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Master’s Thesis

Study on waste lithium-ion batteries recycle technology by hydrothermal method

「水熱処理による廃リチウムイオン電池のリサイクルに関する検討」

Submitted February 12,2019
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1. Introduction

1.1 Introduction of lithium ion battery

1.1.1 Composition and mechanism of Li-ion battery

Lithium-ion battery or Li-ion battery (abbreviated as LIB) is a type of rechargeable battery, in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging [1].

(1) composition

As is shown in Figure 1-1, Li-ion batteries contain 5 basic parts: cathode, anode, electrolyte, organic separator and iron shell.

Cathode is usually made of aluminum covered with some binder and positive electrode active material (e.g. $LiCoO_2$). Anode is usually made of copper covered with binder and negative electrode active material (graphite). Cathode and anode are separated by organic separator.

Electrolyte is the organic solution containing Li^+. $LiPF_6$ is a kind of common electrolyte salt. To improve the performance, $LiAsF_6$, $LiBF_4$, $LiClF_4$ are also used in some cases though they are more expensive.

Iron shell is made of Fe or aluminum in some products.

(2) mechanism

During the charge of Li-ion battery, Li^+ ion escapes form positive electrode and is embedded into negative electrode. While during the discharge, it moves from negative to positive electrode. [2]

The mechanism of Li-ion battery could be described as the reaction formula below:

$$\mathrm{LiMO_2} + n\mathrm{C} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_{1-x}\mathrm{MO_2} + \mathrm{Li}_x\mathrm{C}_n$$

The electrochemical expression is: (-) C_n | $LiPF_6$ -EC + DEC | $LiMO_2$ (+)

In the formula, M means metals in cathode material, such as Co, Ni, Mn, Fe.

The organic solvent EC (Ethylene Carbonate, $C_3H_4O_3$) and DEC (Diethyl Carbonate, $C_5H_{10}O_3$) could also be replaced or mixed by PC (Propylene Carbonate, $C_4H_6O_3$) and DMC (Dimethyl Carbonate, $C_3H_6O_3$).

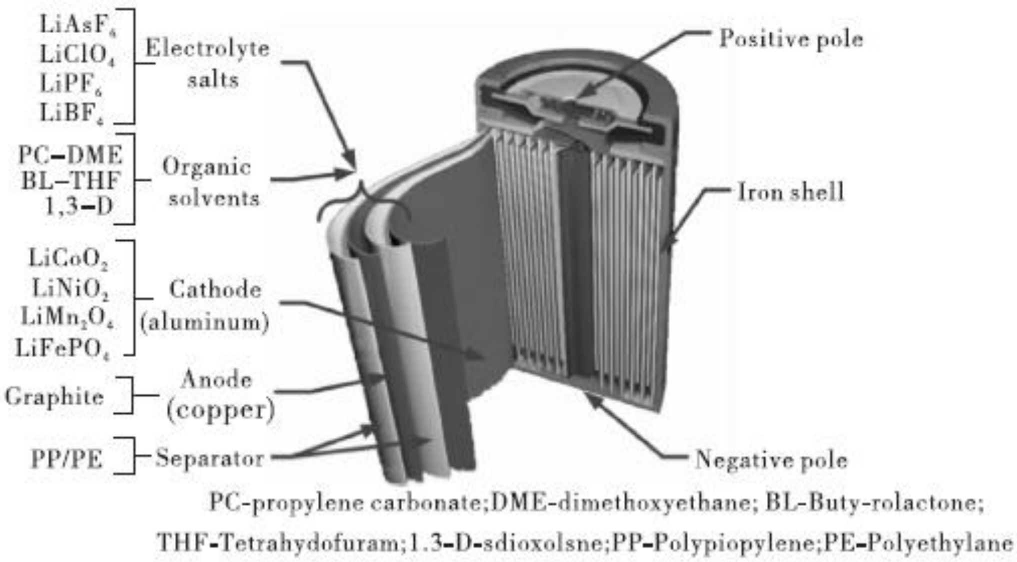


Figure 1-1. The structure of the lithium ion battery [1]

1.1.2 Application of Li-ion battery

As is shown in Figure 1-2, compared with other batteries, the energy density of Li-ion battery is much higher, which means to provide the same electricity, Li-ion is much lighter and easier to carry. Of course the energy density of Li metal battery is the highest, but it is a kind of non-rechargeable battery and safety issues should be noticed [3].

Besides, higher work voltage, wider temperature range, quick charge and discharge rate, no memory effect, long cycle life are also advantage of Li-ion battery [5]. Thus, since Li-ion battery is first commercialized by Sony and Asahi Kasei in 1991 [6], it has been gradually applied widely in mobile electronic device, such as smart phone, laptop computer and digital camera [1].

In recent years, with the energy crisis and the development of alternative fuel vehicle, Li-ion battery is also researched and applied in hybrid electric vehicles.

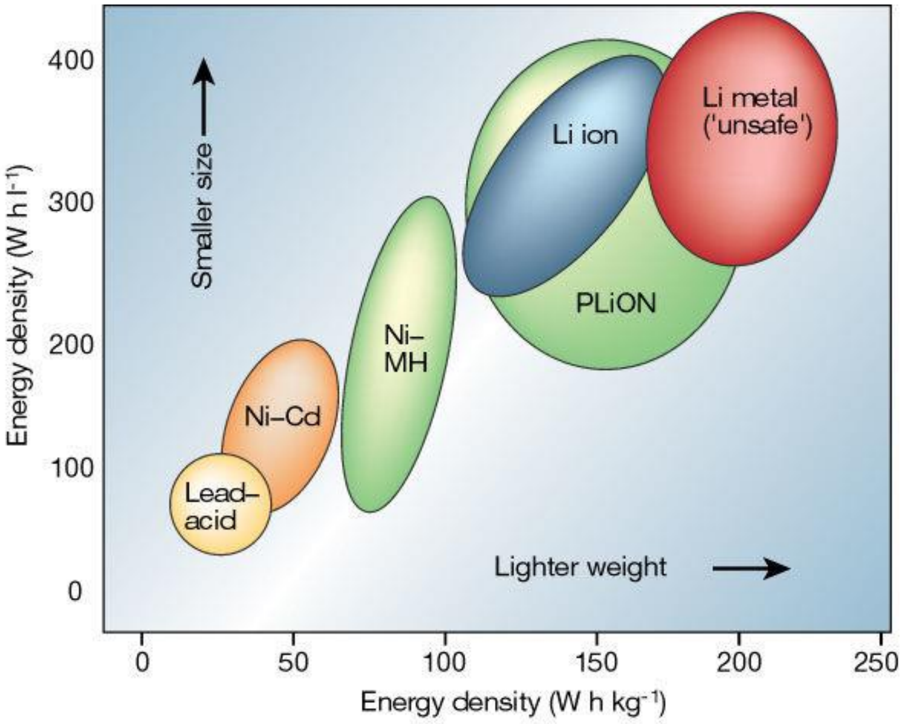


Figure 1-2. Comparison of volumetric and gravimetric energy density of the important NiMH, lead-acid (PbA), Ni-Cd, Na/S, and Li–ion batteries [4]

1.2 Significance of waste lithium ion battery recycle technology

In recent years, the demand for Li-ion battery keeps increasing. According to some researches [7-8], the global Li-ion battery consumption has increased from 500 million single batteries in 2000 to 7000 million in 2015. While in the future, the demand is predicted to keep increasing rapidly as shown in Figure 1-3 because of the popularization of hybrid electric vehicles and the prohibition of traditional gasoline cars in several countries in the future 10 to 30 years.

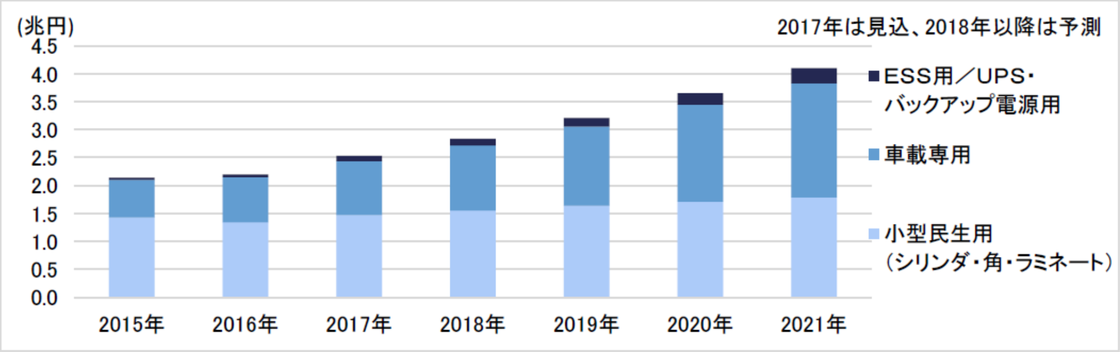


Figure1-3. Predicted Li-ion battery global market [9]

At the same time, since the service life of Li-ion battery is usually about 3 to 5 years, the huge amount of production will unavoidably lead to huge amount of waste batteries. So, it is quite necessary to treat this part of waste Li-ion battery properly considering economic benefit and potential pollution, which is researched by many researchers in the world [1, 2, 10].

1.2.1 Value of waste Li-ion battery

Nowadays, most of the Li-ion batteries are produced in China, Korea and Japan as shown in Figure 1-4. A suitable recycle technology of waste Li-ion battery could make positive effects on reducing the cost of production by recovering useful materials from waste batteries, such as Li, Ni, Co.

Table 1-1 shows raw material contents in some type of hybrid electric vehicles. It indicates that in a single hybrid electric vehicle, several kilograms of valuable metals are used.

Table 1-2 shows major metal contents and potential value of common lithium ion batteries. It indicates that in 1 ton waste LIB, the potential value of Co, Cu, Al in the battery might be 5734.134 dollar. (The market price of metals comes from London Metal Exchange, 2014.12.5.)

If these metals could be recycled and reused, it will reduce the huge amount of metal cost since these metal concentrations in LIB are much higher than natural ore [11]. It is especially meaningful for countries which are lack of natural resources, such as Japan.

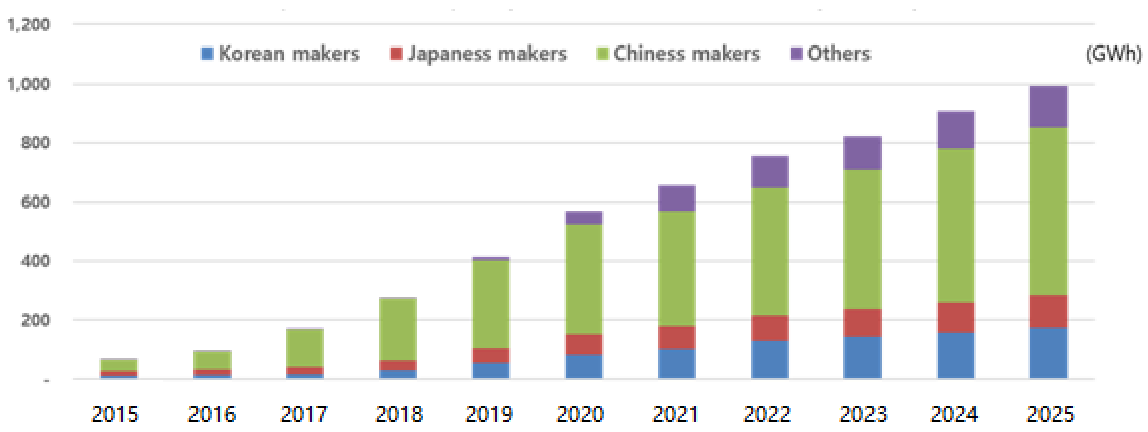


Figure 1-4. Annual production capacity of lithium-ion battery [12]

Table 1-1. Raw material contents per unit of electric vehicles (kg/unit) [13]

Type of the vehicle	Li	Ni	Co	Mn	Cu	Al
Tesla Model S	7.7	53.5	9.9	/	26.6	12.3
BMW i3 Gen2	6.1	14.6	12.0	10.7	15.8	6.9
GM BOLT	13.4	26.3	26.4	43.9	39.7	24.5

Table 1-2. Major metal contents and potential value of lithium ion battery [1]

Metal	Co	Cu	Al	Fe	Li	Summary
Contents (Wt%)	15	14	4.7	25	0.1	58.8
Market price (dollar/ton)	31500	6536	2002	-	-	-
Element price in waste LIB (Dollar / ton battery)	4725	915.04	94.094	-	-	5734.134

1.2.2 Security risks and potential pollution during recycle

As has been mentioned in 1.1.1, the composition and structure of LIB is complicated, which makes it difficult to prevent secondary pollution during treatment.

Table 1-3 shows the composition and potential environmental pollution of LIBs. It indicates that the main environmental problems of LIBs are metals, volatile organic compounds (VOCs), dust and fluorine, which have to be considered and dissolved in the process of treatment.

Metal pollution could pollute the land and soil. VOCs and dust can cause sensory irritation symptoms. Fluorine is also harmful to human as well as that is able to corrode metals of the instruments during treatment [1].

Besides, the residual electricity in LIBs is also security risk, which will lead to heat release and explosion, hurting employees who treat the waste LIBs [15].

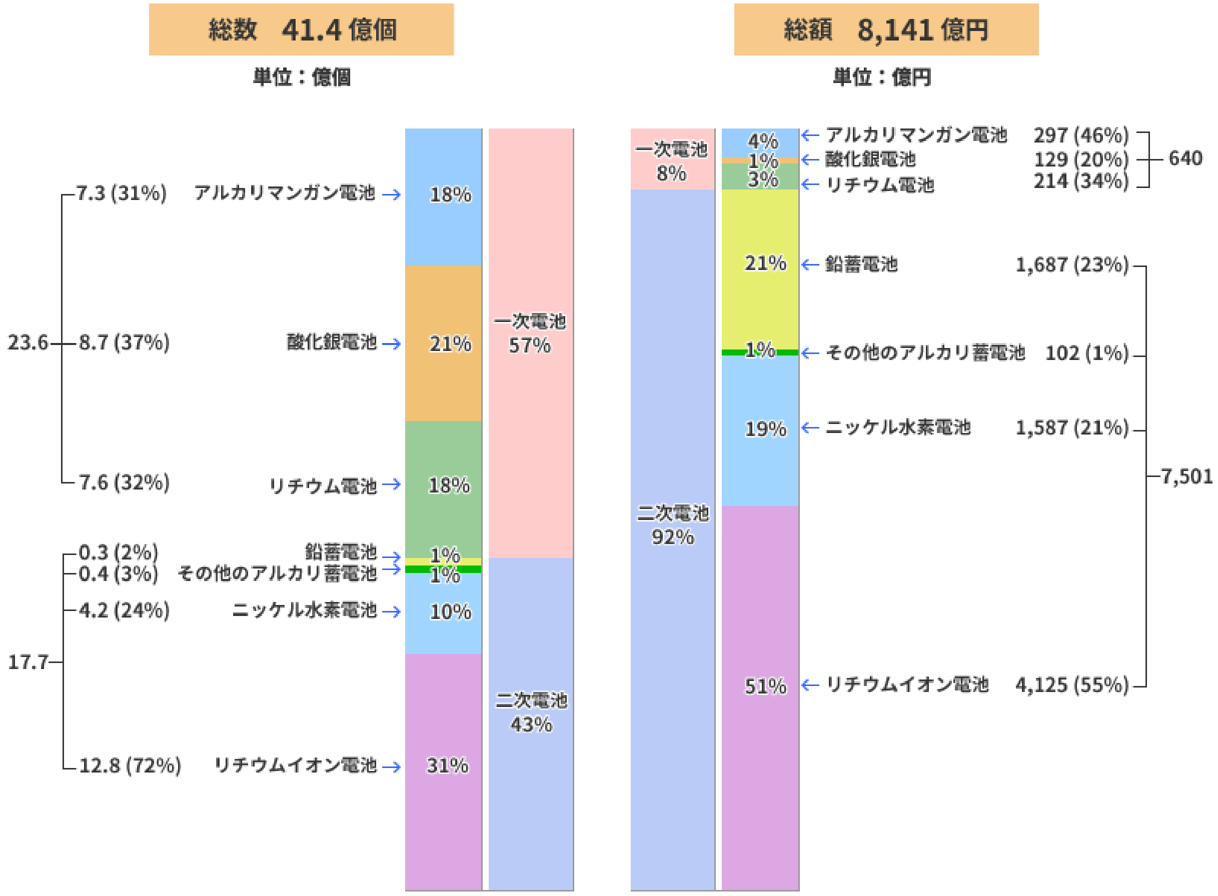


Figure 1-5. Total production of battery in Japan (2017) [14]

Table 1-3. Composition and potential environmental pollution of LIBs [1]

part	composition	main chemical properties	potential pollution
Cathode	$Al+LiCoO_2/LiMn_2O_4/LiNiO_2$	Strong reaction with H_2O/acid/reductants/strong oxidants, forming toxic oxide	Pollution of heavy metals
Anode	Cu + C(graphite)	Explosion when dust get fire or high temperature	Dust pollution
Electrolyte salts	$LiPF_6/LiBF_4/LiAsF_6$	Strong corrosive, forming HF in H_2O	Fluorine
Electrolyte solvents	EC+PC+DC+DEC	Combustible	VOCs
Organic separator	PP/PE	Combustible	VOCs
Binder	PVDF/VDF/EPD	Thermal decomposition produces HF	Fluorine

1.3 Current technology to treat waste Li-ion battery

Several recycle methods have been researched to recover metal resources from waste LIBs. Figure 1-6 shows a quite complete metals recovery process from waste LIBs.

Usually, a complete recycle procedure includes 4 stages:

①. Pretreatment of the battery

In this stage, NaCl solution or low-temperature freezing are usually used to pretreat waste LIB to avoid explosion or fire during next procedure.

②. Material sorting of the battery

In this stage, several methods are able to get useful materials from waste LIBs.

Mechanical separation could separate metal materials from the waste LIBs by density and magnetism. It is the easiest way to be used for large-scale processing. So, it is the most common method currently. However, electrolyte salt will volatilize, causing VOCs pollution. Dust and noise are also problems.

Heat treatment makes use of high temperature to remove organics and graphite powder, which are hard to treat in waste LIBs, to separate cathode materials (metals) and other materials effectively. This method could also treat huge amount of waste LIBs in large scale. But it consumes much energy to reach the target temperature (600℃) for long time (at least 5 hours). Besides, gas cleaning device is necessary to treat the toxic gas from the electrolyte salt in high temperature, which also increases the treatment cost [16-18].

Solvent dissolution method and alkaline dissolution method consume little energy for heat, while the organic solvent and alkaline solution will cause secondary pollution, such as toxic waste solution and gas, and make the next treat procedure much more complicated [19].

Manual disassembly could separate materials much smartly by workers. But the treatment efficiency is low and if organics leak from the waste battery, workers will get hurt.

③. Enrichment of the metals in cathode

Enrichment is to collect target metals from the separated materials. Acid leaching and bioleaching are researched most.

For acid leaching, inorganic acid, such as HCl, H_2SO_4 and HNO_3 are usually used to dissolve metals into liquid as metal ions. According to related researches [20-22], HCl and HNO_3 will release toxic gas (Cl_2 and NO_x). So, in real operation, H_2SO_4 is preferred with reducing agent for higher leaching speed rate [10]. The reaction formula is : $2LiCoO_2 + 2H_2SO_4 + 3H_2O_2 \rightarrow Li_2SO_4 + 2CoSO_4 + 4H_2O + O_2 \uparrow$. In some researches [23], leaching rate of Co and Li could reach 98% and 100%. However, inorganic acid will release acid waste solution and corrode the device. Some researchers [24, 25] have tried organic acid, which will not cause secondary pollution, but organic acid are much expensive and it is much difficult to separate metal ions from the leaching solution.

Bioleaching method is still being researched in laboratory. It is very promising with the characteristics of low cost and non-pollution, but it needs long time and the application condition is hard to control [26].

④. Separation and purification of metal ions.

After the three stages above, Co, Li, Ni, Mn exist as ions in leaching solution. Then, further treatment will be applied to separate, purify and recover metals thoroughly.

Solvent extraction utilize organic extracting agents to react with metal ions, forming stable complex and the complex will separate from the leaching solution, which is able to separate different metal ions. Obviously, different extracting agents will be used for different metal ions. Figure 1-7 shows a schematic of metal ions separation by using different extracting agents. Solvent extraction has characteristics of superior selectivity, low energy consumption, easy operation condition, high recover rate and purity. But the use of chemical agents will increase the cost of treatment and cause potential environmental pollution.

Chemical precipitation utilizes precipitating agent to react with metals ions, forming stable precipitate to separate different metal ions. Common precipitating agent include $NaOH$ [28], $(NH_4)_2C_2O_4$, $H_2C_2O_4$ [29], $KMnO_4$ [30], Na_2CO_3, Na_3PO_4 [31] etc. This method could recover most metals with low cost, low demand of device and high economic benefits. But sometimes, different metals ions will precipitate together. So, to raise separation efficiency, selective precipitating agent is being researched now [10].

Electrochemical deposition uses electrochemical reaction to get metals. For example, Myoung et al. [32] used electrochemical method to treat waste solution containing Co and summarized the reaction formula below:

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$

$Co^{3+} + e^- \rightarrow Co^{2+}$

$Co^{2+} + 2OH_{ad}^- / Ti \rightarrow Co(OH)_2 / Ti$

$3Co(OH)_2 / Ti\cdot 2H_2O + 0.5O_2 \rightarrow Co_3O_4 / Ti + 3H_2O$

This method could get metals in high purity. But it consumes much energy for electricity.

Since there are so many methods mentioned above with different advantages and disadvantages, researchers usually combine different methods together to get better treatment results.

However, there is no method which could treat waste LIBs in low energy consumption, with no secondary pollution and high efficiency.

