solutions (sample No. 3 and 4), and the foil with PVDF also could not dissolve in H_2O (sample No. 2). Consequently, it was clarified that the electrolysis effect must be involved in the Al^{3+} dissolution process during the hydrothermal treatment under the electrolyte (*e.g.*, Li^+ and OH^-) present conditions.

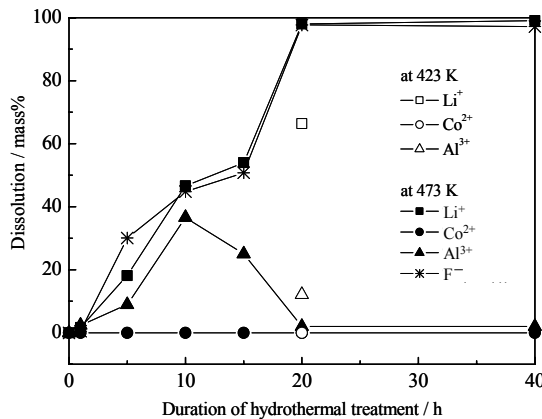


Figure 3: Dissolution of lithium, cobalt, aluminum and fluorine ions into the solution after the hydrothermal treatments of the cathode electrode at 423 and 473 K for various treatment times.

Table 1: Al^{3+} dissolution from Al foil under hydrothermal condition.

Sample No.	Sample ^{*1)}	Solution	Dissolution (mass%)
1	Al foil with PVDF	1M NaCl aq.	79.1
2	Al foil with PVDF	H_2O	0.1
3	Al foil	H_2O	Not detected
4	Al foil	1M NaCl aq.	Not detected

*1) Size of Al foil was 1×1 cm for each sample.

3.1.2 Analyses of the solid residues obtained after hydrothermal treatment

Figure 4 shows XRD profiles of (a) the as-prepared cathode, and hydrothermally treated cathodes with 30 mL of deionized H_2O for (b) 1, (c) 5, (d) 10, (e) 15, (f) 20 and (g) 40 h. XRD profiles in Figs. 4(a) and (b) were acquired from the cathode surface cast by the mixture of LiCoO_2 , conductive carbon black and PVDF. Only peaks derived from the layered rock salt structure of LiCoO_2 were detected on the as-prepared cathode. After the hydrothermal treatments for 1, 5, 10 and 15 h, new peaks of hydrogen cobaltate (HCoO_2) and/or spinel-type cobalt aluminates ($\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$)) were identified in addition to LiCoO_2

peaks, and an unknown peak at around 17° (assigned as +) appeared also for the samples treated for 5 and 10 h. The unknown peak was derived from a reactant between the carbon black and LiCoO_2 because the peak at around 17° appeared when a green compact of carbon black and LiCoO_2 mixture was treated under the above hydrothermal condition. Metallic Al peaks were observed in the process of the treatment for 5 and 10 h (Figs. 4(c) and (d)) due to the disintegration of the cathode sample, and the Al peaks entirely disappeared when the treatment time was 15 h and more (Figs. 4(e), (f) and (g)), which were in good agreement with the result of appearance change shown in Figure 1. Only a spinel-type $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$) was formed when the treatment time was 20 and 40 h, as seen in Figs. 4(f) and (g). Taking the ICP-AES and XRD results into consideration, it was implied that all cobalt existed in the solid phase, i.e., LiCoO_2 , HCoO_2 or $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$, depending on the treatment time. It was found that a spinel-type Co_3O_4 with no Al formed from a green compact of LiCoO_2 and carbon black mixture by a hydrothermal treatment. The diffraction peaks of $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ and Co_3O_4 could not be distinguished each other because their peaks generally overlapped.