Table 1-4. Comparison on treatment process [1]

Process	Efficiency	Capacity	Consumption	Potential pollution
Discharge	high	large	low	waste water containing metals, thermal pollution
Mechanical separation	medium	large	high	dust, noise, VOCs, thermal pollution
Heat treatment	medium	large	very high	thermal pollution, dust, VOCs
Alkaline solution dissolve	medium	medium	high	waste water containing alkaline and metals, alkaline gas,
Organic solvent dissolve	very high	medium	very high	VOCs
Manual disassembly	low	low	low	waste water containing metals, VOCs
Solvent extraction	high	medium	high	organic and inorganic waste water
Chemical precipitation	medium	large	low	inorganic waste water, waste residue
Electrochemical deposition	high	large	medium	waste water, waste gas

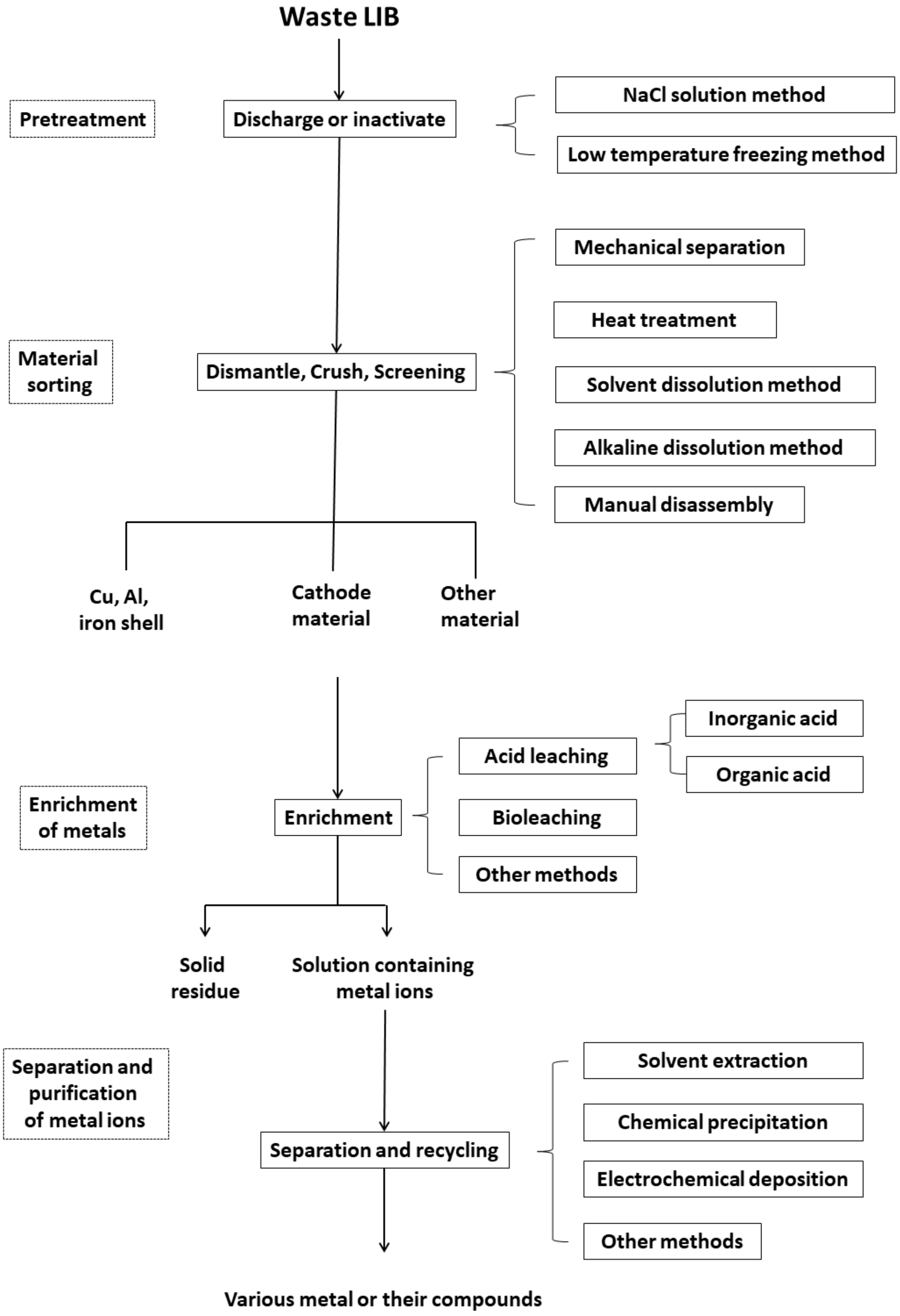


Figure 1-6. Schematic representation of metals recovery from waste lithium-ion batteries [10]

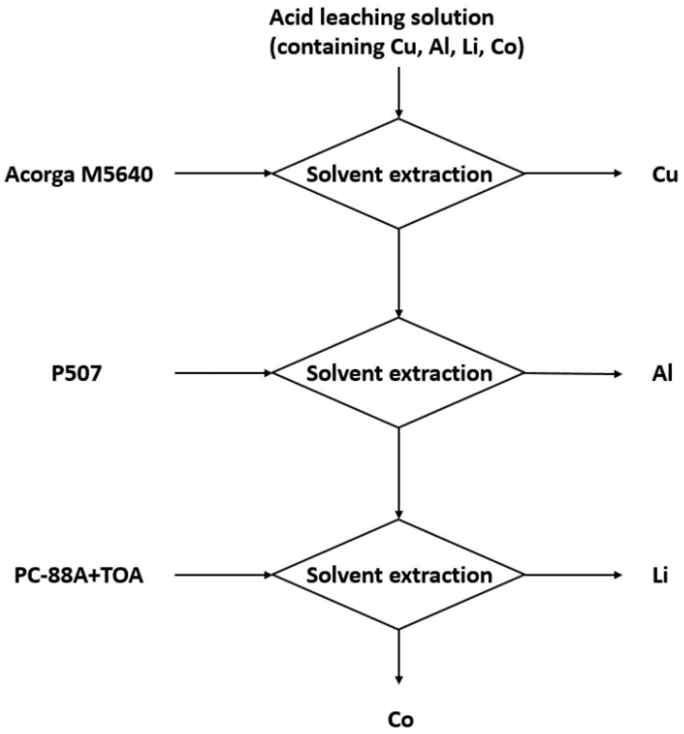


Figure 1-7. Schematic representation of copper, aluminum, lithium and cobalt separation by using different extracting agents [27]

1.4 Hydrothermal technology

1.4.1 Characteristics

Hydrothermal technology is the technology utilizing high-temperature aqueous solutions at high vapor pressures. It could be divided into subcritical water and supercritical water based on the temperature and pressure.

The state of substance will change with the change of temperature and pressure. Figure 1-8 shows the phase diagram of water. The critical point of water is 374℃, 22.1MPa. The water in the condition over the critical point is called supercritical water while the water near the critical point is called subcritical water.

The characteristics of subcritical water and supercritical water are quite different from that of normal water.

Figure 1-9 shows that over critical point of water, the dielectric constant of water decreases obviously. Higher dielectric constant means better dissolution capacity of polar substance (inorganic compounds) while lower dielectric constant means better dissolution capacity of nonpolar substance (organic compounds). Thus, compared with water in room temperature and pressure, sub and supercritical water could dissolve organic compounds easily while inorganic compounds will precipitate.

Figure 1-10 shows ionic product of water increases with the rise of temperature and pressure, which means water dissociates into more H^+ and OH^-. In subcritical water, the concentrations of these two ions are about 30 times larger than that of water in room temperature. These ions are helpful to promote hydrolysis reaction [35].

Thus, subcritical water and supercritical water could be utilized to dissolve organic compounds and accelerate some reaction, such as gasification and oxidation.

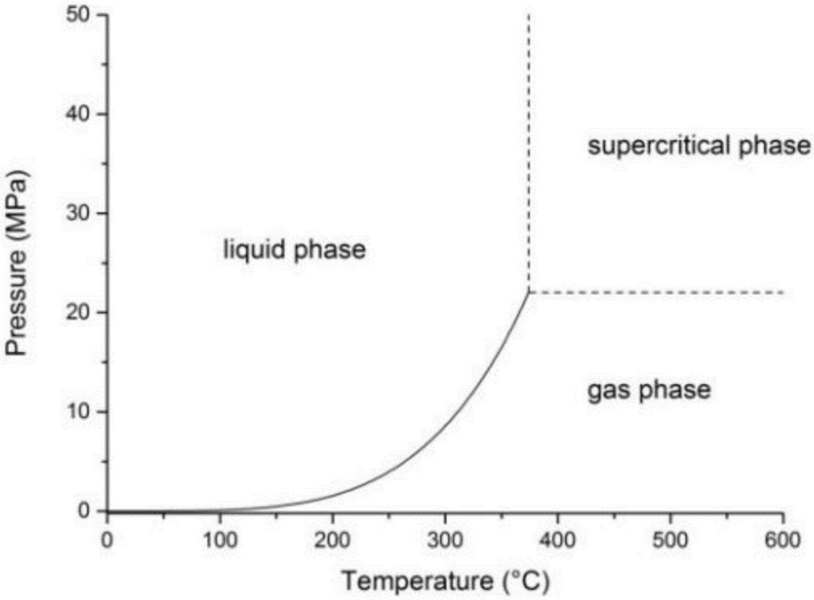


Figure 1-8. Phase diagram of water [33]

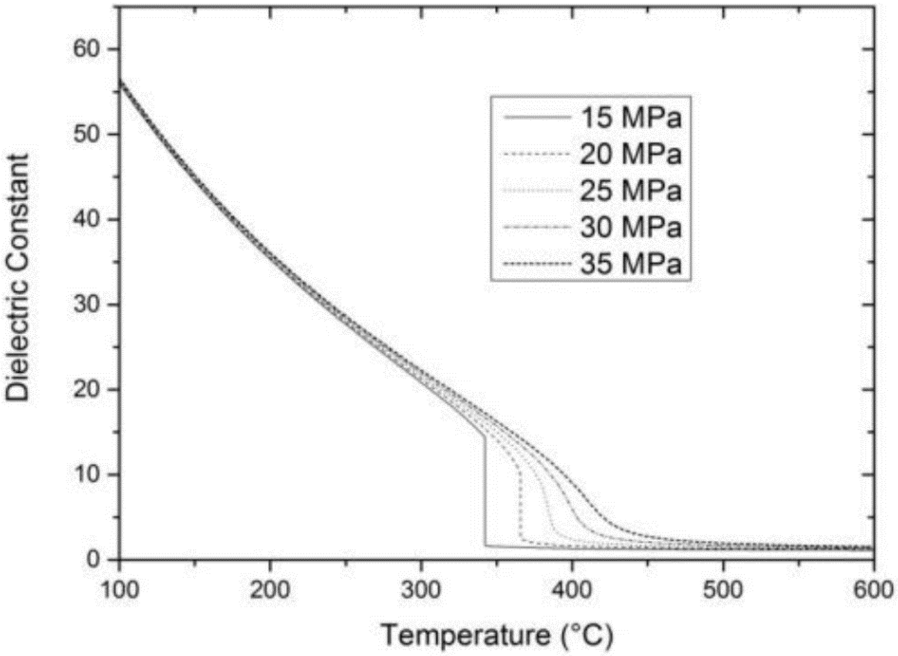


Figure 1-9. Dielectric constant of water at various temperature and pressure [33]

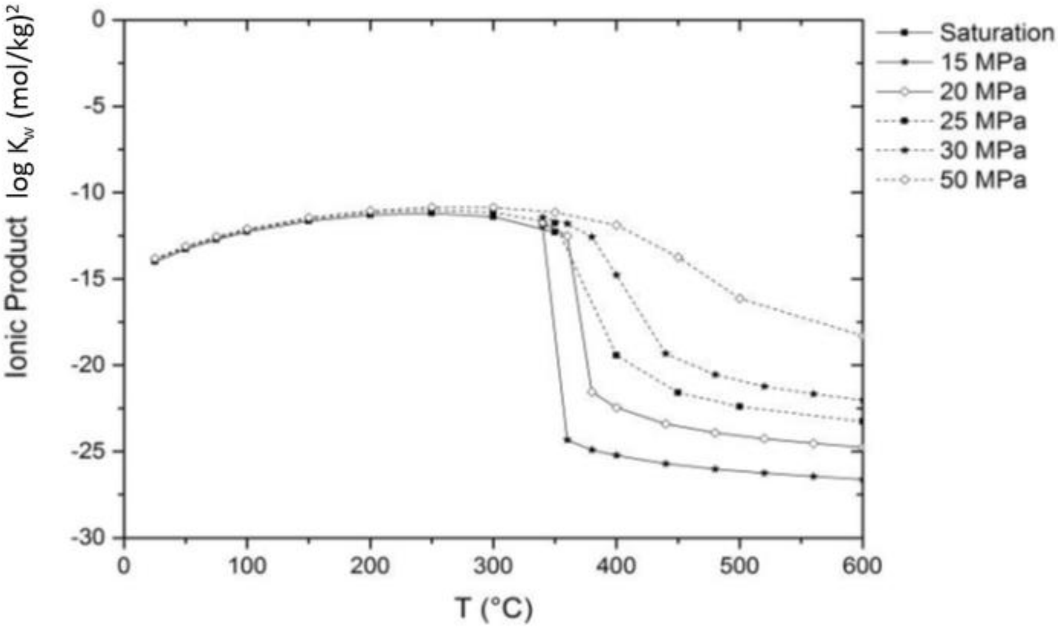


Figure 1-10. Ionic product of water at various temperatures and pressure [34]

1.4.2 Supercritical water gasification

In supercritical water condition, organic compounds could be easily dissolved and decomposed quickly. So, application of hydrothermal technology in organic waste treatment is being researched. Supercritical water gasification is the process in which organics decompose to gas finally. Although the decomposition could happen even without catalyst, generally metal catalyst, carbon-based catalyst or alkali catalyst is applied. In supercritical water, organic compounds containing C, H,O etc will decompose completely and generate fuel gas, such as H_2, CH_4 and CO. Related reaction formulas are shown below [36-39]:

Combustion: $C + O_2 \rightarrow CO_2$

$2H_2 + O_2 \rightarrow 2H_2O$

Partial oxidation: $2C + O_2 \rightarrow 2CO$

Furnace gasification: $C + CO_2 \rightarrow 2CO$

Aqueous gasification: $C + H_2O \rightarrow CO + H_2$

Hydrogenation: $C + 2H_2 \rightarrow CH_4$

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

Methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$

1.4.3 Supercritical water oxidation

Supercritical water oxidation (SCWO) is a kind of oxidation method utilizing supercritical water as reaction field to treat organic waste. There are 3 advantages of SCWO [40]:

① Complete oxidation

In high temperature and pressure, molecules react more fiercely, making it possible to oxidize all organic compounds to CO_2.

② No toxic gas generate

SCWO will not generate NO_x, SO_x or dioxin, which are common pollutants in combustion treatment of waste.

③ Closed reaction system

SCWO should be conducted in a closed reactor to provide high pressure. The closed reaction system could prevent the leakage of any toxic product during the reaction.

With the characteristics mentioned in 1.4.1, SCWO could dissolve the organic compounds which are hard to dissolve by normal water or solvent. Then, these organic compounds could be oxidized quickly and completely by SCWO. In some cases, with enough oxidant (such as H_2O_2 or O_2), organic compounds could be oxidized 100% in only one minute [40].

Common SCWO reaction could be shown as the formula below [37]:

$$[C, H, O] + nO_2 \rightarrow xCO_2 + yH_2O$$

1.5 Related researches

1.5.1 About supercritical water

There are many researches utilizing supercritical water to treat hardly decomposable waste safely and quickly.

Xiu [41] pretreated waste printed circuit boards by SCWO to remove organic compounds in printed circuit boards and then recover metals. The optimum SCWO treatment conditions were 60 min, 713 K, 30 MPa, with electrokinetic treatment time of 11 h and constant current density of 20 mA/cm^2. The recovery rate of Cu and Pb under the best treatment conditions were around 84.2% and 89.4%. In the best treatment with only electrokinetic, 74% of total Cu was recovered as solid product on the cathode with a purity of 97.6%. At the same time, Pb was recovered in liquid phase near either anode (23.1%) or cathode (66.3%) but almost no Pb was found existing as solid substance on the electrodes. It is believed that this SCWO method with electrokinetic is effective and realizable for Cu and Pb recovery from waste electric and electronic waste.

Endo [42] utilized supercritical gasification to treat fish waste. The result shows that Ni catalyst in the condition of 500°C, 25 MPa could help promote gasification reaction, forming organic acid, such as acetic acid and propionic acid.

Hirai [35] utilized SCWO to treat waste liquid containing Os. It was found that with the oxidant (H_2O_2), Os could be oxidized quickly to OsO_4, proving it is effective to treat Os waste liquid by SCWO while Os is quite hard to treat by traditional methods.

Matsunaga [43] utilized high pressure superheated steam and supercritical water oxidation to treat cow manure. In the optimum condition (600°C, 15 MPa, 15min, oxygen ratio=1.2), the cow manure was completely oxidized without generating ammonia or NO_x. At the same time, it was also proved that to avoid generating N_2O during the treatment, 650°C, 12.5 MPa, 13 min and oxygen ratio=1.2 are necessary.

Chen [44] treated copper waste water and gasified biomass waste CDR (Cornstalk Depolymerization Residual) at the same time with the use of supercritical water. Under the temperature of 923 K and pressure of 22 MPa, with 2.5mmol Cu^{2+} in solution, the CO_2 fraction in the gas phase could reach about 99.2%. The carbon gasification efficiency could even be over 99.9%. Meanwhile, Cu^{2+} were transferred into metallic copper and Cu_2O. And almost all of the Cu was recovered.

Although hydrothermal methods are expected to treat the waste safely, for real application, there are still some topics need to be researched.

Firstly, supercritical water could treat organic waste quite efficiently compared with traditional combustion method, but it is not able to treat inorganic waste so well. Then, for huge amount of waste water in which concentration of hazardous substance is high, supercritical water technology performs weakly as well. So, several methods are utilized together to treat the hazardous waste [39].

1.5.2 About catalyst in hydrothermal method

To reduce the high-temperature and high-pressure condition, researches using metal catalyst, carbon-based catalyst and alkali catalyst are being conducted [36]. With the function of catalyst, if lower temperature could be enough to get the same results as that in higher temperature, it will make hydrothermal technology much safer and save much energy.

Selhan Karagöz [45] conducted catalytic hydrothermal treatment of wood biomass at 553 K for 15 min with the use of alkaline solutions (NaOH, Na_2CO_3, KOH and K_2CO_3). Oil products were taken out from both liquid and solid phases by different solvents. Based on the conversion and analysis results of the liquid products, the catalytic activity of the alkaline solutions can be known as follows: K_2CO_3 > KOH > Na_2CO_3 > NaOH. In hydrothermal reaction, the yield of solid residue was nearly 42% while it was only 4.0% in the case of utilizing K_2CO_3. The main product by catalytic hydrothermal treatment of biomass was phenolic compounds. In hydrothermal reaction, furan derivatives were found, which was not be found in catalytic runs. The volatility distribution of hydrocarbons was analyzed by using C-NP gram and the result indicated that most substance of hydrocarbons for all conditions were organic carbon-containing substance with carbon number of eleven (n-C11).

Shirin Falamarzian [46] investigated the application of subcritical and supercritical water technology for decomposition of pharmaceutical compounds (carbamazepine, metoprolol and sulfamethaxazole). The experiments were conducted by a kind of batch-type reactor as reaction field. The experiment conditions ranges from 200 to 500 ℃ with reaction time of 5 to 50 minutes. The experiment and analysis results indicated that carbamazepine, metoprolol and sulfamethaxazole could be decomposed by 98.84%, 90.27% and 99.99% under the reaction time of 20 min with temperature of 300℃, 350℃ and 400℃. Compared with the conventional methods of pharmaceutical waste treatment, the current method provides a higher decomposition efficiency (over 90%) with shorter durations. NaOH and $CuSO_4 \cdot 5H_2O$ were also utilized as catalyst in the experiments with temperature range of 200 to 450℃. By analyzing the effects of these catalysts, $CuSO_4 \cdot 5H_2O$ lead to a higher treatment efficiency even in the lower temperature. Based on the proposed mechanism, the products of decomposition were judged as the compounds which will not increase environmental burden. The results indicated that this treatment method can be used as a green treatment for efficient removal of pharmaceutical compounds from wastewater.

1.5.3 About treatment of fluorine-containing waste

Fluorine is the only hazardous substance in waste LIB which might cause security problem. So, it is meaningful to research about the behavior of fluorine during the treatment process.

A. Toyoda and T. Taira [47] found a new method to treat fluorine-containing wastewater for reducing the amount of sludge and cost of running. The method utilized $Al(OH)_3$ not only as a precipitant to generate CaF_2 deposit (solid) from the F^- in the wastewater (liquid), but also as an effective adsorbent to assemble fluorine. This new method was able to treat the wastewater with high fluorine concentration effectively and simply to get treated water with extraordinarily low concentration of fluorine. A real treatment system was built based on this method by changing and replacing some parts of an existing wastewater treatment system. According to the real treatment results, this new treatment system was proved to effectively reduce the amount of total generated sludge. In addition, it could cut about 90% of the running costs compared with the treatment system used before.

Kurosaki [48] used AlO_2 as treatment agent to absorb fluorine from fluorine-containing waste and convert the fluorine into AlF_3. By this method, the fluorine concentration in waste could be reduced to a low concentration. After that, another treatment agent, $Ca(OH)_2$, was used to convert AlF_3 into CaF_2, a common final solid product usually observed in fluorine treatment technology. By this method, fluorine concentration in the waste could be reduced to about 25%, indicating effective fluorine treatment capacity. In addition, the aluminum treatment agent could be reused, reducing the cost of the treatment and avoiding secondary pollution from chemical agent emissions.

Tamura [49] used combustion method to treat waste LIB. During the treatment, fluorine became HF gas and reacted with $CaCO_3$, transferring into CaF_2 to reduce the emission of fluorine. By this method, concentration of generated HF could be reduced from 210 mg/ Nm^3 to 0.9 mg/ Nm^3.

1.6 Research purpose

This research is to make out whether hydrothermal method is suitable to treat waste LIB in mechanism. In this research, batch type reactor is used to treat waste Li-ion battery by subcritical water and supercritical water. With the characteristics of hydrothermal method, organic compounds in LIB might be oxidized completely, which could be separated from metal materials, making metal recovery easier to conduct.

The treatment result is judged by 3 issues:

① How much organic compounds could be oxidized and removed from metal materials?

② Will fluorine, the only hazardous element in waste LIBs, make security risk?

③ Will metals become much easier to be recovered from waste LIBs by acid leaching?

The expected result is that all of the organic compounds are oxidized to CO_2 and H_2O in gas phase. The hazardous fluorine keeps in liquid phase as ions. In the solid phase, there is only graphite and metals, which could be reused as metal ore in factory or recovered by other methods introduced in 1.3.

In this situation, hydrothermal method might be able to replace the effect of material sorting and enrichment of metals in schematic representation of metals recovery from waste lithium-ion batteries (Figure 1-6). Compared with the methods mentioned in Figure 1-6, hydrothermal method has advantages of less energy cost (lower temperature than heat method), no secondary pollution from added chemical agents and short reaction time consumption.

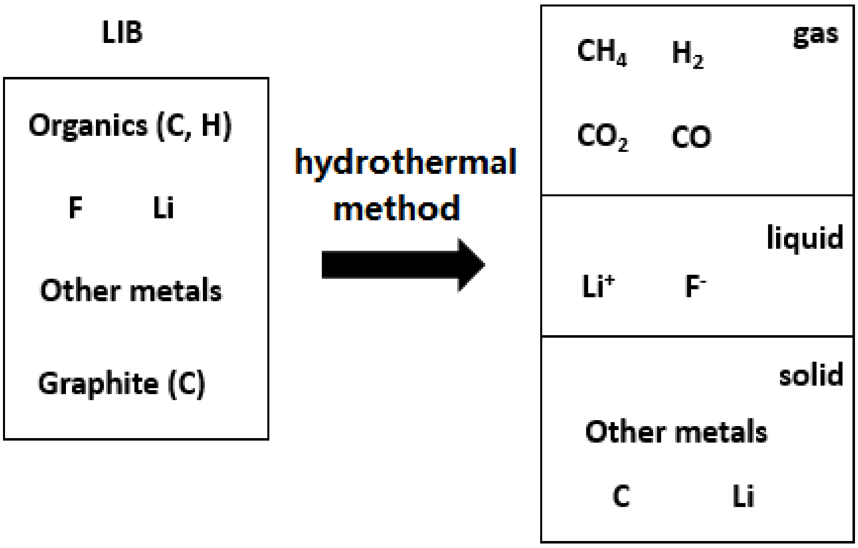


Figure 1-11. Expected treat results by hydrothermal method

1.7 Structure of the thesis

The thesis is composed of six chapters.

In chapter 1, waste Li-ion batteries, significance of waste LIB recycle technology, current treat methods of waste LIB, hydrothermal methods and research purpose are introduced.

In chapter 2, research methodology, device, instruments and safety issues are introduced.

In chapter 3, behavior of organic compounds are reported and discussed.

In chapter 4, behavior of fluorine are reported and discussed.

In chapter 5, behavior of metals are reported and discussed.

In chapter 6, research conclusions and recommendations are written.

In the end of the thesis, there is reference.

2. Methodology

2.1 Preparation of Li-ion battery

2.1.1 Choice of experiment battery

In this research, small type Li-ion battery is chosen as experiment battery because the larger type battery (for electric vehicles) seems easier to be treated in another way [50]. While for small type battery, there are button type and cylinder type. To conduct experiment, cylinder type is easier to pretreat.

However, the element concentration of waste cylinder Li-ion battery is hard to be proved the same in different single battery. So, in this research, to make sure all of the single batteries contain the same amount of every element, completely new Li-ion batteries are chosen to be used.

Of course, the element concentration of new battery is different from the waste battery. The component difference between new and waste battery is shown in Figure 2-1 and Figure 2-2.