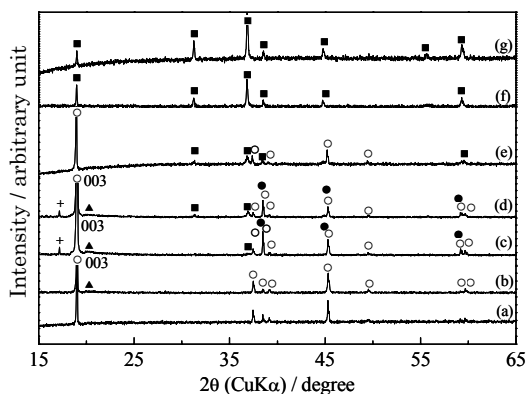


Figure 4: XRD profiles of (a) as-prepared cathode, and hydrothermally treated cathodes in H_2O at 473 K for (b) 1, (c) 5, (d) 10, (e) 15, (f) 20 and (g) 40 h. Symbols are (■) $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$), (□) Co_3O_4 , (●) Al, (○) LiCoO_2 , (▲) HCoO_2 and (+) unknown peak.

Figure 5 shows representative (a) secondary electron image (SEI), and EDX element maps corresponding to (b) Co, (c) O, (d) Al and (e) C on the hydrothermally treated cathode. The EDX maps clearly verified that particles consisting of Co, Al and O existed in the treated cathode, while particles consisted of carbon were originated from carbon black and PVDF. Although the $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ particles were confirmed by the EDX analysis, the Co_3O_4 particles were not observed. The hydrothermally treated cathode was believed to contain Co_3O_4 particles, but the amount of Co_3O_4 seemed too small to be identified by EDX analysis.

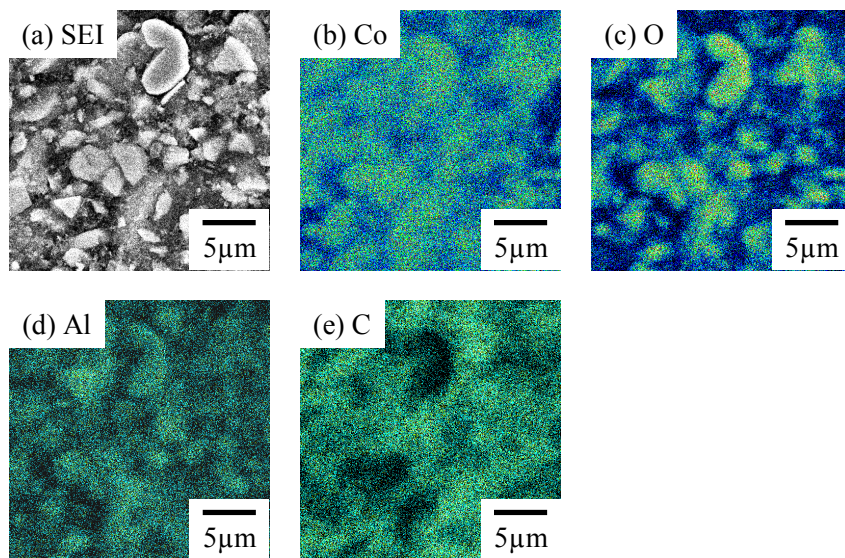


Figure 5: Representative (a) secondary electron image (SEI) and element distributions of (b) Co, (c) O, (d) Al, and (e) C on hydrothermally treated cathode at 473 K for 40 h.

3.1.3 Optimum condition of hydrothermal treatment

The hydrothermal treatment at 423 K for 20 h was carried out in order to lower the treatment temperature, but the Li^+ dissolution was found insufficient (see Figure 3). Therefore, it was found that the treatment temperature at 473 K or more was required for the separation of Li from Co and Al. Taking the results of ICP-AES, IC, XRD and XPS analyses into consideration, the hydrothermal treatment at 473 K for 20 h was determined as an optimum condition for the separation of Li and F from the cathode electrode, when more than 99.9 mass% of Co and 98 mass% of Al were efficiently reclaimed as a form of solid-state $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$), and most of Li and F could be dissolved into the solution. XPS analysis exhibited that no fluorine was detected on the solid residue after the hydrothermal treatment over 20 h, corresponding to the result of F^- dissolution shown in Fig. 3. Residual carbon analysis by CHN coder revealed that the recovered spinel compound contained nearly 12 mass% of carbon, which originated from the conductive carbon black and PVDF. This carbon contamination has no problem in the subsequent pyrometallurgical treatment because the carbon can be used as a reductant.