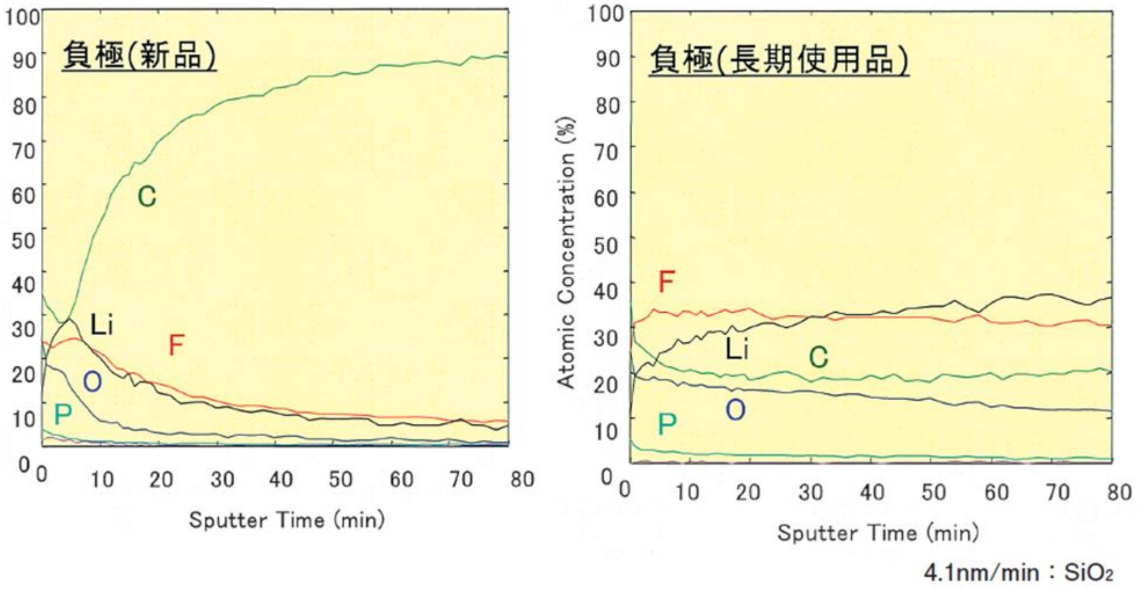


Figure 2-1. Element analysis result of negative electrode by XRD [51]

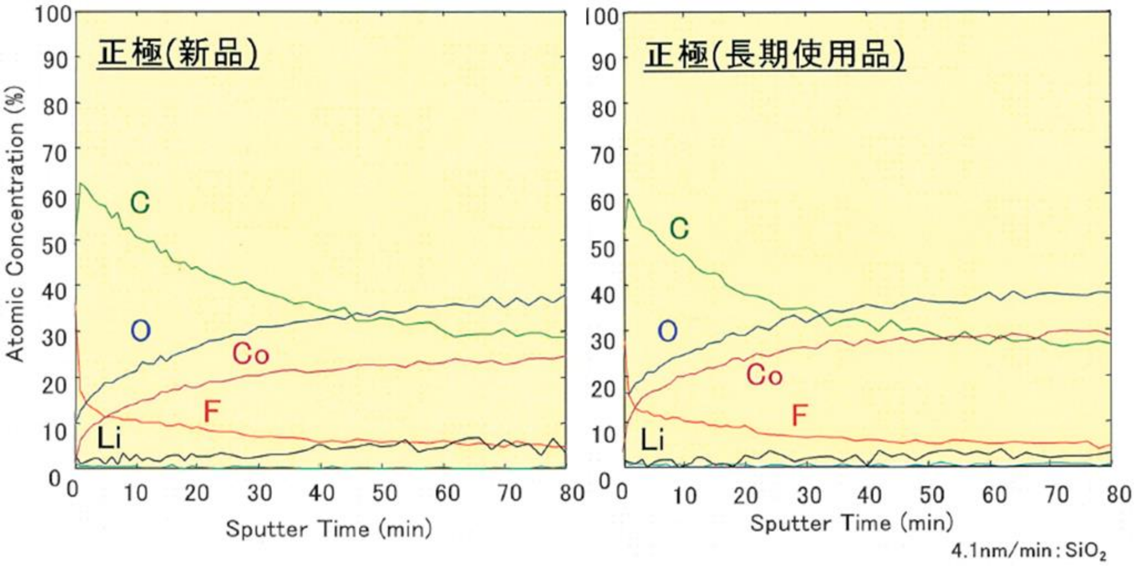


Figure 2-2. Element analysis result of positive electrode by XRD [51]

Figure 2-1 and Figure 2-2 indicate that the carbon concentration in negative electrode of waste LIB is much lower than that of new LIB. In addition, the concentrations of other elements are quite different between positive and negative electrode as well. Thus, the LIB should be pretreated into evenly distributed shape to make sure the initial element concentration is the same for different single experiments.

2.1.2 Dismantle method of Li-ion battery pack

In this research, a kind of laptop computer Li-ion battery is used for experiment. It is produced by Janri Ltd. with model number of HSTNN-IB52 HSTNN-IB89 HSTNN-XB89 as shown in Figure 2-3.

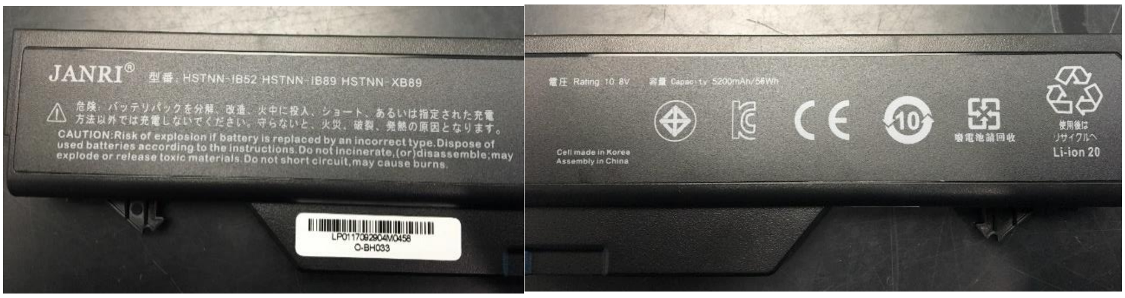
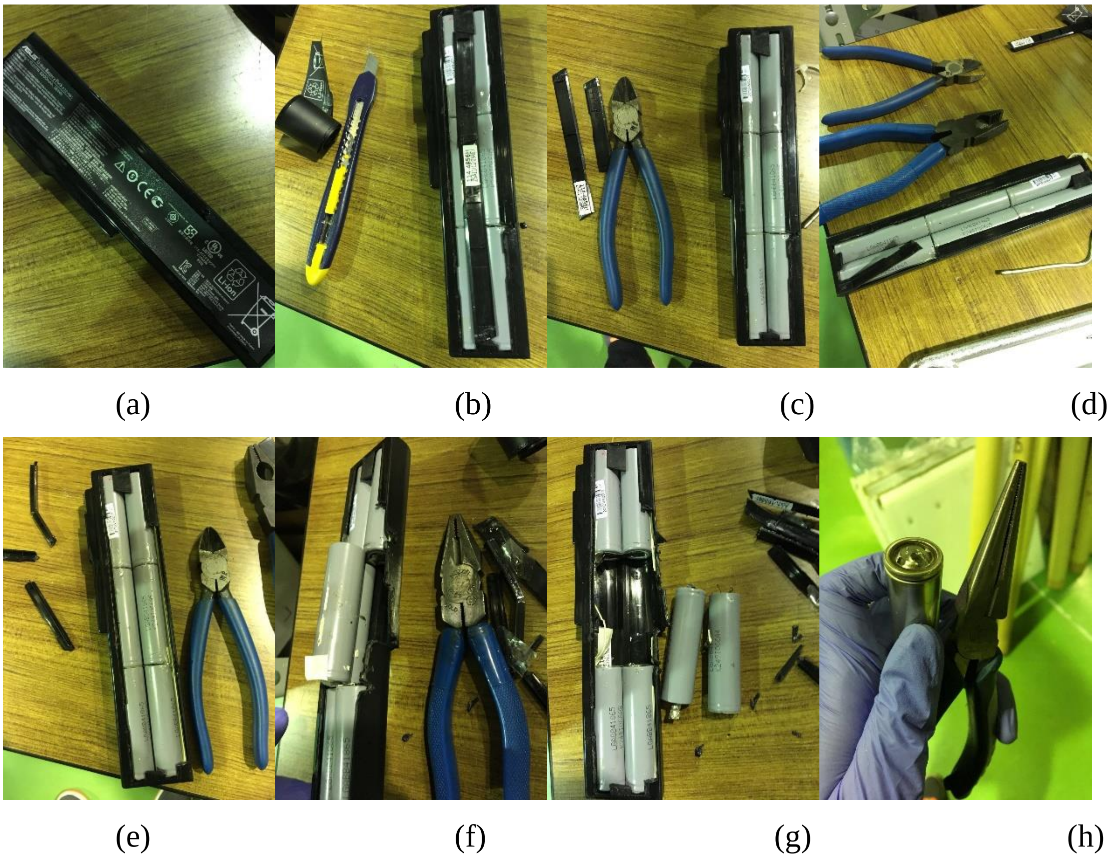


Figure 2-3. The Li-ion battery pack used in the research



(a) (b) (c) (d)

(e) (f) (g) (h)

Figure 2-4. Dismantle of the whole battery pack

The dismantle method of the battery pack is shown in Figure 2-4.

In Figure 2-4,

(a) → (b): Remove the label by cutter

(c) → (f): Cut the black plastic part by diagonal plier and remove it by sharp nose plier. During this process, the metal part of the plier may cause short circuit if it touches the two ends of battery

(g) Take out the single cylinder batteries

(h) Peel the plastic package of a single cylinder Li-ion battery

By the procedure mentioned above, a single Li-ion battery is prepared.

2.1.3 Discharge method of a single LIB

If there is residual electricity in the battery, it is quite dangerous to dismantle the battery because fire or explosion may happen, which is mainly caused by the sudden temperature rise inside the battery, while the temperature rise is due to the exothermic reaction of organic solvent with Li salt[2,52]. The reaction will happen when the temperature is about 230-280°C($LiPF_6$) or 290-310°C($LiClO_4$)[53].

Thus, to dismantle a single LIB, discharge is essential. Discharge could consume the residual electricity in the battery. Then, the short circuit during dismantle will not release too much heat to cause explosion, and it will be safe. Usually, the voltage should be about 2 to

2.5V through discharge [54].

In related researches, waste LIB could be put into salt solution (NaOH, NaCl, K_2CO_3, Na_2SO_4) to discharge [15,54]. But it will cause some problems, including electrolytes leak, gas pollution and metal corrosion, which will make negative effect on the element analysis of the battery. Low temperature discharge [55] method and conductor-metal powder short circuit method [16] have also been researched. But the discharge device is not available.

In this research, every single battery is discharged by light bulb and resistance, as is shown in Figure 2-5. The resistance is composed of several 1Ω-resistances.

The discharge efficiency could be calculated by the formula $P = \frac{U^2}{\mathrm{R}}$. U is the voltage of the battery and R is the resistance of the whole circuit. The resistance has to be changed as the voltage decrease to get higher discharge efficiency. The related discharge data is showen in Table 2-1.

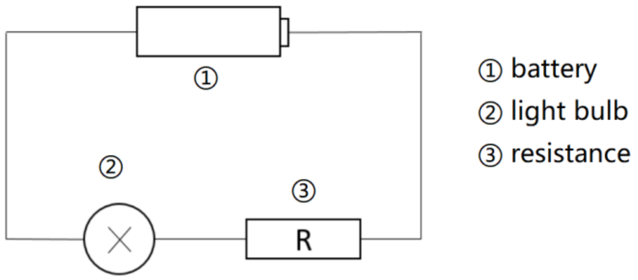


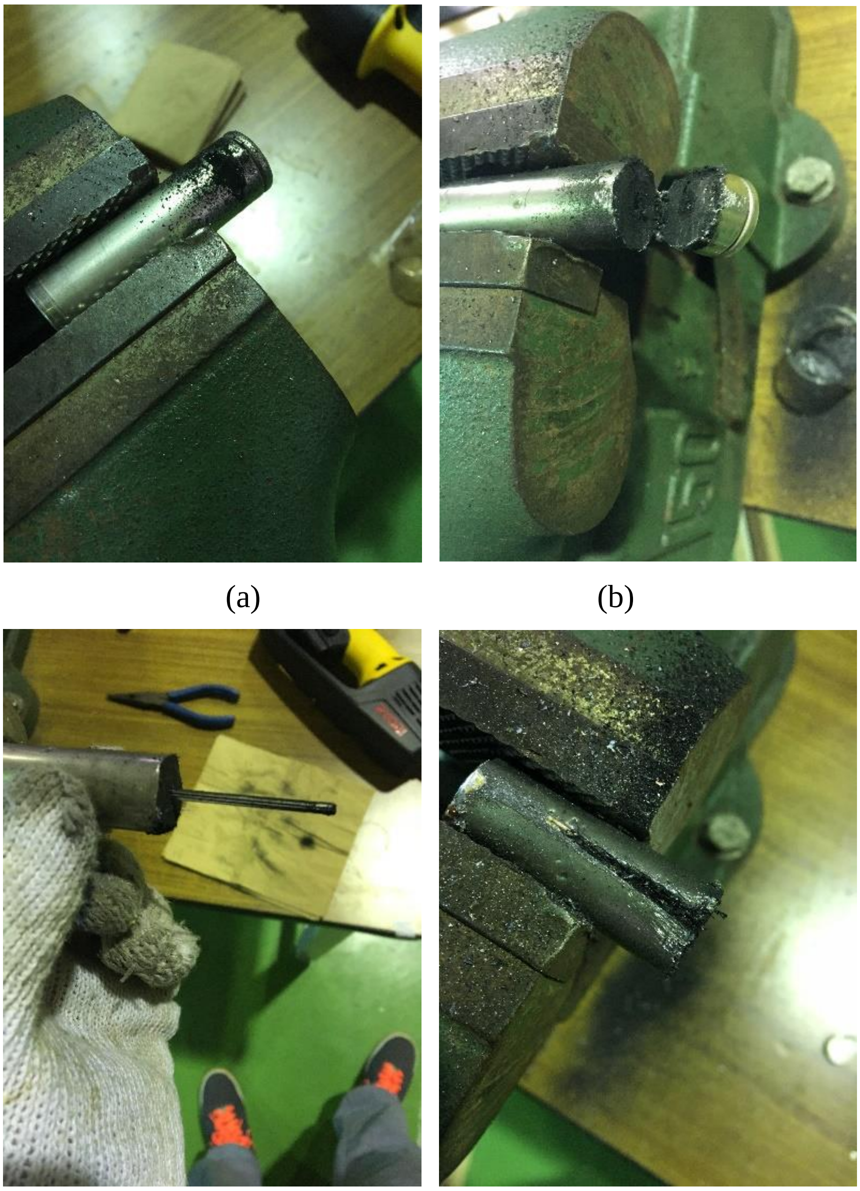
Figure 2-5. Discharge schematic

Table 2-1. Discharge data

Initial voltage of battery	Resistance of light bulb	The extra resistance	Electric current	Discharge time
3.7 V	5Ω	5Ω	0.37 A	60min
3.5	5Ω	3Ω	0.4375 A	30min
3 V	5Ω	1Ω	0.5 A	40min
2.5 V	5Ω	0	0.5 A	30min
1.8 V	0	4Ω	0.45 A	90min
0.6-1 V	/	/	/	/

2.1.4 Dismantle method of single battery

After the discharge, the single battery will be dismantled into evenly distributed shape for experiment.



(a) (b)

(c) (d)

Fig 2-6. Dismantle of a single battery

(a)-(b): Cut down both sides of the battery by electric saw;

(c): Take out the thin iron stick inside the battery;

(d): Make a longer cut to separate the iron shell and the substance inside.

Then, crush the substance inside battery into two shapes (powder and ribbon) by food mixer as shown in Figure 2-7.

Separate and keep the powder and ribbon in two plastic bags as shown in Figure 2-8.

Store the sample with desiccant in refrigerator as shown in Figure 2-9 for experiment.

Figure 2-7. Crushed LIB

Figure 2-8. Ribbon (left) and powder (right) LIB sample

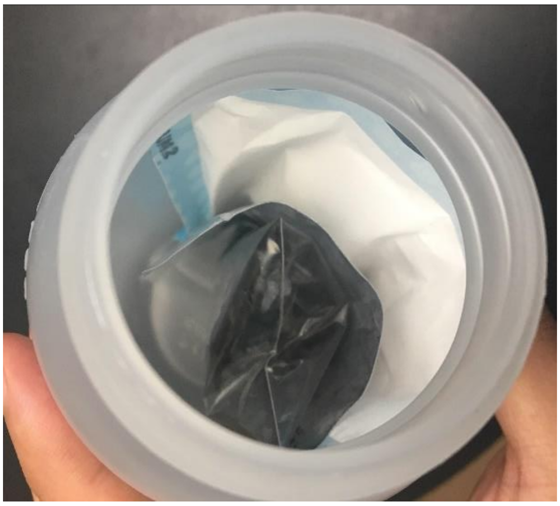


Figure 2-9. Stored LIB sample with desiccant

2.2 Experiment device

2.2.1 Batch type reactor

In this research, a kind of batch type reactor is used for experiment to research about the treatment result by hydrothermal method. The schematic diagram of the reactor is shown in Figure 2-10.

The reactor is made of SUS316. The reaction part is a 10-cm tube with diameter of 3/4 inch and thickness of 2.11mm. In one side of the tube, a 3/4-inch cap is attached. In the other side, a 3/4-inch to 1/2-inch reducing union is connected with a 1/2-inch to 1/8-inch reducer. Then, it is connected to a 1/8-inch T-piece with a 20-cm 1/8-inch tube. The left two sides of the T-piece are connected to a pressure transducer (AP-V80 type produced by KEYENCE CORPORATION) and a sampling valve, which is used for collecting gas sample after reaction.

The total volume of the reactor is 23.303mL. The maximum use pressure of the reactor is 28.9 MPa below 93℃ and 22.83 MPa in 426℃.

Besides, to monitor the temperature, SD16A21-05 indicator (produced by SHIMADEN CO. LTD.) is used.

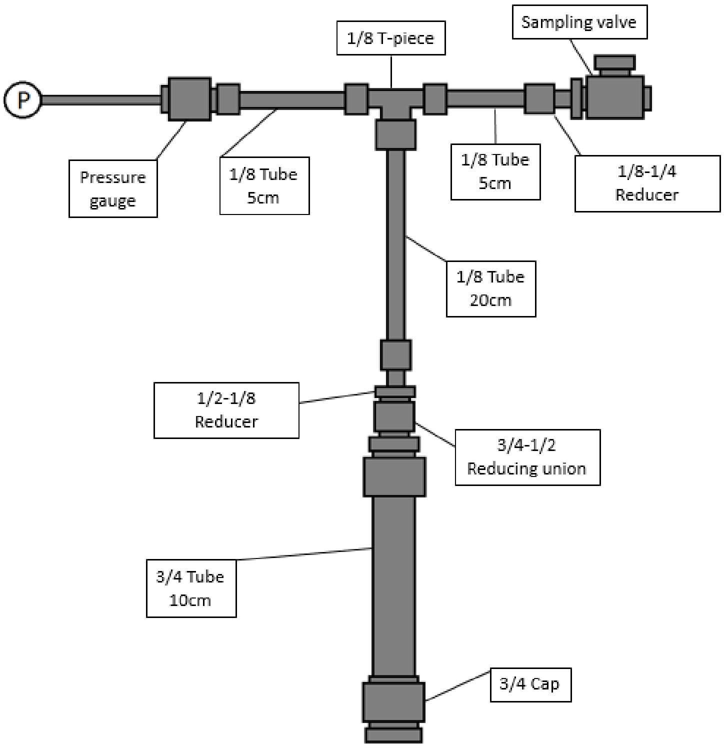


Figure 2-10. The batch type reactor

2.2.2 Salt bath device

In the hydrothermal reaction of this research, a salt bath device is used to heat up the reactor.

In the salt bath, there are mixed KNO_3, $NaNO_2$, $NaNO_3$, of which the mass ratio is 6:5:1. The temperature of salt bath is controlled by thermocouple and T-35 type sheath thermocouple (produced by SAKAGUCHI E.H VOC CORP.). In addition, an air pump is also used to blow air into the melted salt to ensure the temperature is distributed evenly in the salt bath. The salt bath device is shown in Figure 2-11.

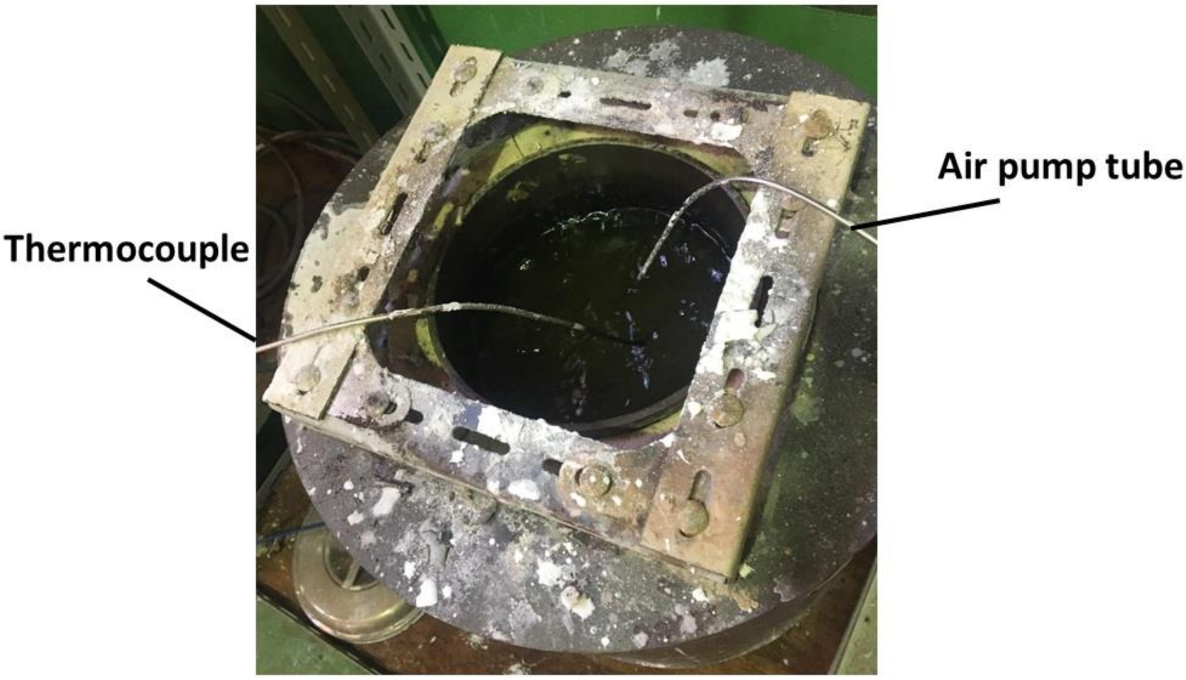


Figure 2-11. Salt bath device

Of course, it will take some time to heat up the sample inside reactor until it reaches set temperature. So, it is essential to know the heating time of the salt bath. Thus, a series of blank experiments are conducted to find it out by monitoring the change of pressure inside the reactor. The result is shown in Figure 2-12.

The result shows that after about 4min, the temperature of the water inside the reactor could reach a relatively closer temperature to the set temperature.

So, for experiment with reaction time of 30 minutes, the reactor should be put into the salt bath for 34 minutes.

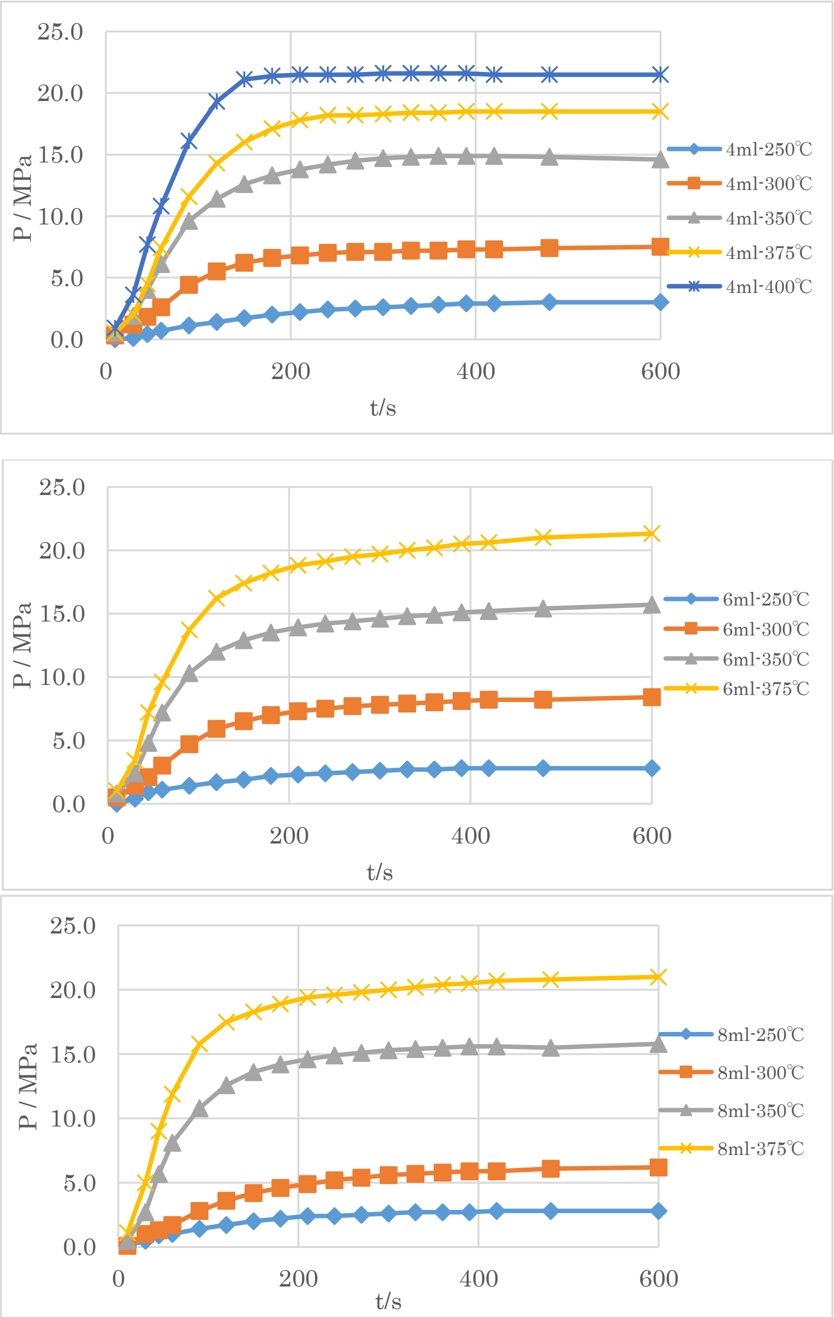


Figure 2-12. Pressure curve inside the reactor since the salt bath start heating up with 4mL, 6mL, 8mL H_2O only in the reactor.

2.3 Initial element analysis of LIB

The first dismantled and crushed LIB sample has been separated into ribbon (4.4101g) and powder (23.3359g). So, in all of the experiment, added LIB sample will be made in this ratio (0.2518g powder and 0.0482g ribbon to compose 0.3g sample). Of course, initial element analysis will also be prepared by this ratio.

2.3.1 Metals

Analysis procedure of initial metals in LIB is shown as follows:

① Weigh 0.2518g powder and 0.0482g ribbon LIB sample into a Teflon beaker
② Add 5 mL HNO_3 and 3 mL H_2SO_4
③ Put the Teflon beaker on a magnetic stirrer (without rotation)
④ Set the temperature of the stirrer to 190°C
⑤ Heat for 5 hours
⑥ Cool down the Teflon beaker
⑦ Filter the liquid sample and collect it in a polypropylene volumetric flask
⑧ Dilute it and analyze metals concentration by ICP-MS

2.3.2 Fluorine

Total fluorine in waste LIB is analyzed by combustion-ion chromatography method in the Microanalytical Laboratory of the University of Tokyo[56].

2.3.3 Carbon and hydrogen

Total carbon and hydrogen concentration is analyzed by CHN coder in the Microanalytical Laboratory of the University of Tokyo.

Organic carbon concentration is also necessary to assess the treatment result. However, organic carbon could not be analyzed by CHN coder.

Organic carbon exists as separator (solid), adhesive (solid) and electrolyte (liquid) in LIB. After crushing LIB into powder and ribbon, separator almost exists in ribbon part. Electrolyte is easy to volatile. As for adhesive, PolyVinylidene DiFluoride (PVDF, $-(C_2H_2F_2)n-$) is usually used, in which organic carbon concentration is hard to analyze because of its low thermal conductivity, high chemical corrosion resistance and heat resistance.

Since fluorine exists as electrolyte ($LiPF_6$) and adhesive (PVDF) in LIB, in the research, organic carbon is analyzed by calculating fluorine concentration.

Procedure:

① Weigh a clean dry crucible (m_1) and crucible with LIB powder sample (m_2);
② Add some HNO_3 into crucible and heat it to 280°C in muffle furnace for 3h (to volatile the F in electrolyte while PVDF still remains in solid);
③ Put the crucible into desiccator for cooling down for one night;

④ Weigh the crucible (m_3);

⑤ Collect and send the sample to the Microanalytical Laboratory for C and F analysis by the method mentioned above;

⑥ Get volatile C concentration and F concentration to calculate.

The organic carbon concentration could be calculated by the formula below:

$$m_v = (m_2-m_1) * C_{c1} - (m_3-m_1) * C_{c2}$$

$$m_p = (m_3-m_1) * C_{f2} * 12 / 19$$

$$m_{oc} = m_v + m_p + m_r$$

m_v: organic carbon in volatile organic compounds

m_1: weight of clean dry crucible

m_2: weight of powder LIB sample and crucible before muffle furnac

m_3: weight of powder LIB sample and crucible after muffle furnace

m_p: organic carbon in PVDF

m_{oc}: total organic carbon in LIB sample

m_r: carbon in ribbon sample analyzed by CHN coder (all of which is seen as organic carbon)

C_{c1}: carbon concentration in powder sample before muffle furnace

C_{c2}: carbon concentration in powder sample after muffle furnace

C_{f1}: fluorine concentration in powder sample before muffle furnace

C_{f2}: fluorine concentration in powder sample after muffle furnace

Through the analysis method mentioned above, the initial element analysis result is shown in Table 2-2.

Table 2-2. Initial element analysis result

Element	In total (%)	
	In powder (%)	In ribbon (%)
F	2.71	
	2.12	5.79
Organic carbon	13.27	
	3.04	66.67
Inorganic carbon	25.16	
	29.98	0
H	2.30	
Li	4.32	
Mn	8.04	
Co	3.90	
Ni	4.90	
Cu	2.97	

2.4 Experiment method

2.4.1 Experimental condition

Table 2-3 shows the experimental condition of hydrothermal reaction to treat waste LIB sample.

In 0.3g LIB sample (0.2518g powder and 0.0482g ribbon), there is 39.8mg organic carbon. To oxidize them into CO_2, 3.317mmol O_2 is necessary. For the experiments, diluted H_2O_2 was prepared, in which 6 mL solution could provide 6.633mmol O_2, twice as the demand O_2 to oxidize 100% of the organic carbon in 0.3g LIB sample. So, the 6mL H_2O_2 means 200% H_2O_2 concentration mentioned in Table 2-3. While for experiments with 100% H_2O_2, 3mL of the diluted H_2O_2 solution and 3mL H_2O were added.

However, the real concentration of H_2O_2 is different from the calculated concentration because the initial H_2O_2 concentration changed a little from the concentration in label. After analysis by UV-Vis [57], it was found that 6mL of the diluted solution could provide 232.7% demand O_2.

So, although the marks in Table 2-3 are 100% and 200% H_2O_2, the real concentrations are 116.3% and 232.7%.

Table 2-3. Experimental condition

No.	T/℃	Amount of added H_2O & H_2O_2 /mL	H_2O_2 concentration / %demand H_2O_2	Reaction time/min	Target pressure/MPa
1	250	4	0	30	3.97
2	300				8.59
3	350				16.53
4	375				21.70
5	400				25.25
6	250	6			3.97
7	300				8.59
8	350				16.53
9	375				22.32
10	400				27.96
11	250	8			3.97
12	300				8.59
13	350				16.53
14	375				22.37
15	400				29.68
16	250	6	100%		4.60
17	300				9.28
18	350				17.28
19	375				23.10

20	400				28.77
21	250		200%		5.23
22	300				9.97
23	350				18.03
24	375				23.88
25	400				29.59
26	250		100%	60	4.60
27	300				9.28
28	350				17.28
29	375				23.10
30	400				28.77
31	250			90	4.60
32	300				9.28
33	350				17.28
34	375				23.10
35	400				28.77

2.4.2 Experimental procedure

① Heat up the salt bath to the set temperature and turn on the air pump
② Weigh 0.2518g powder LIB sample and 0.0482g ribbon LIB sample
③ Add the 0.3 g sample into the 3/4-inch tube of the reactor
④ Close the sampling valve
⑤ Add H_2O and H_2O_2 into the tube
⑥ Tighten the connection part between tube and 3/4-inch to 1/2-inch reducing union
⑦ Put the reactor into the salt bath to start the reaction
⑧ Take out the reactor when reaction finishes
⑨ Cool down the reactor by tap water
⑩ Collect the sample

2.4.3 Collecting method of sample

2.4.3.1 Collection of gas sample

After reaction and cooling down, gas sample is collected and analyzed first. Thus, a gas sampling system is used as shown in Figure 2-13.

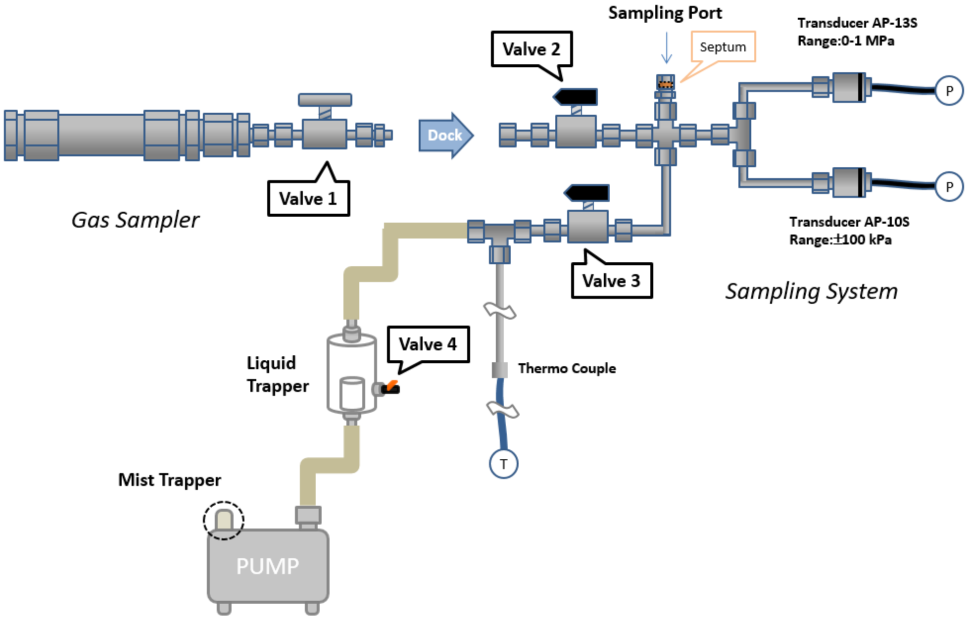


Figure 2-13. Gas sampling system

Collecting procedure:

① Dock the reactor (valve 1) to the gas sampling system (valve2 side).
② Keep valve1 closed.
③ Open valve 2 and 3. Close valve 4.
④ Turn on the vacuum pump.
⑤ Wait until the whole system is evacuated.
⑥ Shut valve 3.
⑦ Turn off the vacuum pump.
⑧ Open valve 4 immediately.
⑨ Open valve 1 and wait until the gas flows into the sampling system.

Then, gas sample will be analyzed by the procedure below:

① Take 0.5mL gas by syringe
② Analyze that part of gas sample by GC-TCD
③ Get analysis result and calculate

The amount of total gas in the reactor could be calculated by the formula below：

$$n=\frac{(V_1+V_c+V_2-V_w)*(P_2+P_a)-V_2*(P_1+P_a)}{(273+T)*R}$$

n: amount of total gas in the reactor (mol)
V_1: volume of reactor (23.303 mL)
V_2: volume of sampling system (6.5 mL)

Vc: volume changed when valve closed and opened (0.65 mL)
V_w: volume of water input
P_1: pressure of sampling system before opening valve 1 (Pa)
P_2: pressure of sampling system after opening valve 1 (Pa)
P_a: atmosphere pressure (Pa)
T: room temperature (℃)
R: gas constant (8.314 $kg \cdot m^2/s^2 \cdot K \cdot mol$)

In some conditions, P_1 will be over the measuring range of the pressure gauge (100kPa) because too much O_2 generated from the added H_2O_2. In this situation, an extra gas cylinder is connected between valve 1 and valve 2 in Figure 2-13 to expand the volume, reducing P_1 below 100kPa. If the extra gas cylinder is used, the volume of sampling system (V_2) will change. So, it is necessary to measure V_2 after connecting gas cylinder.

For the 0.5mL gas sample taken by the syringe, it is essential to calculate that amount because it is not in atmosphere pressure. The real amount of that part could be calculated by the formula below:

$$n_s = \frac{(P_3 - P_2) * (V_1 + V_2 + V_c - V_w)}{(273 + T) * R}$$

n_s: amount of gas taken by syringe (mol)
P_3: pressure of sampling system after taking sample (Pa)

2.4.3.2 Collection of liquid sample

Procedure:

① Filter the sample in the reactor after the reaction by filter paper to separate the solid phase and liquid phase.
② Dilute the liquid phase into a volumetric flask
③ Filter the liquid sample by hydrophilicity syringe filter (0.45μm)
④ Store the liquid sample for analysis later

2.4.3.3 Collection of solid sample

Procedure:

① Dry the solid sample and filter paper in 2.4.3.2①
② Crush the solid sample into powder by mortar
③ Store the solid sample for XRD analysis later

2.5 Analysis method

2.5.1 CHN coder

Initial LIB sample is sent to the Microanalytical Laboratory of University of Tokyo for analysis. The analytical instrument is CHN coder (MT-6) produced by YANAKO Co Ltd.

2.5.2 GC-TCD

Gas Chromatography –Thermal Conductivity Detector (GC-TCD) is used to analyze H_2, O_2, N_2, CO, CH_4 and CO_2 in gas sample. The instrument is GC-2014 Gas Chromatography produced by SHIMADZU Corporation. The analysis condition is shown in Table 2-4 and Table 2-5.

To make the calibration line, standard gas produced by TOKYO KOATSU Co., Ltd is used. Concentration of standard gas is shown in Table 2-6. In addition, air (78% N_2 and 21% O_2) is also used.

During the analysis, the instability of base line sometimes happens. In this situation, the temperature should be set about 20°C higher than the highest temperature in analysis program to bake the column for several hours or even one night. If the problem could not be solved, the glass wool inside the injection port should be replaced.

Table 2-4. Instrument data of GC-TCD

Column type	PORAPAQ N
Carrier gas	Ar
Carrier gas flow rate	30 mL / min
Temperature of detector	170 ℃
Temperature of inject	170 ℃

Table 2-5. Temperature program of column during analysis

No.	Initial Temperature	Final temperature	Rise rate	Time
1	50 ℃	50 ℃	0 ℃/min	7 min
2	50 ℃	120 ℃	10 ℃/min	7 min
3	120 ℃	120 ℃	0 ℃/min	7 min

Table 2-6. Standard gas concentration

CO_2	CO	CH_4	H_2	N_2
20.38%	16.23%	5.11%	4.80%	balance

2.5.3 IC

Ion Chromatography (IC) is used to analyze fluorine in liquid phase. The instruments are DX-120 Ion Chromatograph and AS50 Autosampler produced Thermo Scientific™ Dionex™. The analysis method is shown in Table 2-7.

For the column AS 18, the eluent (KOH) must be filtered by 0.45μm filter paper first and be degassed by ultrasonic wave for one hour to prevent the interference of CO_3^{2-} from dissolved CO_2.

Table 2-7. Analysis method of IC

Column type	AS 18
Headspace gas for eluent	N_2
Eluent	23 mmol/L KOH
Standard chemicals for calibration	NaF

2.5.4 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used to analyze metal concentrations in liquid sample. The instrument is ICPM8500 produced by SHIMADZU Corporation.

To make the calibration line, 1000ppm standard solutions of Li, Ni, Mn, Co, Cu are used, which are all produced by FUJIFILM Wako Pure Chemical Corporation. Tuning solution is made of lithium, bismuth and indium standard solution.

Analysis procedure is:

① Dilute the metal standard solution by 1%wt HNO_3 into 50, 100, 200, 400ppb
② make the calibration line
③ dilute liquid sample and analyze it by ICP-MS
④ calculate the metal concentration in liquid sample

2.5.5 TOC analyzer

TOC analyzer is used to analyze total organic carbon (TOC), inorganic carbon (IC), total carbon (TC) in liquid sample. The instruments are TOC-5000A total organic carbon analyzer and ASI-5000A auto sampler produced by SHIMADZU Corporation. The instruments belong to Oshima Laboratory of the Department of Environment System, the University of Tokyo.

Standard solution of TC is potassium hydrogen phthalate. Standard solution of IC is $NaHCO_3$ and Na_2CO_3.

Analysis procedure is:

① Dissolve 2.125 g potassium hydrogen phthalate into 1 L volumetric flask to make 1000 mg-C/L standard solution of TC.
② Dissolve 3.50 g $NaHCO_3$ and 4.41 g Na_2CO_3 into 1 L volumetric flask to make 1000 mg-C/L standard solution of IC.
③ Dilute the standard solution to 10 to 100 ppm
④ Analyze the IC and TC of standard solution and sample by TOC analyzer
⑤ Make calibration line to get the IC and TC of sample
⑥ Calculate the TOC of sample by the formula: TOC = TC - IC

2.5.6 XRD

X-Ray Diffractometer (XRD) is used to analyze the metal oxidation result of solid sample after reaction. The instrument is in the X-ray analysis laboratory of the Institute for Solid State Physics, the University of Tokyo. For analysis, the voltage is 40kV and electric current is 30.0 mA. The degree range is 10 to 90 degree and the analysis rate is 4 degree/min.

The solid sample will be analyzed as the procedure below:

① Separate solid sample from liquid by filter paper and dry it in room temperature
② Crush solid sample into powder by mortar
③ Separate powder and larger particles by 180μm sieve
④ Put the powder sample on the glass plate and make it into the correct shape
⑤ Analyze the sample by XRD
⑥ Analyze the data of the peaks

2.6 Safety issue

During the experiment, quite a lot of issues should be noticed to ensure safety.

2.6.1 Safety operation

(1) During the preparation of LIB sample

Safety operation during the preparation of LIB sample is shown in Table 2-8.

Table 2-8. Safety operation during the preparation of LIB sample

Stage	Safety operation	Potential accident
Dismantle the battery pack	Wear work gloves	Cut and hurt by tools
Discharge a single battery	Wear rubber gloves	Electric shock
	Use rubber tape to fix wires	Leakage of electric
Dismantle a single battery by electric saw	Wear both rubber gloves and work gloves	Cut and hurt by tools; Electric shock; burn of finger by the temperature rise of battery
	Wear mask which could resist organics	Breathe in volatile organic compounds (VOCs)
Crush the battery into powder and ribbon	Operate in the fume hood	Release of VOCs in the room
All of the stages	Wear protective glasses	Hurt of eyes by VOCs

(2) During the reaction in salt bath

Safety operation during the reaction is shown in Table 2-9.

During the reaction, besides the operation in Table 2-9, it is also necessary to monitor the pressure inside the reactor to make sure that no leakage happens during the reaction.

Usually, if there is no leakage of the solution inside the reactor, the pressure inside the reactor will not change too much during the reaction. Sometimes the pressure will increase a little in total (about 0.1 MPa to 0.2 MPa) as some gas generate, such as H_2, CO or CH_4, but it will not increase very quickly.

While if leakage happens, the pressure inside the reactor will decrease in a certain rate (about 0.2 MPa/min).

As long as a leakage happens, the reaction should be stopped and the reactor should be taken out of the salt bath immediately because the solution leakage will affect the composition of the salt bath and the water will evaporate from the bottom of salt bath, becoming water vapor bubble and making the hot salt spill.

Table 2-9. Safety operation during the reaction

Procedure	Safety operation	Potential accident
Ture on the salt bath	Use protective shield	Splash of the hot salt
	Paste a notification on the shield	Accident for the person who did not know the use of salt bath and passed by
Put the reactor into the salt bath	Wear thick heat-resistant work gloves	Burn of finger from the heat of salt bath
	Wear protective head shield	Splash of the hot salt
Take out the reactor from salt bath and cool down	Wear thick heat-resistant work gloves	Burn of finger from the heat of salt bath
Open the reactor	Keep the open side upwards	Liquid phase spill, causing sample loss and chemical corrosion
All the procedure	Wear rubber gloves	Skin corrosion by chemicals

Figure 2-14. Thick heat-resistant work gloves

Figure 2-15. Protective head shield

Figure 2-16. The protective shield of the salt bath

Figure 2-17. The protective shield and the notification

2.6.2 Safety treatment of liquid sample for analysis

Because of the existence of fluorine, the liquid sample after reaction must be treated carefully.

(1) Material of the tools

Firstly, as mentioned in 2.4.3.2, after the reaction, sample will be filtered to separate the solid phase and liquid phase. The funnel used for filter should be made of polypropylene, which is resistant to acid and alkali corrosion.

Then, the volumetric flask used for dilution is also made of polypropylene.

Besides, the hydrophilicity syringe filter is made of PTFE, which is also resistant to acid, alkali and fluorine corrosion.

(2) Concentration and pH

To avoid corrosion to the analysis instruments, the liquid sample should be diluted to a certain concentration.

For IC analysis, the limit concentration is shown in Table 2-10.

However, 1/10 of the limit concentration is a much more suitable concentration, which could avoid overlapping peaks and analysis error.

Table 2-10. Limit concentration for IC analysis

	Limit concentration / ppm
F^-	100
Cl^-	200
NO_3^-	500
SO_4^-	1000
PO_4^{3-}	500

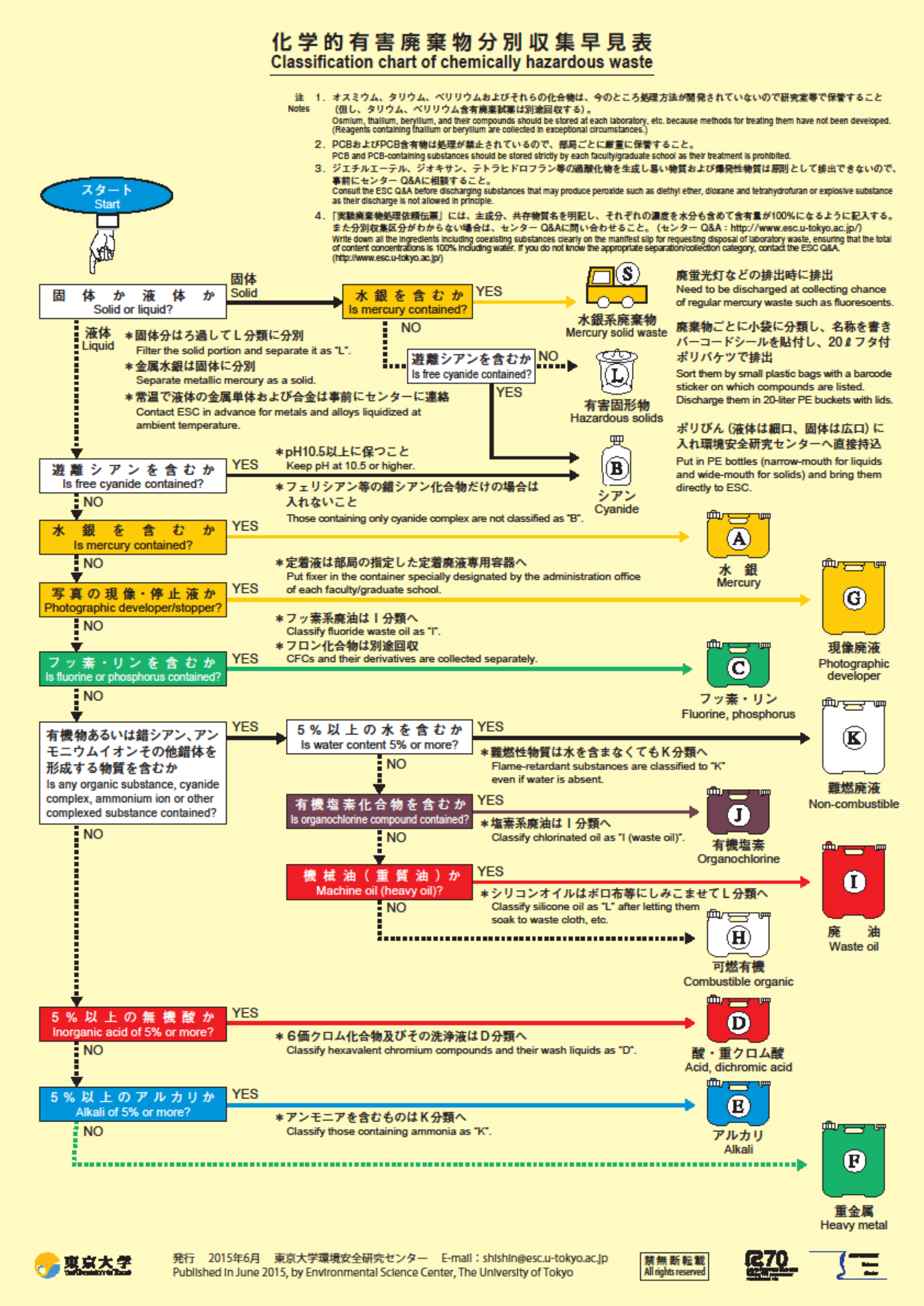
For ICP-MS analysis, the fluorine concentration should be below 0.5 ppm to avoid corrosion.