3.2 Recovery of metal cobalt by pyrometallurgical method

Figure 6 shows XRD profiles of the mixture of SiO_2 , CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$, CoAl_2O_4 and carbon black before (a) and after (b) a pyrometallurgical treatment at 1623 K for 5 h in Ar flow. The peaks of SiO_2 , CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$ and CoAl_2O_4 , which were the components of the starting mixture, were identified in Fig. 6(a). On the

other hand, the peaks of calcium silicate, larnite, gehlenite and metallic cobalt were identified with no peaks of the starting components, as seen in Fig. 6(b). Hence, by adding the SiO_2 , CaCO_3 and $\alpha\text{-Al}_2\text{O}_3$ to the CoAl_2O_4 and carbon black mixture, we succeeded in incorporating Al into the slag phase and obtaining the metallic Co without formation of any alloy. The effect of such additives is explained by the difference in Gibbs free energy change for the formation of each oxide from metallic Co and Al. As generally known, the more negative a free-energy change for oxidation is, the easier the formation of an oxide is. The free-energy change for the formation of aluminum oxide is more negative than that for the formation of cobalt oxide according to the Richardson-Jeffes diagrams [9]. In addition, $\alpha\text{-Al}_2\text{O}_3$ can form a liquid slag phase with the additives at 1623 K in terms of the equilibrium phase diagram of the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system [8]. Thereupon, Al was transferred into the slag phase and Co was separated as a pure metal.

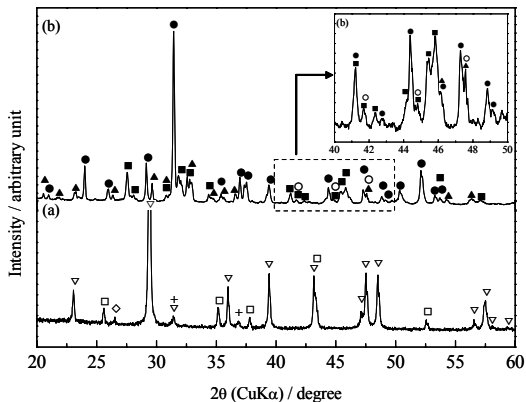


Figure 6: XRD profiles of the mixture (a) before and (b) after a pyrometallurgical treatment at 1623 K for 5 h. Symbols are (∇) SiO_2 , (\square) CaCO_3 , (\square) $\alpha\text{-Al}_2\text{O}_3$, (+) CoAl_2O_4 , (\bullet) $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite), (\blacktriangle) Ca_2SiO_4 (calcium silicate), (\blacksquare) Ca_2SiO_4 (larnite) and (\circ) Co.

Considering the results of the hydrothermal and the pyrometallurgical treatments, we propose a novel cobalt recovering process. This new process consisted of two stages; the first is the hydrothermal treatment for the dissolution of Li and F into the solution and the second is the pyrometallurgical treatment for the reduction and condensation of cobalt from the spinel compound. It is quite obvious that the hydrothermal treatment can operate at temperatures lower than the present pyrometallurgical process for the gasification of Li and F with no corrosive gas generation and with no utilization of toxic or expensive solvents such as acid or alkali solution. Thus, a cost for equipment maintenance of damaged furnace wall is expected to be reduced by preventing the corrosive gas generation. Additionally, the energy consumption in hydrothermal treatment can be compensated by the utilization of waste heat generated from the subsequent pyrometallurgical treatment. In the second pyrometallurgical step, the present-

operating furnace is probably utilized without any modification, which means that an investment for new equipments is expected to be reduced. Therefore, taking all advantages into account, this new process can be recommended as an environmental-friendly and low-cost process.

4 Summary

- (1) Metallic cobalt was successfully reclaimed from a cathode electrode by a hydrothermal treatment in pure water at 473 K for 20 h and subsequent pyrometallurgical treatment at 1623 K for 5 h under Ar flow.
- (2) More than 99.9 mass% of Co and 98 mass% of Al in the cathode sample was converted to solid state spinel $\text{Co}(\text{Co}_x\text{Al}_{2-x})\text{O}_4$ ($0 < x \leq 2$) and most of Li and F could be dissolved in the solution after the hydrothermal treatment under the optimum condition at 473 K for 20 h.
- (3) The hydrothermal treatment for the separation of Li and F in the cathode electrode could lower the treatment temperature from 1273 K to 473 K with no corrosive gas generation and with no utilization of toxic and expensive solvents.

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