For both IC and ICP-MS analysis, pH of the liquid sample had better be adjusted to around 7.

2.6.3 Waste liquid management

Experimental waste liquid should be classified according to the classification chart of chemically hazardous waste (as shown in Figure 2-18). In the research, any waste liquid containing LIB sample is stored in C type waste liquid tank because it contains fluorine. Other waste liquid, such as the standard solution of metals for ICP-MS analysis, is stored in F type waste liquid tank. Then, the composition, concentration and pH should be written on the application note and the tank will be submitted to the Environmental Science Center of the University of Tokyo.

Besides, any used chemicals should be recorded in the UTCRIS (University of Tokyo Chemical Registration Information System).



化学的有害廃棄物分別収集早見表
Classification chart of chemically hazardous waste

注 Notes
1. オスミウム、タリウム、ベリリウムおよびそれらの化合物は、今のところ処理方法が開発されていないので研究室等で保管すること（但し、タリウム、ベリリウム含有廃棄試薬は別途回収する）。
Osmium, thallium, beryllium, and their compounds should be stored at each laboratory, etc. because methods for treating them have not been developed. (Reagents containing thallium or beryllium are collected in exceptional circumstances.)
2. PCBおよびPCB含有物は処理が禁止されているので、部局ごとに厳重に保管すること。
PCB and PCB-containing substances should be stored strictly by each faculty/graduate school as their treatment is prohibited.
3. ジエチルエーテル、ジオキサン、テトラヒドロフラン等の過酸化物を生成し易い物質および爆発性物質は原則として排出できないので、事前にセンター Q&Aに相談すること。
Consult the ESC Q&A before discharging substances that may produce peroxide such as diethyl ether, dioxane and tetrahydrofuran or explosive substance as their discharge is not allowed in principle.
4. 「実験廃棄物処理依頼伝票」には、主成分、共存物質名を明記し、それぞれの濃度を水分も含めて含有量が100%になるように記入する。また分別収集区分がわからない場合は、センター Q&Aに問い合わせること。（センター Q&A：http://www.esc.u-tokyo.ac.jp/）
Write down all the ingredients including coexisting substances clearly on the manifest slip for requesting disposal of laboratory waste, ensuring that the total of content concentrations is 100% including water. If you do not know the appropriate separation/collection category, contact the ESC Q&A. (http://www.esc.u-tokyo.ac.jp/)

廃蛍光灯などの排出時に排出
Need to be discharged at collecting chance of regular mercury waste such as fluorescents.

廃棄物ごとに小袋に分類し、名称を書きバーコードシールを貼付し、20ℓフタ付ポリバケツで排出
Sort them by small plastic bags with a barcode sticker on which compounds are listed. Discharge them in 20-liter PE buckets with lids.

ポリびん（液体は細口、固体は広口）に入れ環境安全研究センターへ直接持込
Put in PE bottles (narrow-mouth for liquids and wide-mouth for solids) and bring them directly to ESC.

＊固体分はろ過してＬ分類に分別
Filter the solid portion and separate it as "L".
＊金属水銀は固体に分別
Separate metallic mercury as a solid.
＊常温で液体の金属単体および合金は事前にセンターに連絡
Contact ESC in advance for metals and alloys liquidized at ambient temperature.

＊pH10.5以上に保つこと
Keep pH at 10.5 or higher.
＊フェリシアン等の錯シアン化合物だけの場合は入れないこと
Those containing only cyanide complex are not classified as "B".

＊定着液は部局の指定した定着廃液専用容器へ
Put fixer in the container specially designated by the administration office of each faculty/graduate school.

＊フッ素系廃油はＩ分類へ
Classify fluoride waste oil as "I".
＊フロン化合物は別途回収
CFCs and their derivatives are collected separately.

＊難燃性物質は水を含まなくてもＫ分類へ
Flame-retardant substances are classified to "K" even if water is absent.

＊塩素系廃油はＩ分類へ
Classify chlorinated oil as "I (waste oil)".

＊シリコンオイルはボロ布等にしみこませてＬ分類へ
Classify silicone oil as "L" after letting them soak to waste cloth, etc.

＊6価クロム化合物及びその洗浄液はＤ分類へ
Classify hexavalent chromium compounds and their wash liquids as "D".

＊アンモニアを含むものはＫ分類へ
Classify those containing ammonia as "K".

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Figure 2-18. Classification chart of chemically hazardous waste

3. Behavior of organic compounds and discussion

In this chapter, the behavior of organic compounds will be shown and discussed. The target of treatment result is that 100% of the organic compounds in waste LIB could be oxidized into CO_2 and water, which means they are separated from metals.

Series of experiments have been conducted as described in 2.4.

3.1 Carbon and hydrogen gasification efficiency

3.1.1 Carbon gasification efficiency

The analysis result of gas sample after hydrothermal reaction is shown in Figure 3-1 and Figure 3-2.

In the figures, the amounts of six kinds of gases in room temperature are calculated out based on the amount of the gas sample taken by syringe. The amount of unknown gas is calculated by subtracting the amounts of these gases from the amount total of total gas in the reactor (as mentioned in 2.4.3.1). Thus, the amount of unknown gas sometimes is below 0. And the unknown gas might come from the little error of analysis and the calculation of the volume of reactor and gas sampling system. A part of the known gas might be other gases probably.

Figure 3-1 shows the gas sample analysis result in the experiments without using H_2O_2 (No.1-15 in Table 2-3). These fifteen experiments are conducted to research about the effect of water amount to the reaction and to find out the optimum water amount. The result indicates that for 4 mL and 8 mL H_2O, most H_2 and CO_2 are generated under 375℃. For 6 mL H_2O, the max amount of generated H_2 and CO_2 are very close in 350℃ and 375℃.

The gas sample data of experiments with 4 mL and 6 mL H_2O are similar in total gas amount. But they are both more than 8mL. In the reactor, more H_2O will cause less initial gas (air) inside before the reaction. After checking the data, it is found that 8 mL H_2O still generated less gas than 6mL H_2O. And 6mL generated more gas than 4mL H_2O ignoring the original gas amount.

So, 6 mL seems the optimal amount of added H_2O and H_2O_2 in generating gas.

Figure 3-2 shows the gas sample analysis result in the experiments with 100% H_2O_2 for 30, 60, 90 minutes and 200% H_2O_2 for 30 minutes. These twenty experiments are conducted to research about the effect of the extra O_2 generated from H_2O_2 and reaction time on the treatment result.

The result of Figure 3-2 indicates that huge amount of O_2 generated from the added H_2O_2, oxidizing more organic compounds to CO_2 compared with that in experiments without H_2O_2. However, after the hydrothermal reaction, still a lot of O_2 remained in the reactor as shown in Figure 3-3, which means the extra provided O_2 has not been completely utilized to oxidize the organic compounds in LIB sample. In the expectation, the O_2 from added 100% H_2O_2 should be completely consumed and become CO_2 with oxidized organic compounds.

Figure 3-4 shows the amount of generated CO_2 in gas phase after hydrothermal reaction. And Figure 3-5 shows the carbon gasification efficiency (CGE). The calculation formula of CGE is: $CGE=(n_{CO2}+n_{CO}+n_{CH4})/n_{TOC}$. ($n_{TOC}$ is the total organic carbon in LIB sample)

By comparing Figure 3-4 and Figure 3-5, it could be known that the main carbon gasification product is CO_2 because the curve of CGE is quite similar to that of generated CO_2. The amounts of generated CO and CH_4 are so little that could be almost ignored.

Figure 3-4 indicates that the use of H_2O_2 could help oxidize more organic compounds to CO_2 compared with the experiments without H_2O_2. Besides, more O_2 by adding more H_2O_2 (200%) increased CGE significantly. In lower temperature, longer reaction time (60 and 90min) is positive to increase the CGE while as temperature rises, longer reaction time makes negative effect. At the same time, with more H_2O_2, the change of temperature affects more obviously on CGE.

The highest CGE is 28.78%, appearing under 350℃ with 200% H_2O_2, 30min.

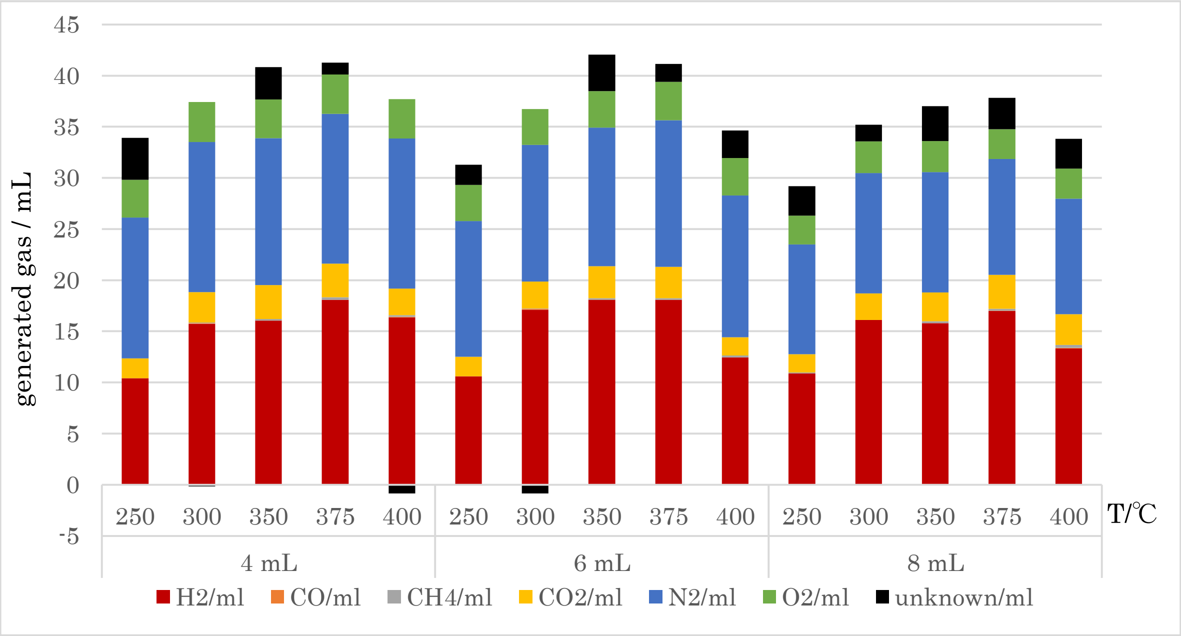

Figure 3-1. Gas sample analysis in experiments without H_2O_2

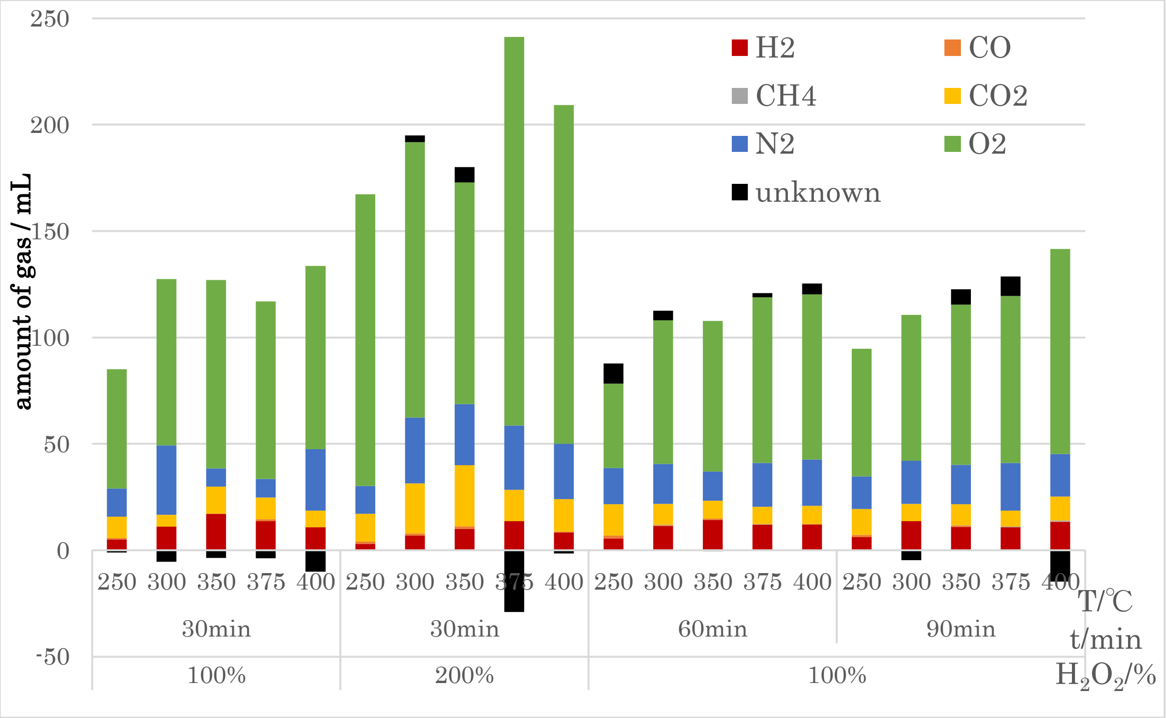

Figure 3-2. Gas sample analysis in experiments with H_2O_2

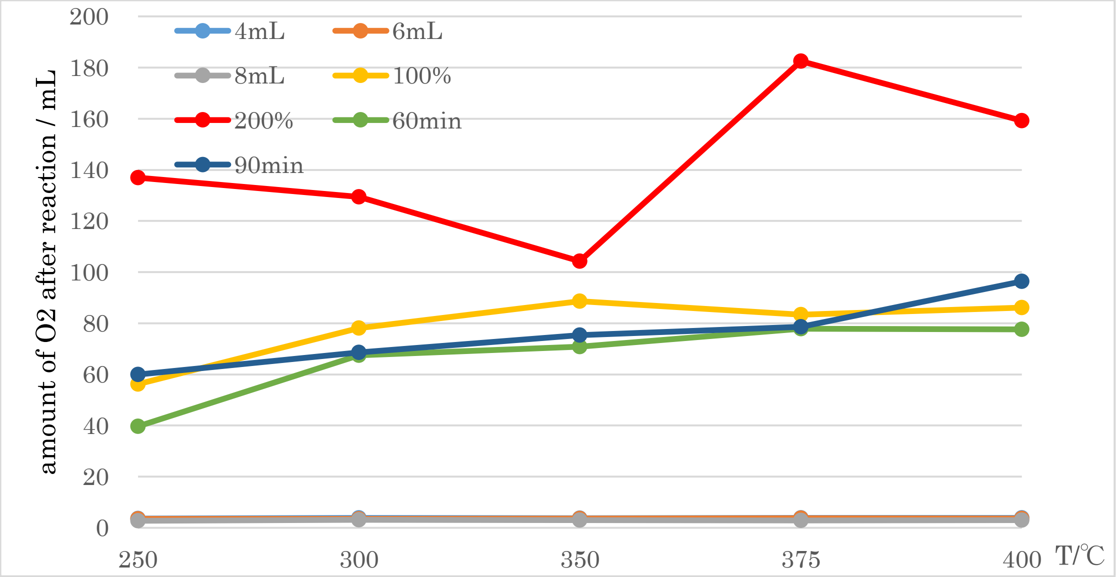

Figure 3-3. Amount of O_2 in gas phase after reaction

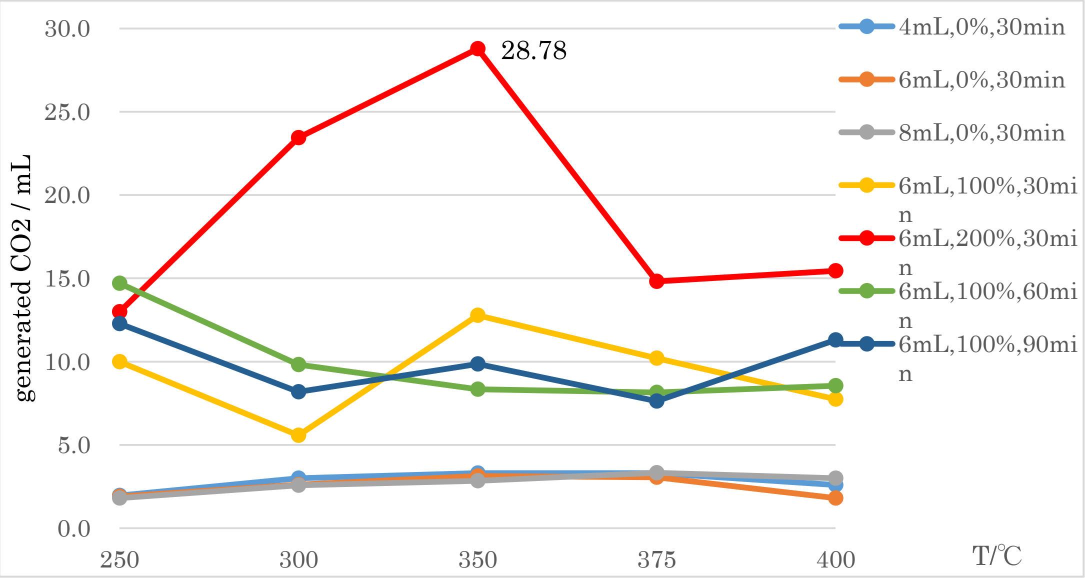

Figure 3-4. Amount of generated CO_2 in gas phase after reaction

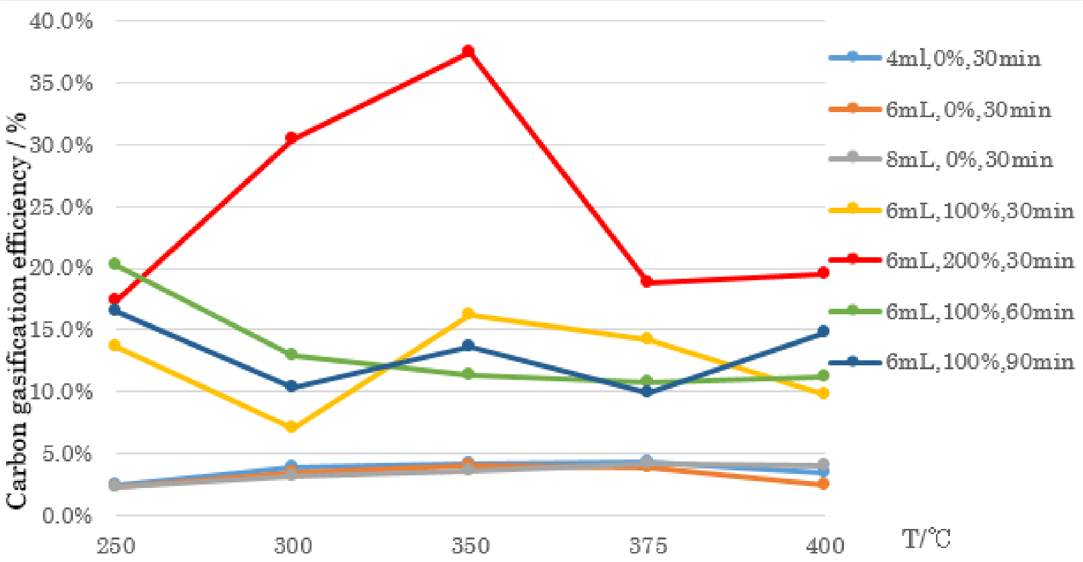

Figure 3-5. Carbon gasification rate

3.1.2 Hydrogen gasification efficiency

Figure 3-6 presents the amount of generated H_2 after hydrothermal reaction. Figure 3-7 presents the hydrogen gasification efficiency (HGE). The calculation formula of HCG is: HGE= $(2n_{H2}+4n_{CH4})/n_H$. (n_H is the total hydrogen in LIB sample)

By comparing Figure 3-6 and Figure 3-7, it could be known that the main hydrogen gasification product is H_2 because the curve of HGE is quite similar to that of generated H_2. The amount of generated CH_4 is so little that could be almost ignored.

The change of HGE indicates it is affected by temperature and the amount of added H_2O_2. For temperature, under 300 to 375℃, most hydrogen is gasified, becoming fuel gas which is helpful to increase the economic benefit in this research.

The use of H_2O_2 seems to be able to oxide the generated H_2 and CH_4 into H_2O and CO_2, reducing HGE. As shown in Figure 3-8, the more H_2O_2 is added, the lower HGE is.

Reaction time also makes some effect. Under 350℃ and 375℃, HGE decreased as reaction time becomes longer.

The highest HGE is 21.43%, appearing under 375℃ without H_2O_2, 30min.

It has been mentioned in 3.1.1 already that longer reaction time and more amount of H_2O_2 are both positive on the oxidation of organic compounds in LIB sample, which is directly connected to the treatment result of organic compounds. While it will make negative effects on HGE, which means less fuel gas could be got. When judging the optimal experimental condition, CGE is much more important than HGE because the economic benefits from generated fuel gas is not the main target in the research. Besides, if H_2 concentration is inside the flammability limit (4% ~75%), it will cause security risk.

Although the reason of the change of HGE has been known as described above, the mechanism of the generation of H_2 is still unknown. It is not clear that whether the gasified hydrogen comes from the organic compounds or added water. According to a series of blank experiments using only 6 mL water inside the reactor, it is found that only a little H_2 generated. The data is shown in Table 3-1. So, the material of the reactor is not the reason generating so much H_2. Possible reaction to generate H_2 might be related to supercritical water gasification mentioned in 1.4.2 and the reaction formulas are:

Aqueous gasification: $C + H_2O \rightarrow CO + H_2$

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

However, further experiments are necessary to confirm it.

Table 3-1. Generated H_2 in blank experiments without LIB sample

T / °C	Amount of generated H_2 / mL (in room temperature)
250	0.03843
300	0.035633
350	0.006259
375	0
400	0.06503

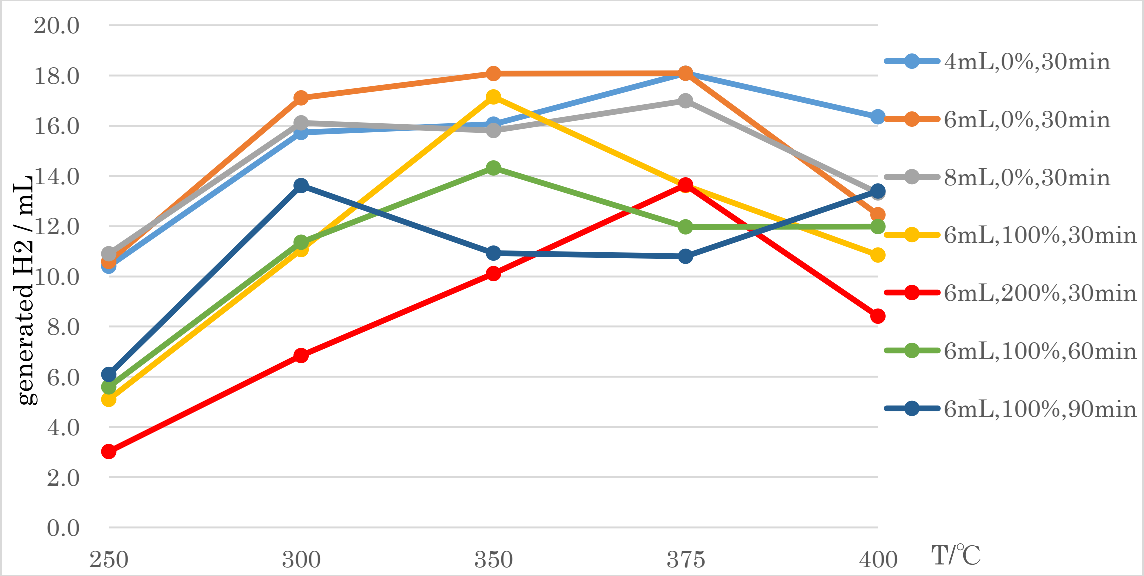

Figure 3-6. Amount of generated H_2 in gas phase after reaction

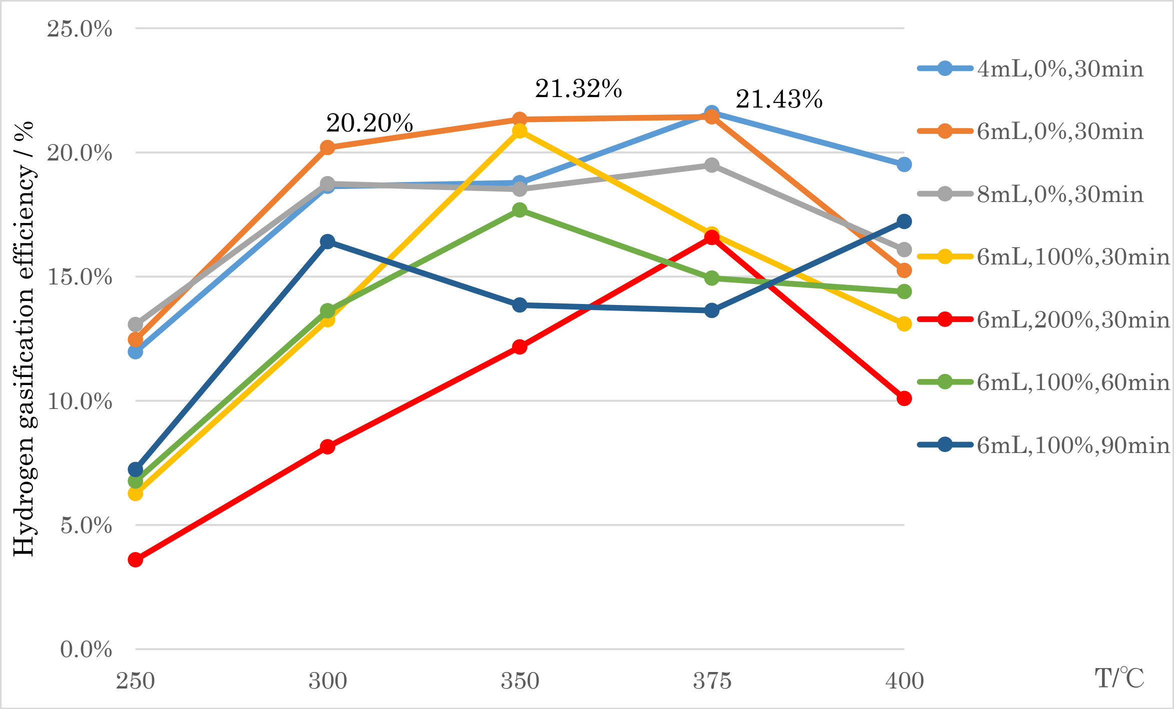

Figure 3-7. Hydrogen gasification efficiency

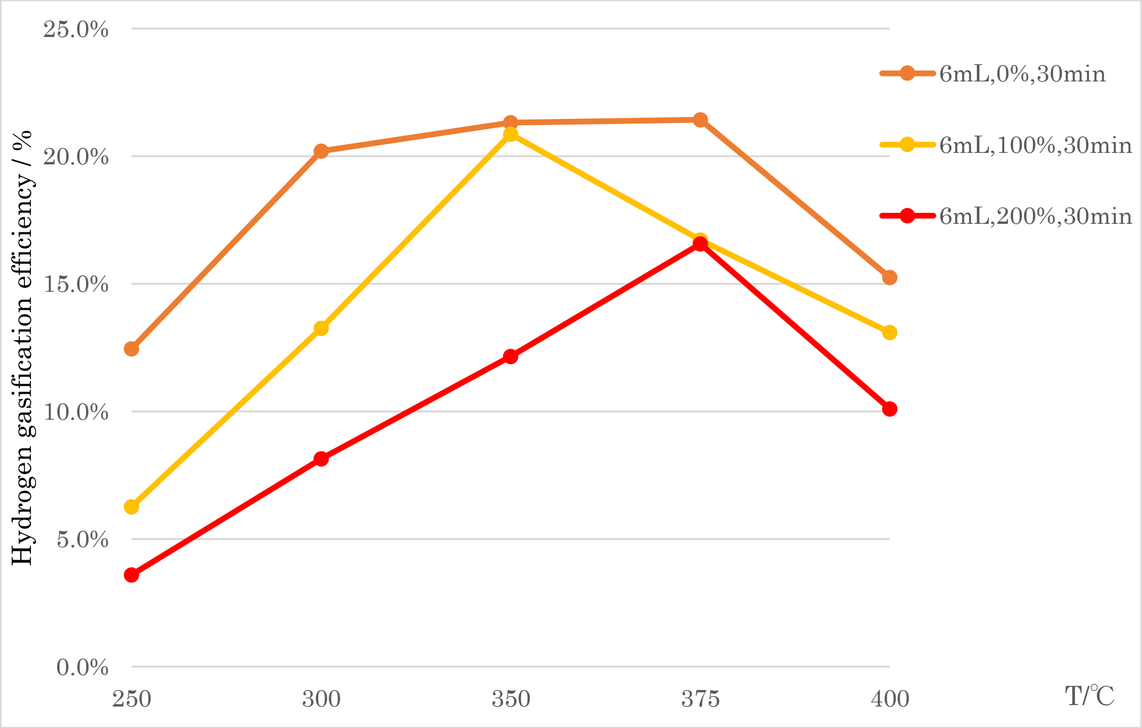

Figure 3-8. Change of HGE with different amount of H_2O_2

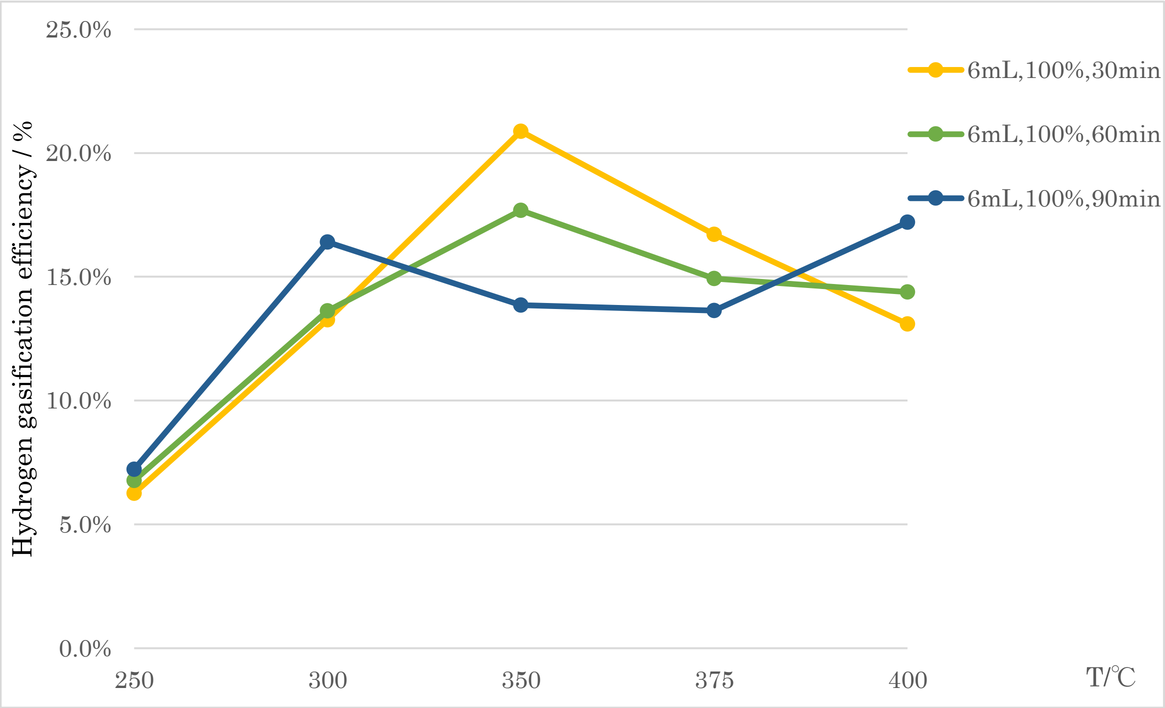

Figure 3-9. Change of HGE with different reaction time

3.2 TOC conversion

Total organic carbon (TOC) in liquid phase after hydrothermal reaction is analyzed by TOC analyzer. Figure 3-10 and Figure 3-11 show TOC analysis result of liquid phase after hydrothermal reaction.

In the two figures, it seems that inorganic carbon (IC) in liquid increases as temperature rises. The curve of TOC is irregular in experiments without H_2O_2 but in cases using H_2O_2, TOC decreases as temperature rises. IC should be the dissolved CO_2 in liquid and TOC should come from the dissolved organic compounds. So, both of the increase of IC and the decrease of TOC in liquid phase mean the oxidation of organic compounds in LIB sample.

To assess the whole organic compounds treatment result, the organic carbon conversion rate in all phases is shown in Figure 3-12. Considering that only the carbon concentration in liquid phase and gas phase are directly analyzed, carbon concentration in solid phase is named as "unknown" because that part is calculated by the formula: $C_{unknown} = 100\%- C_{liquid} - C_{gas}$. It might not be equal to the real carbon concentration in solid phase because of some experimental and calculation error.

The result in Figure 3-12 presents that even in the best case, only 57.86% organic carbon is recovered into gas and liquid phase, separated from metals in solid phase. While in the comparison experiment using only water in room temperature, 11.16% of organic carbon transferred in liquid phase.

For further analysis, Figures 3-13, 3-14, 3-15 show carbon separation rate (carbon in gas and liquid phase after hydrothermal reaction) and its change in different experimental conditions. It could be known that the use of H_2O_2 could increase the carbon separation rate greatly. However, as temperature rises, it decreases a little, which means a part of the separated organic carbon transferred into solid phase.

Although the highest carbon separation rate (57.86%) appears under 350℃ with 200% H_2O_2, 30min, the experimental condition 250℃ with 100% H_2O_2, 60 min also performs good, separating 51.70% organic carbon from solid phase.

So, both higher temperature with more H_2O_2 and lower temperature with longer reaction time are positive to decompose organic compounds and separate them from metals in solid phase, which is expected in the research. But much higher temperature and much longer reaction time might be negative, transferring organic compounds to solid phase though it is unknown what this part of carbon is.

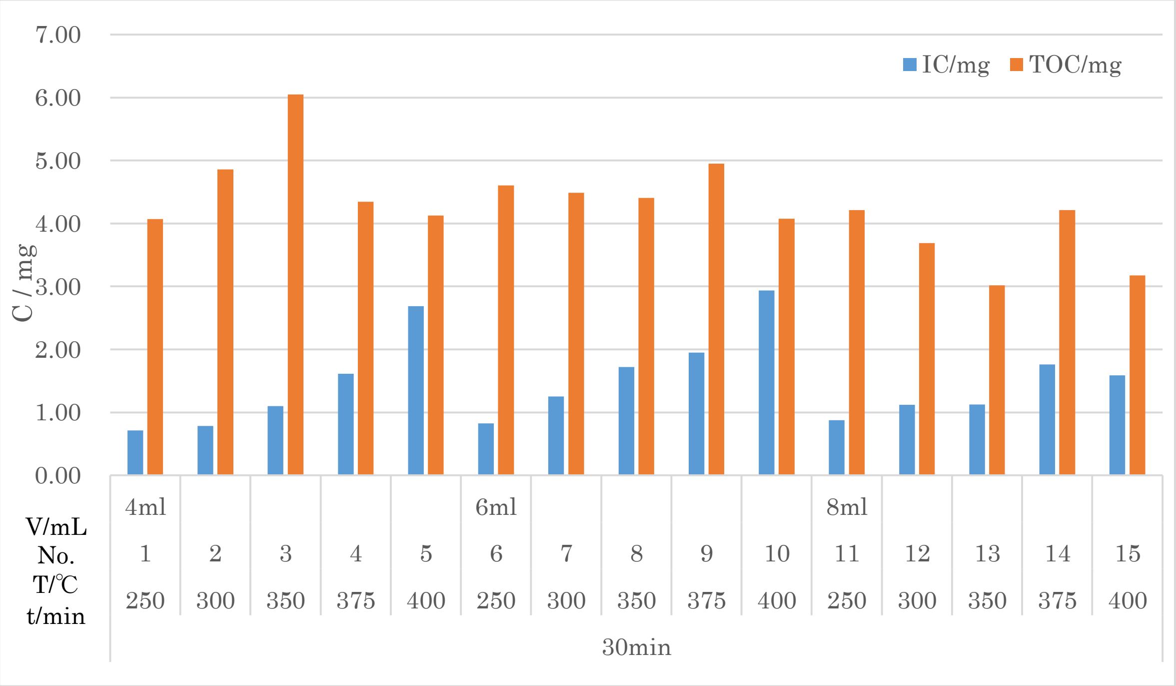

Figure 3-10. TOC analysis result of liquid phase in experiments without H_2O_2

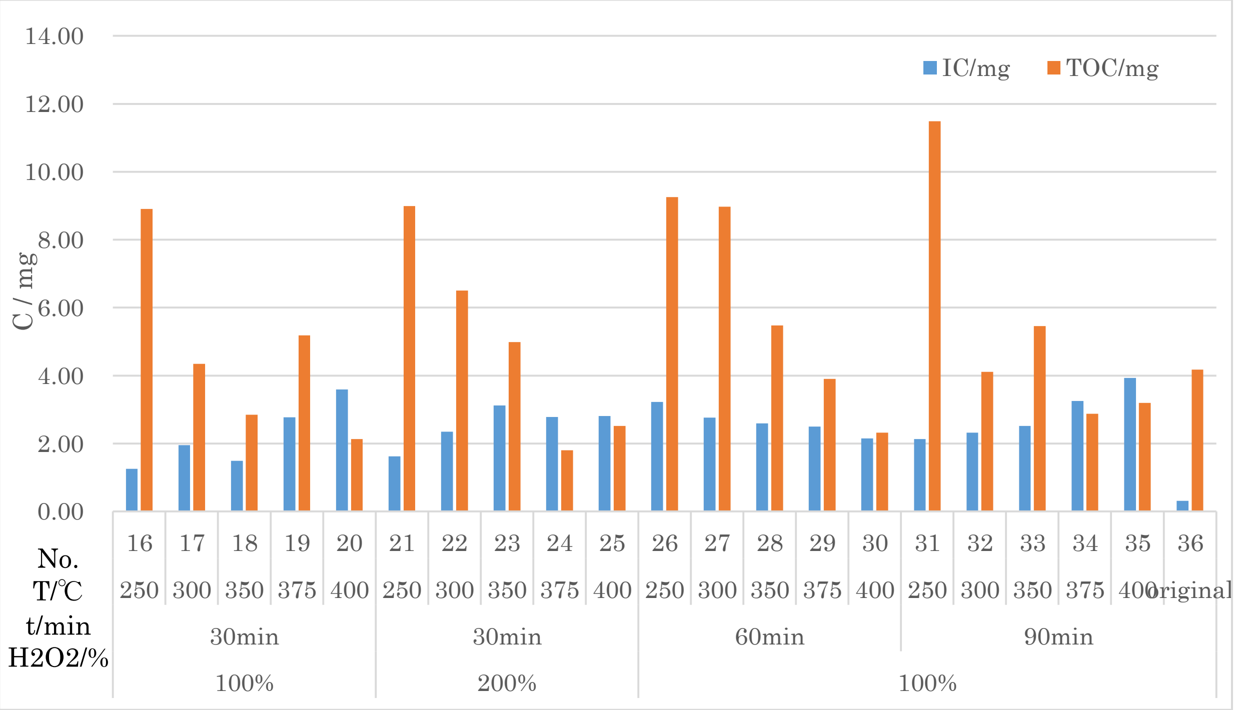

Figure 3-11. TOC analysis result of liquid phase in experiments with H_2O_2

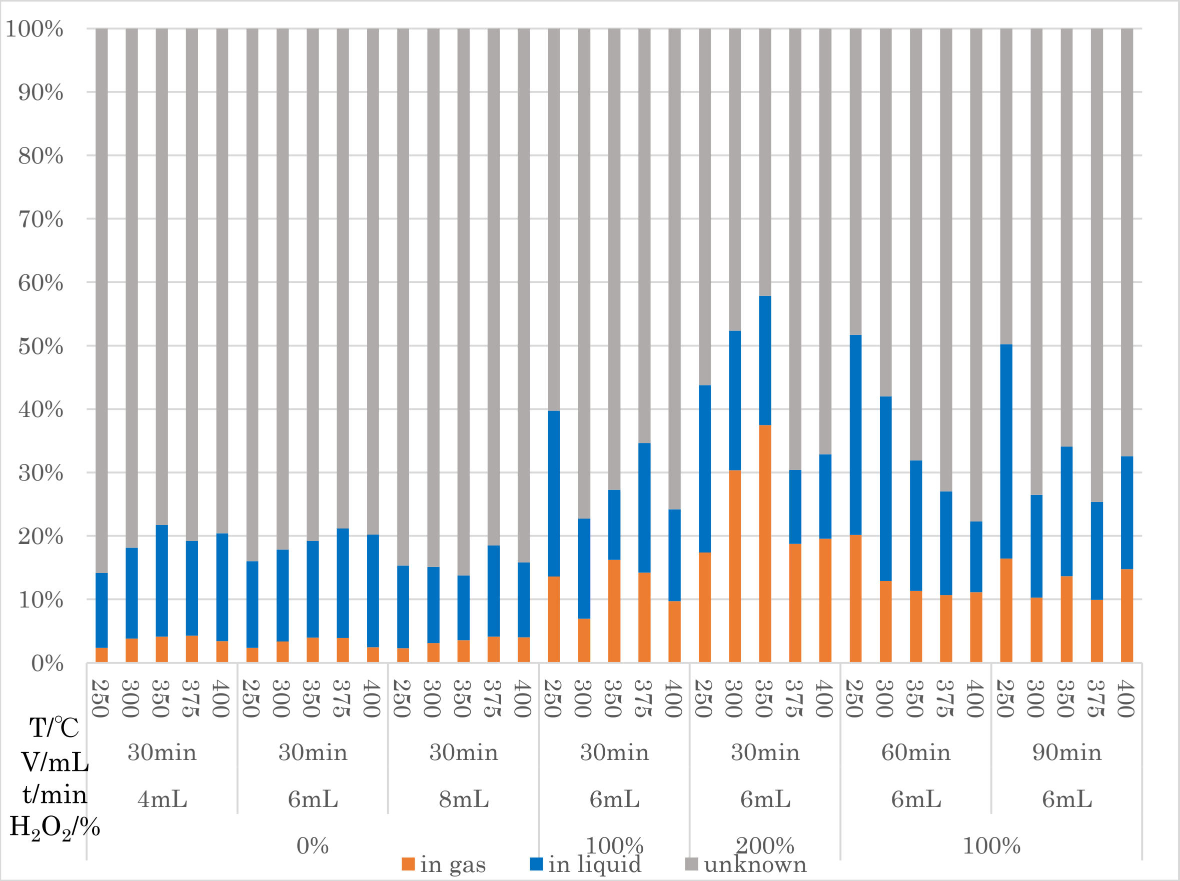

Figure 3-12. Organic carbon conversion rate in all phases

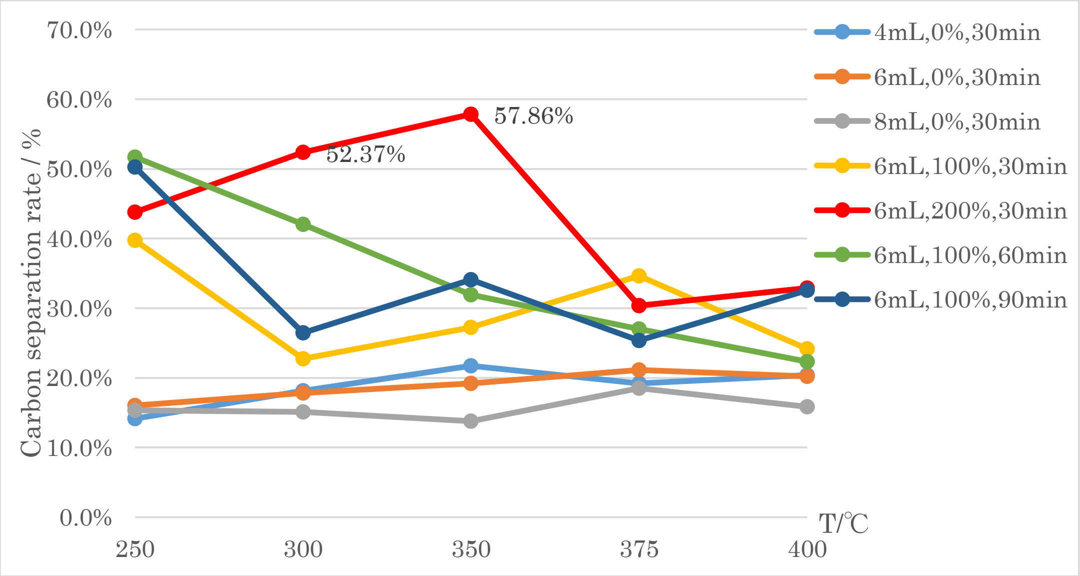

Figure 3-13. Carbon separation rate in all experiments

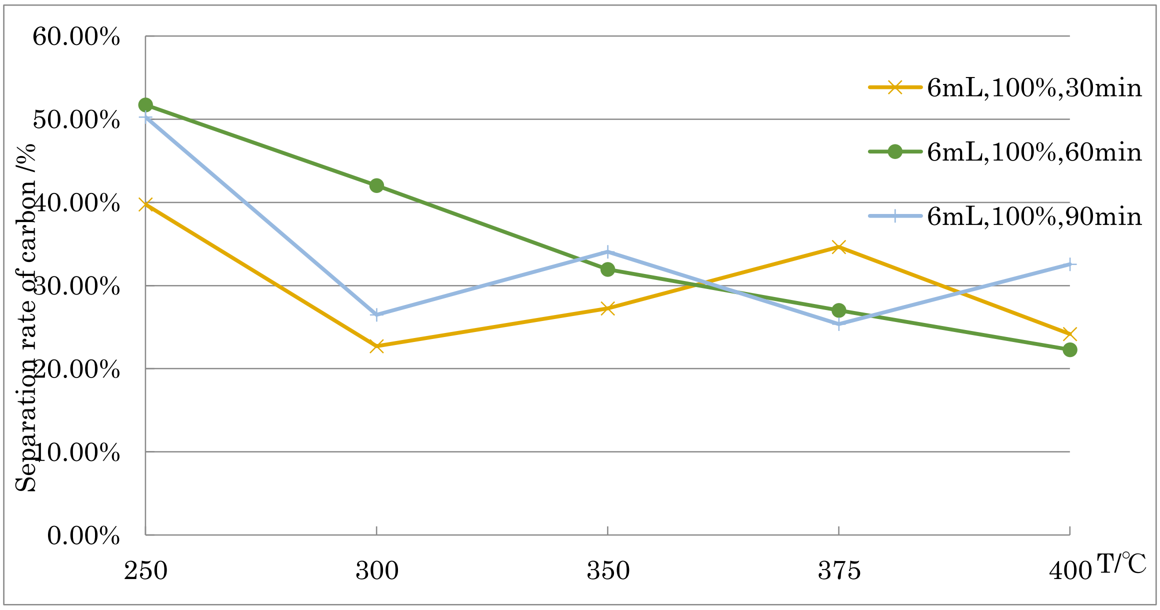

Figure 3-14. Change of carbon separation rate with different reaction time

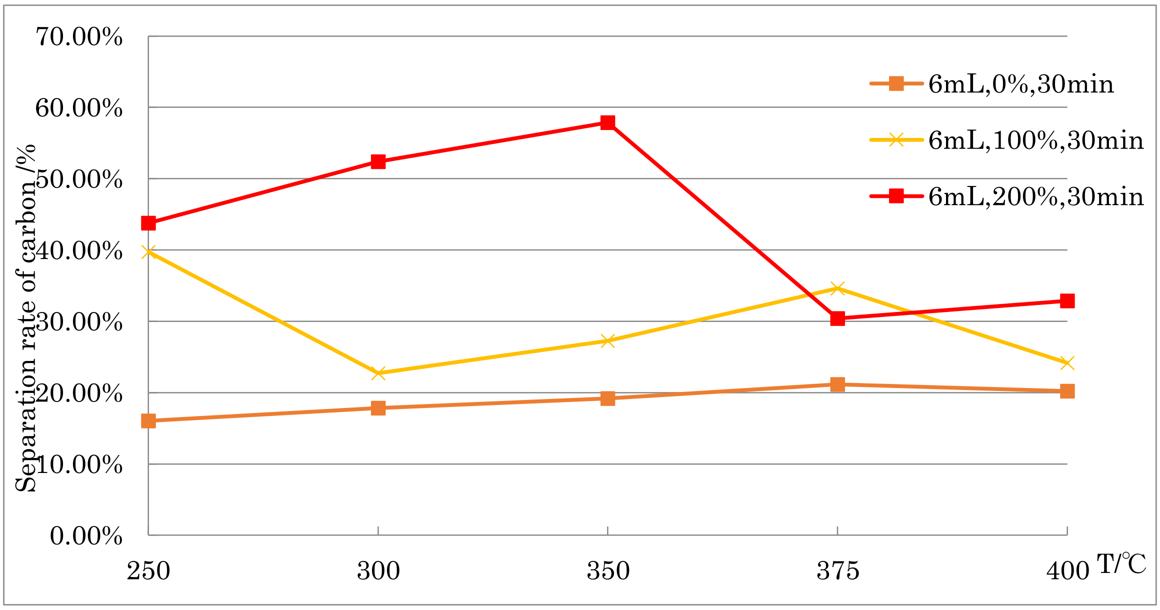

Figure 3-15. Change of carbon separation rate with different amount of H_2O_2

3.3 Summary and discussion

In this chapter, carbon and hydrogen behavior is discussed. In hydrothermal reaction, the utilization of H_2O_2 could help oxidize more organic carbon in LIB sample and separate it from metals in solid phase.

Based on the researches introduced in 1.4, the reaction formula should be:

$$[C, H, O] + nO_2 \rightarrow xCO_2 + yH_2O$$

In lower temperature, longer reaction time also makes some positive effects on carbon separation but in higher temperature, it becomes negative. Higher temperature also helps treat organic compounds in cases with H_2O_2 but when it is over 350℃, higher temperature makes the treatment result worse.

For gasification of hydrogen, higher temperature and no use of H_2O_2 are preferred, generating more fuel gas, H_2 and as economic benefits. The related reaction formula should be:

$$\text{Aqueous gasification: } C + H_2O \rightarrow CO + H_2$$

$$\text{Partial oxidation: } 2C + O_2 \rightarrow 2CO$$

$$\text{Furnace gasification: } C + CO_2 \rightarrow 2CO$$

$$\text{Water-gas shift reaction: } CO + H_2O \rightarrow CO_2 + H_2$$

However, other conditions which help treat organic carbon will decrease HGE. Between treatment results of organic carbon and economic benefits, the former is much important in this research. The reaction formulas which decrease the amount of H_2 should be:

$$2H_2 + O_2 \rightarrow 2H_2O$$

At the same time, the generated H_2 might become security risk as well, causing explosion when the valve of the reactor is opened if the concentration is in the flammability limit of H_2 (4% ~75%).

So, the optimum experimental condition to treat organic compounds is 350℃ with 200% H_2O_2, 30min. In this condition, 57.86% of organic carbon is separated from metals in solid phase and 28.78% of organic carbon is oxidized to CO_2.

However, this is still not enough compared with the initial target of this research, all of the organic compounds could be oxidized into CO_2 in gas or dissolved into liquid phase. There are two main reasons why it did not reach the target:

(1) The O_2 from H_2O_2 is not completely utilized. As was mentioned in 3.1.1, a lot of O_2 still remains in the reactor after hydrothermal reaction. If this part of O_2 could be fully used to oxidize organic compounds, the treatment results of organic compounds ought to be better.

As for the reason why provided O_2 is not consumed efficiently, it might be the design of the reactor. To collect gas sample after reaction, a T-piece is used to connect sampling valve and pressure transducer as shown in Figure 2-10. But these three parts are not put inside the salt bath for security. So, they are exposed to the air, causing it much cooler than set temperature during the reaction and the pressure inside the reactor is much lower than plan as well. The data of pressure is shown in Table 3-2

So, to get better treatment results of organic compounds, this problem should be solved. For example, use another kind of heat device (such as electric furnace [44]) which is able to cover the whole reactor and avoid the loss of heat, ensuring the actual pressure could reach the target pressure.

(2)A part of organic carbon returned into solid phase as temperature rises.

About the mechanism and reason, a reasonable guess is that this part of carbon was carbonized into coal by hydrothermal carbonization. Dewi Agustina Iryani [58] investigated hydrothermal carbonization of sugarcane bagasse using hydrothermal water to treat the solid material to understand the occurring decomposition reactions. The experiments were conducted in a batch type reactor with inner volume of 14 mL under experimental conditions with reaction time of 3 to 30 min and temperature of 473 to 573 K. The analysis result of the solid residues separated from liquid sample indicated that nearly 34 to 88 wt% of raw material converted into solid products. By characterizations, it was found that higher treatment temperature and longer reaction time are able to change the structure of the sugarcane bagasse. The final solid product was a lignin-like residue.

Similar reaction may also happened in this research that a part of organic carbon assemble and formed solid particles. To confirm this, further research on solid product is necessary.

Table 3-2. Target pressure and actual pressure in experiments

No.	T/℃	Amount of H_2O /mL	H_2O_2	Reaction time/min	Target pressure/MPa	Actual pressure/MPa
1	250	4	0	30	3.97	2.7
2	300				8.59	4.8
3	350				16.53	10.6
4	375				21.70	14.1
5	400				25.25	19.1
6	250	6			3.97	2.3
7	300				8.59	5.5
8	350				16.53	13.6
9	375				22.32	16.8
10	400				27.96	23.6
11	250	8			3.97	1.9
12	300				8.59	4.6

13	350				16.53	9.3
14	375				22.37	14.7
15	400				29.68	18.1
16	250	6	100%		4.60	2.4
17	300				9.28	5.4
18	350				17.28	10.7
19	375				23.10	17.3
20	400				28.77	24.2
21	250		200%		5.23	3.1
22	300				9.97	5.7
23	350				18.03	11.4
24	375				23.88	17.4
25	400				29.59	22.8
26	250		100%	60	4.60	2.3
27	300				9.28	5.2
28	350				17.28	11.8
29	375				23.10	12.67
30	400				28.77	23.25
31	250			90	4.60	2.4
32	300				9.28	5.2
33	350				17.28	11.5
34	375				23.10	14.72
35	400				28.77	25.32

4. Behavior of fluorine and discussion

4.1 Fluorine dissolved in liquid phase

The liquid samples after hydrothermal reaction are analyzed by IC to know the behavior of fluorine, the only hazardous substance in LIB able to cause security problem.

The fluorine recovery rate in liquid phase is shown in Figure 4-1. And Figures 4-2 to 4-4 shows the change of fluorine recovery rate in different experimental conditions.

Figure 4-1 shows as temperature rises, the fluorine recovery rate decreases first in 350℃ and rise a little later. In 400℃, the fluorine recovery rates are close with 6mL H_2O/H_2O_2, and are all over 90%.

Figure 4-2 shows without H_2O_2, higher temperature is able to increase fluorine recovery rate. The amount of water also affects. 6 mL and 8 mL perform better than 4 mL water.

Figure 4-3 indicates that in lower temperature, more H_2O_2 helps decompose PVDF and convert fluorine into liquid phase. When temperature rises (over 350℃), the fluorine recovery rates are similar with different amount of H_2O_2.

Figure 4-4 presents that longer reaction time (60 and 90min) dissolves less F under 250℃ but dissolves more F in 300,350,375℃ compared with 30min experiment using the same H_2O_2 concentration (100%).

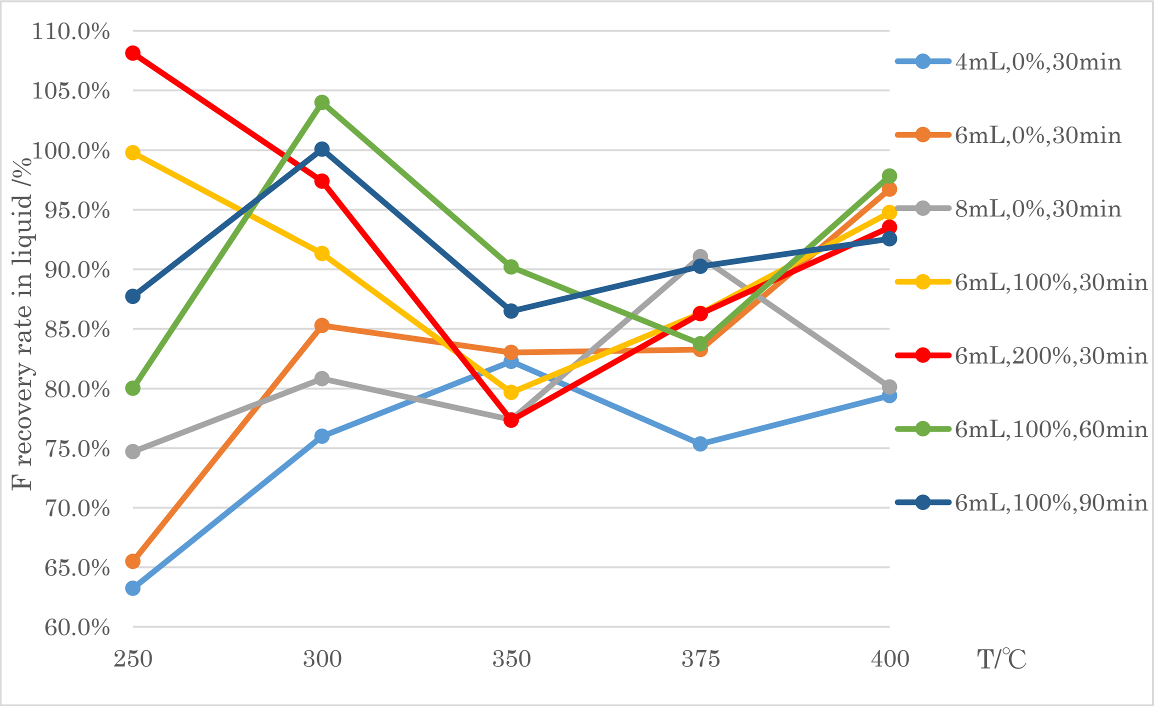

Figure 4-1. Fluorine recovery rate in liquid after hydrothermal reaction

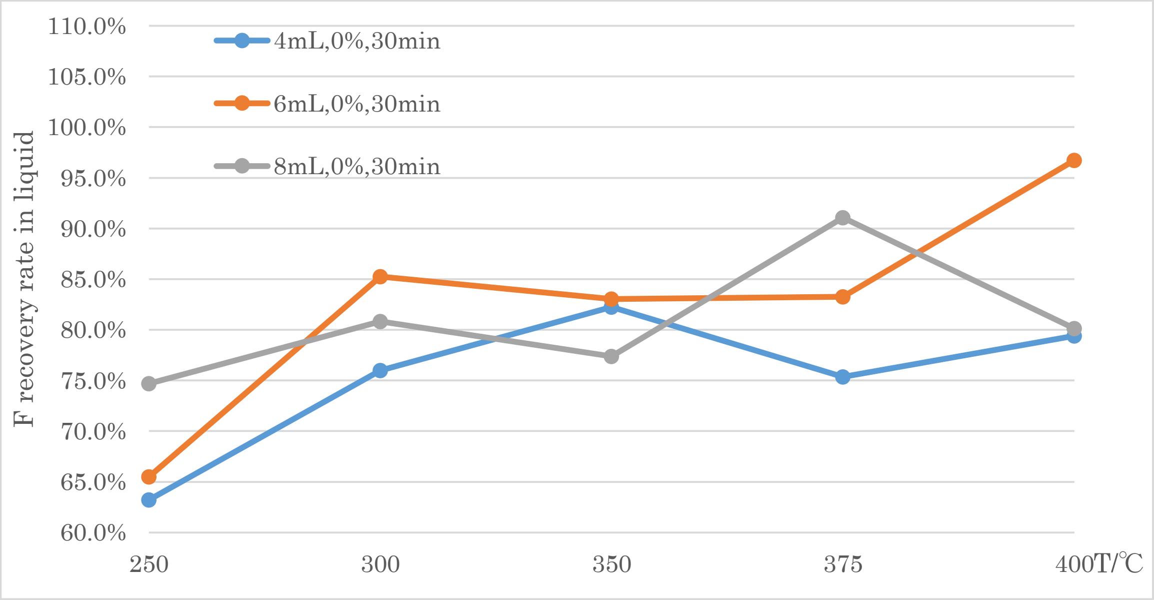

Figure 4-2. Fluorine recovery rate in liquid without H_2O_2

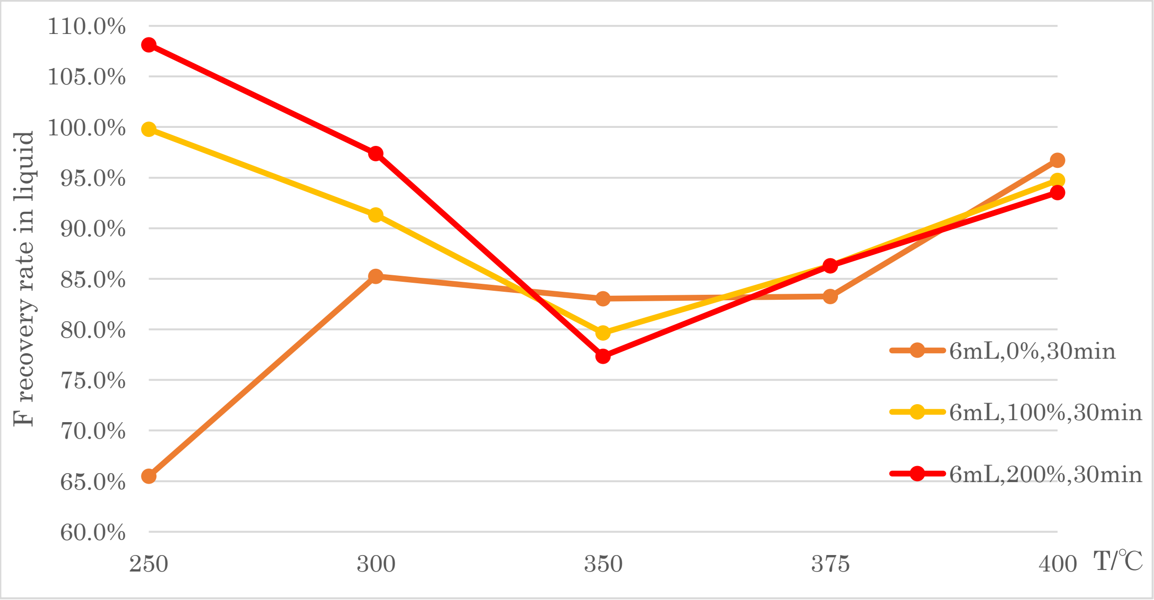

Figure 4-3. Change of fluorine recovery rate in liquid with different amount of H_2O_2

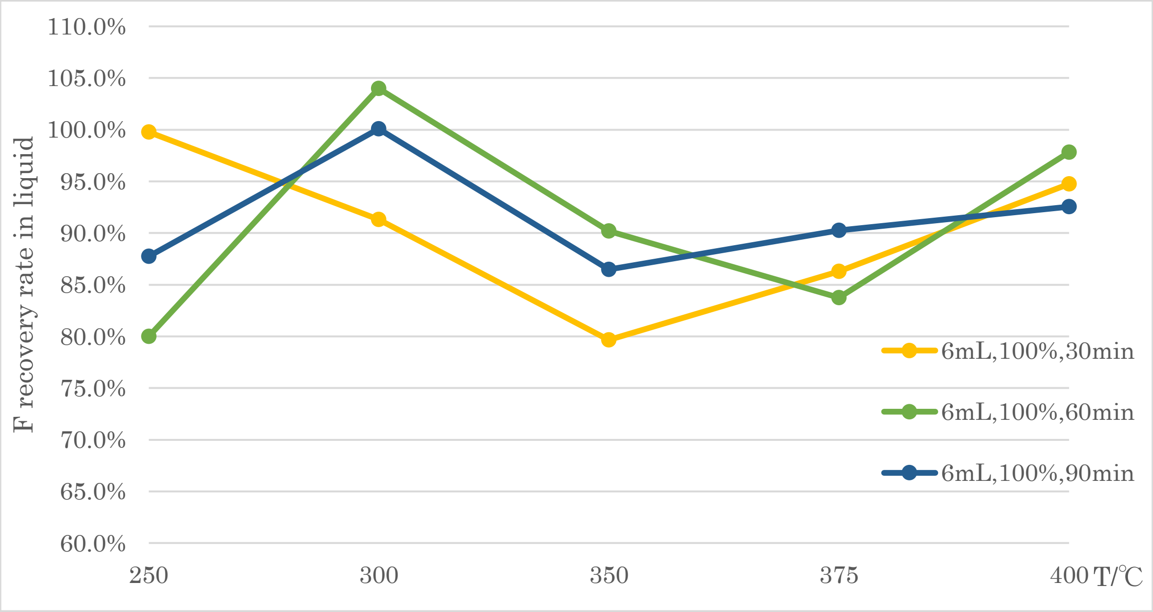

Figure 4-4. Change of fluorine recovery rate in liquid with different reaction time

4.2 Fluorine corrosion

The rise of fluorine recovery rate in liquid means the decomposition of PVDF and the dissolution of fluoride ion. However, the fluorine recovery rate decreases under 350℃ as shown in Figure 4-1. Considering that it rises again under higher temperature, the reduced part of dissolved fluorine should not be gasified to HF. Thus, it is supposed that a little part of fluorine reacts with the reactor in 350℃, moving into solid phase. While in higher temperature, the generated fluorine-containing solid substance decomposes and the fluorine dissolves in liquid again.

To find out whether the fluorine reacts with the metal of reactor, a stainless plate experiment has been conducted. The experimental condition is 350℃ with 6mL H_2O_2 (200%) for 30min, in which the fluorine recovery rate decreased most in Figure 4-1. The experiment procedure is the same as before except that a piece of 10*6*4 mm SUS316 stainless plate (the same material as the reactor) is added into the reactor as well. After the reaction, the surface of the stainless plate was washed and dissolved by acid (5 mL HNO_3 and 2 mL H_2SO_4) for one night.

Then, KOH was added to adjust the pH of solution and the fluorine concentration in the dissolving solution was analyzed by IC. The analysis result shows about 73.42% fluorine in LIB sample was converted into solid phase. So, it could be confirmed that in a certain condition (with H_2O_2 over 300℃), fluorine will react with the metal of reactor.

But the reaction product could not be confirmed yet.

Figure 4-5. Stainless plate before (left) and after (right) reaction

Figure 4-6. Stainless plate after acid dissolving

4.3 Summary and discussion

In this chapter, behavior of fluorine during the hydrothermal reaction is discussed.

In waste LIB, fluorine exists as electrolyte ($LiPF_6$) and adhesive (PVDF). According to related researches [59], $LiPF_6$ could react with H_2O easily, forming HF. The reaction formulas are:

$$LiPF_6 + H_2O \rightarrow LiF \cdot HF + HF\uparrow + POF_3\uparrow$$

$$POF_3 + H_2O \rightarrow H[PO_2F_2]$$

$$H[PO_2F_2] + H_2O \rightarrow H_2[PO_3F] + HF\uparrow$$

$$H_2[PO_3F] + H_2O \rightarrow H_3[PO_4] + HF\uparrow$$

But with the characteristics of high chemical corrosion resistance and heat resistance, PVDF is quite hard to decompose. By hydrothermal reaction and with the utilization of H_2O_2, PVDF is expected to be decomposed, which could both oxidize this part of organic carbon and assemble the fluorine into liquid phase.

So, high fluorine recovery rate means the decomposition of PVDF (solid) in LIB sample and the assembly of fluoride ion in liquid phase, which is helpful for safe treatment after the hydrothermal reaction of the whole waste LIB treatment procedure.

The results show fluorine in waste LIB sample could be easily recovered into liquid phase. Even in the lowest temperature (250°C) without H_2O_2, more than 65% fluorine could be recovered into liquid phase. Most of this part of fluorine should be from $LiPF_6$ based on the reaction with H_2O mentioned above.

As temperature rises, the fluorine recovery rate also increases, indicating the decomposition of PVDF. The use of H_2O_2 is able to accelerate the decomposition of PVDF, increasing fluorine recovery rate under lower temperature (250°C and 300°C) while according to other researches [54], PVDF starts to decompose in 350°C in conditions without adding H_2O_2 and hydrothermal method.

However, high temperature and the use of H_2O_2 might lead to fluorine corrosion of the reactor, causing security risk. Thus, the corrosion mechanism and product should be researched further and more to guarantee the safety both in experiments and real application.

In related researches about fluorine corrosion, M.Nakagawa [60] found the mechanism of fluorine corrosion with Ti :

$$Ti_2O_3 + 6HF \rightarrow 2TiF_3 + 3H_2O$$

$$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O$$

$$TiO_2 + 2HF \rightarrow TiOF_2 + H_2O$$

In addition, pH and fluorine concentration decide whether the corrosion happens as shown in Figure 4-7. It indicates that lower pH of solution could make fluoride ion more corrosive to Ti. In this research, 8.13 mg of fluorine is contained in 0.3 g of waste LIB sample. If 6 mL H_2O is added into the reactor for experiments, if all of the fluorine is dissolved into liquid, the highest fluoride ion concentration could be 1355 ppm, which is corrosive below pH of 5.

As has been introduced in 1.4.1, much more H^+ generates in hydrothermal water, which might decrease pH and make F^- more corrosive according to Figure 4-7. Besides, considering the effect of H_2O_2 and based on the analysis results, it is supposed that the reactor reacts with HF generated from decomposed PVDF. The possible reaction formulas in this research might be:

Generation of O_2 from H_2O_2: $2H_2O_2 \rightarrow 2H_2O + O_2$

Oxidation of surface of the reactor: $2M + O_2 \rightarrow 2MO$

Decomposition of PVDF: $-(C_2H_2F_2)_n- + 2nO_2 \rightarrow 2nCO_2 + 2nHF\uparrow$

Fluorine corrosion with SUS316: $2HF + MO \rightarrow MF_2 + H_2O$

In the reactions, M is the metals in the reactor, including Fe, Cr, Ni and Mo.

However, this is only a speculation now. To confirm it, further experiments should be conducted. For example, use acid (HCl or H_2SO_4) to leach the inner surface of the reactor used for hydrothermal reaction treating waste LIB and a new reactor. Then, analyze the leaching solution by ICP-MS to compare the metal ion composition in the solution. The difference between the metal compositions of inner surface of the reactors might be the evidence to confirm something.

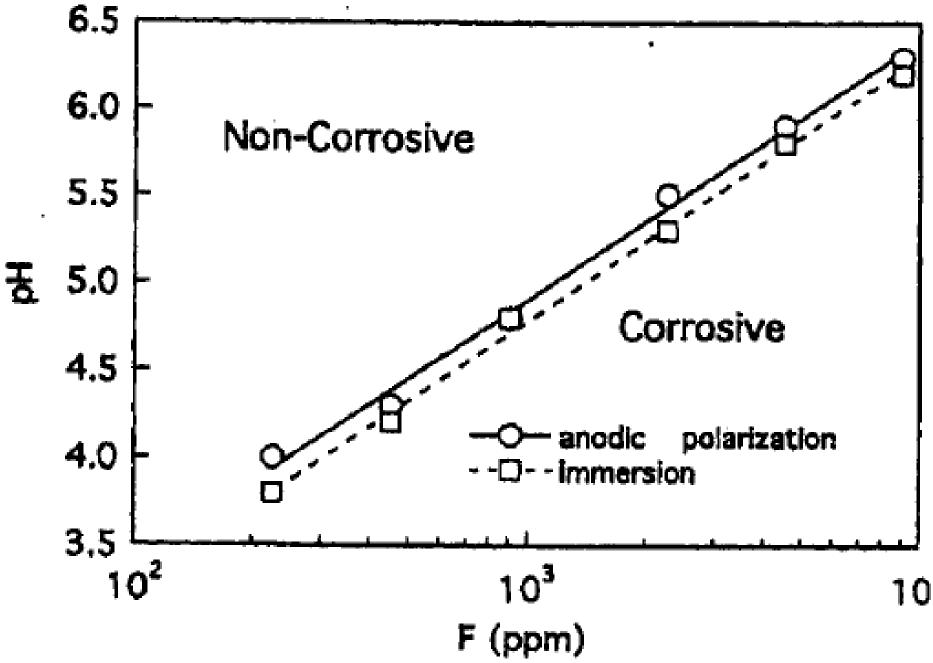

Figure 4-7. The corrosion behavior of Ti with pH and F concentration change [60]

5. Behavior of metals and discussion

5.1 Metals dissolved in liquid phase

The liquid samples after hydrothermal reaction are analyzed by ICP-MS to know the behavior of metals. The result shows only Li is dissolved into liquid phase while Co, Mn, Ni and Cu are not in.

Figure 5-1 presents the Li recovery rate in liquid phase after hydrothermal reaction and Figures 5-2 to 5-4 shows the change of Li recovery rate in different experimental conditions.

Figure 5-1 indicates in average, higher temperature has limited positive effect on the recovery of Li. As temperature rises, Li recovery rate in liquid increases a little.

Figure 5-2 also proves the limited effect from higher temperature in cases without using H_2O_2.

Figure 5-3 shows the utilization of H_2O_2 could increase the Li recovery rate in liquid obviously.

Figure 5-4 shows the effects of reaction time. It indicates that in lower temperature (250℃ and 300℃), the difference of reaction time does not affect too much on the Li recovery. But over 350℃, longer reaction time helps dissolve much more Li into liquid phase. The highest Li recovery rate is 81.42%, appearing under 375℃, 100%H_2O_2, 90min.

About whether dissolving Li into liquid phase is better for recycling or not, in a review [61] about lithium, several Li recovery processes are introduced. Li is mainly collected from Li-bearing ore (solid), clay (solid), brine (liquid) and seawater (liquid). The processes are shown in Figures 5-5 to 5-7. In these real processes, Li is usually transferred into liquid first and then collected as lithium carbonate. Thus, higher Li recovery rate into liquid phase should be better for next recycle treatment in real application. Besides, dissolving Li into liquid is also helpful to separate Li from other metals, reducing the cost of separation (mentioned in 1.3) if they are mixed together.

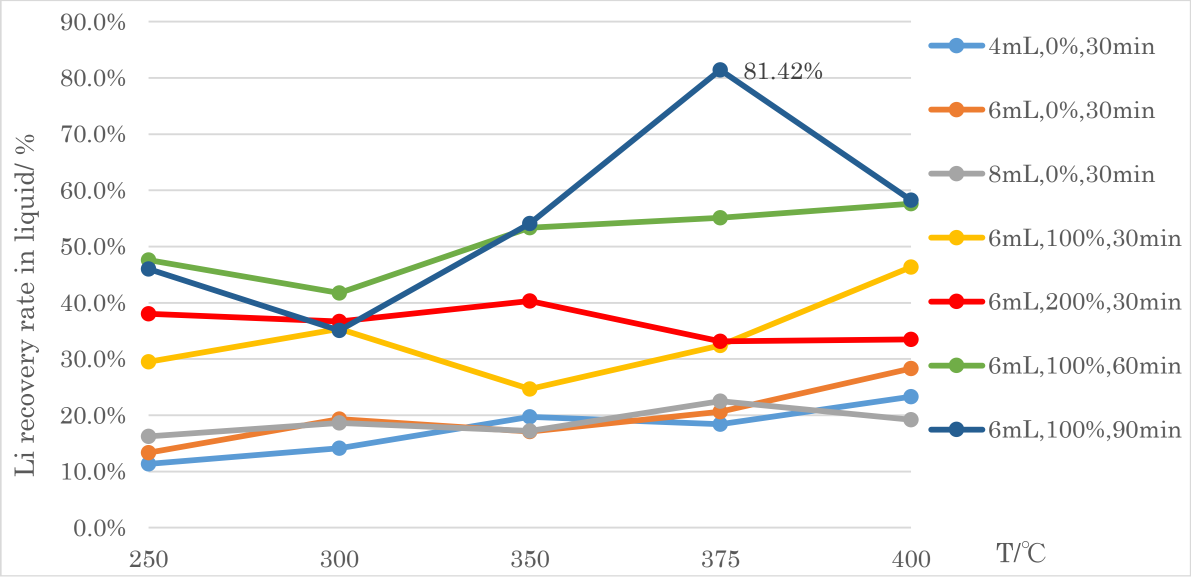

Figure 5-1. Lithium recovery rate in liquid after hydrothermal reaction

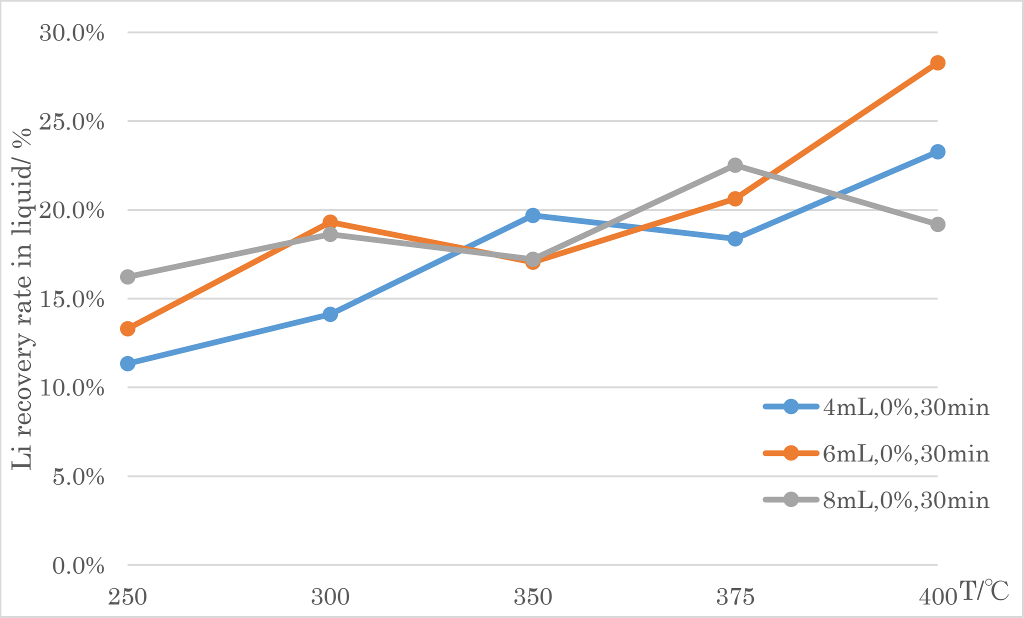

Figure 5-2. Lithium recovery rate in liquid without H_2O_2

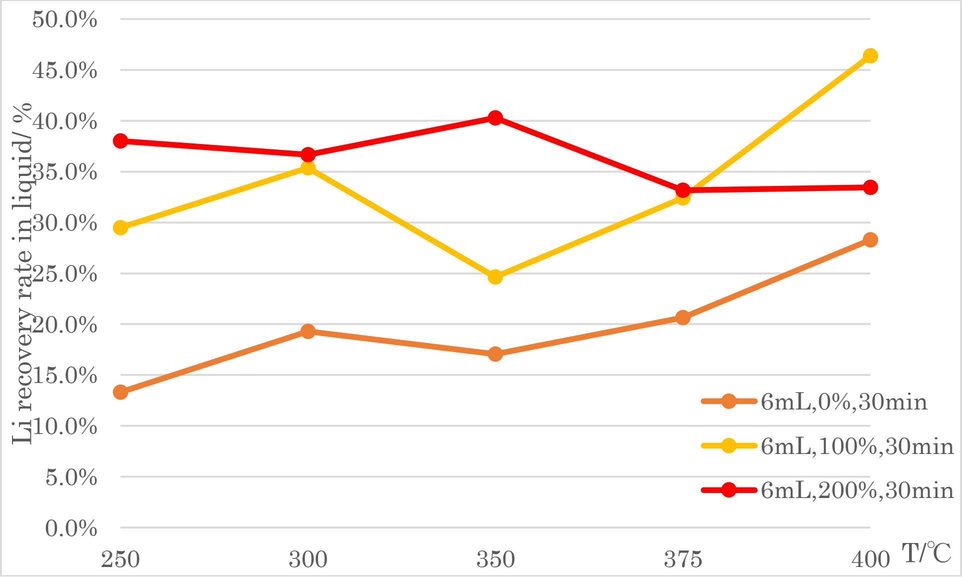

Figure 5-3. Change of lithium recovery rate in liquid with different amount of H_2O_2

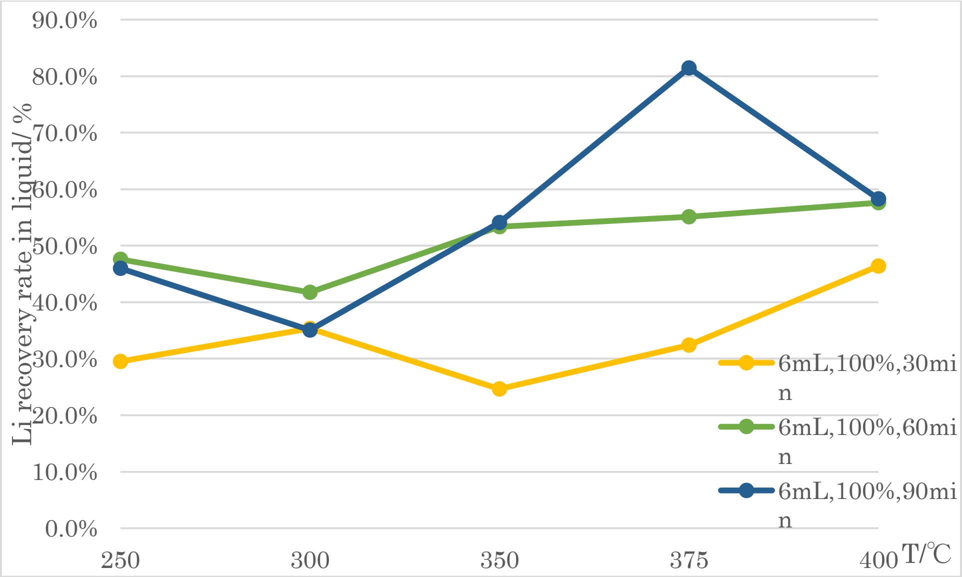

Figure 5-4. Change of lithium recovery rate in liquid with different reaction time

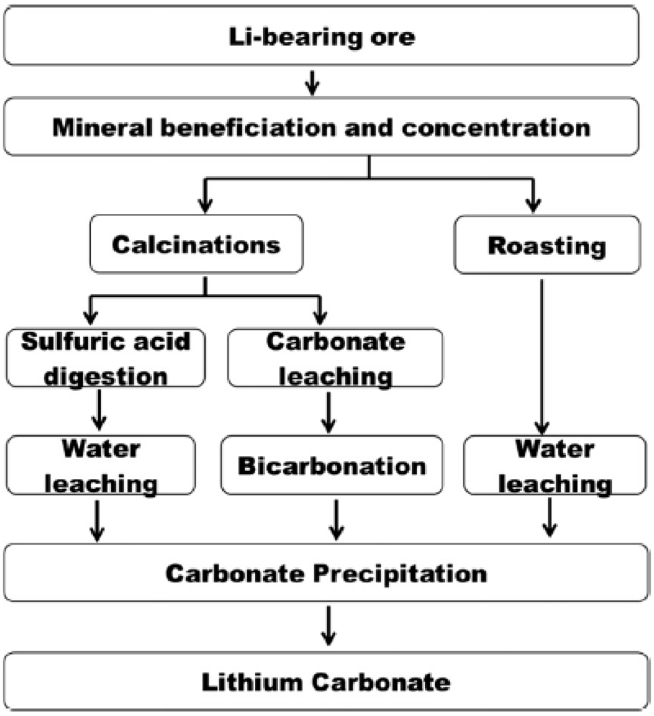

Figure 5-5. Li recovery process from Li-bearing ore [61]

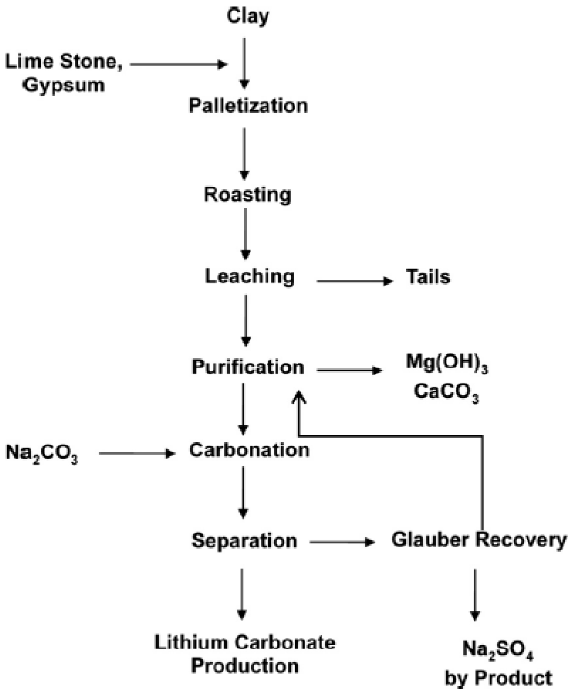

Figure 5-6. Li recovery process from Li-bearing clay [61]

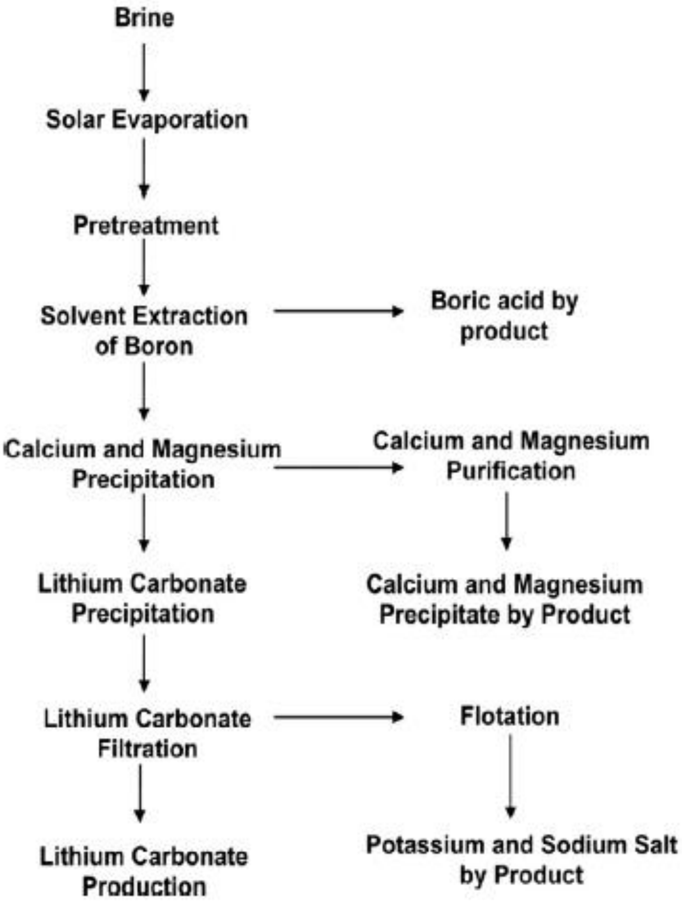

Figure 5-7. Li production technology from brine [61]

5.2 Metals in solid phase

Other target metals in LIB sample (Co, Cu, Mn. Ni) still remain in solid phase after hydrothermal reaction according to the analysis result of ICP-MS. Those metals might just be oxidized in sub- and supercritical water but still exist in solid phase because they could not be dissolved in ambient water without acid. However, because of the existence of fluorine, considering the corrosion of reactor and the experiment safety, acid was not used in this research.

To know the treatment results of metals in solid phase, XRD is used to analyze the solid sample. The procedure is described in 2.5.6 and Figure 5-8 shows the pretreatment result of solid sample before XRD analysis.

Figure 5-9 shows the qualitative XRD analysis result of a solid sample (6 mL H_2O, 250℃, 0% H_2O_2, 30min) and Figure 5-10 describes the metal peaks. It could be known that the peaks around 20 degree and 40 degree are the main peaks of metals. And the highest peak around 25 degree in Figure 5-9 is graphite.

Table 5-1 shows the substance analysis result by XRD. Besides graphite, metal oxide containing Co, Ni, Li and Mn is the main composition. Table 5-1 also shows the substance concentration by Reference Intensity Ratio (RIR) analysis method. However, this quantitative analysis result is not so accurate. For example, Figure 5-11 shows the graphite peaks of powder samples after reaction with 100% H_2O_2, 30min under different temperature. Figure 5-12 shows the RIR analysis result of the same samples. The graphite peaks are quite close, which means the graphite concentration should be similar as well. But the RIR analysis result shows that in the sample under 250℃, there is only 33.7% graphite, about half of the other four samples. Thus, the RIR analysis result is not reliable and the reason might come from the interference of those small peaks of metals.

So, the powder sample could not be quantitatively analyzed. But something could be known through qualitative analysis by comparing main peaks of XRD results.

Figures 5-13 to 5-17 show the main metal peaks around 20 degree of powder samples in different conditions. And the “original” in figures means the LIB sample before hydrothermal reaction. From these figures, it could be known that hydrothermal reaction could effectively decrease the metal peaks around 20 degree, which means decrease the metal concentration in solid powder. And as temperature rises, the peaks become much smaller. Under 375℃ and 400℃, the peak almost disappears.

Figures 5-18 to 5-22 present the main metal peaks around 40 degree of powder samples in different conditions. It is indicated that hydrothermal reaction could decrease the metal peaks around 40 degree. But the peaks only become to about half of the original peak and as temperature rises, the peaks close to 45 degree move to left, smaller degree of XRD. This might mean some reaction or change of the metal substance. The possible reaction product might be NiO according to Table 5-1 but this needs to be confirmed in further research.

To research about the effect of H_2O_2 and reaction time on the metal peaks, Figures 5-23 to 5-27 shows the metal peaks around 20 degree of powder samples in the same temperature. It could be observed that under 250℃ and 350℃, longer reaction time is more effective than the amount of H_2O_2 on reducing metal concentration in powder sample. While under 375℃ and 400℃, the metal peaks are similar, almost disappearing.

Since quite a part of metals disappear from powder sample and do not exist in liquid phase, they are separated from powder by the sieve probably. This means after hydrothermal reaction, a part of metals become larger particles. Although several kinds of metals are still mixed, these larger metal particles could be separated from graphite easily and metal concentration in the particles should be much higher than in waste LIB sample.

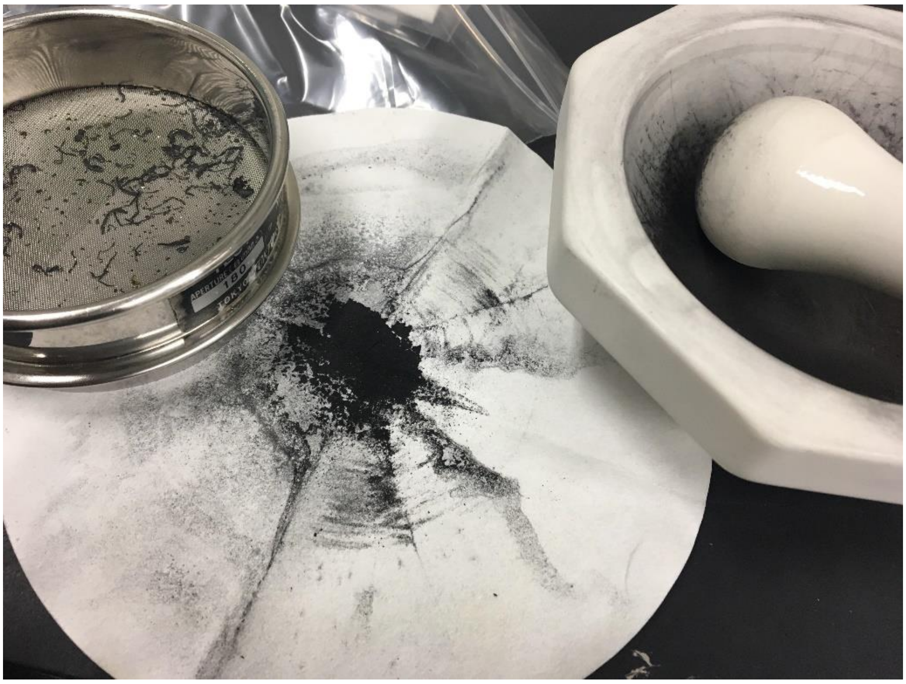

Figure 5-8. Larger particles in 180μm sieve (left),
separated powder sample for XRD analysis (middle) and the mortar (right)

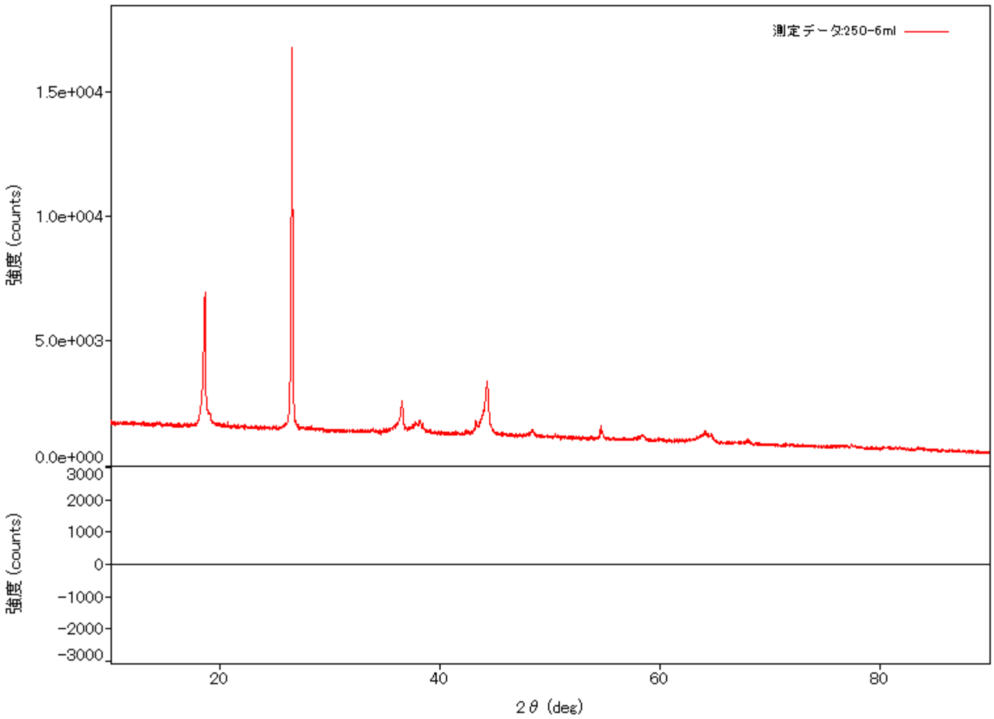

Figure 5-9. XRD analysis result of solid sample (6 mL H_2O, 250℃, 0% H_2O_2, 30min)

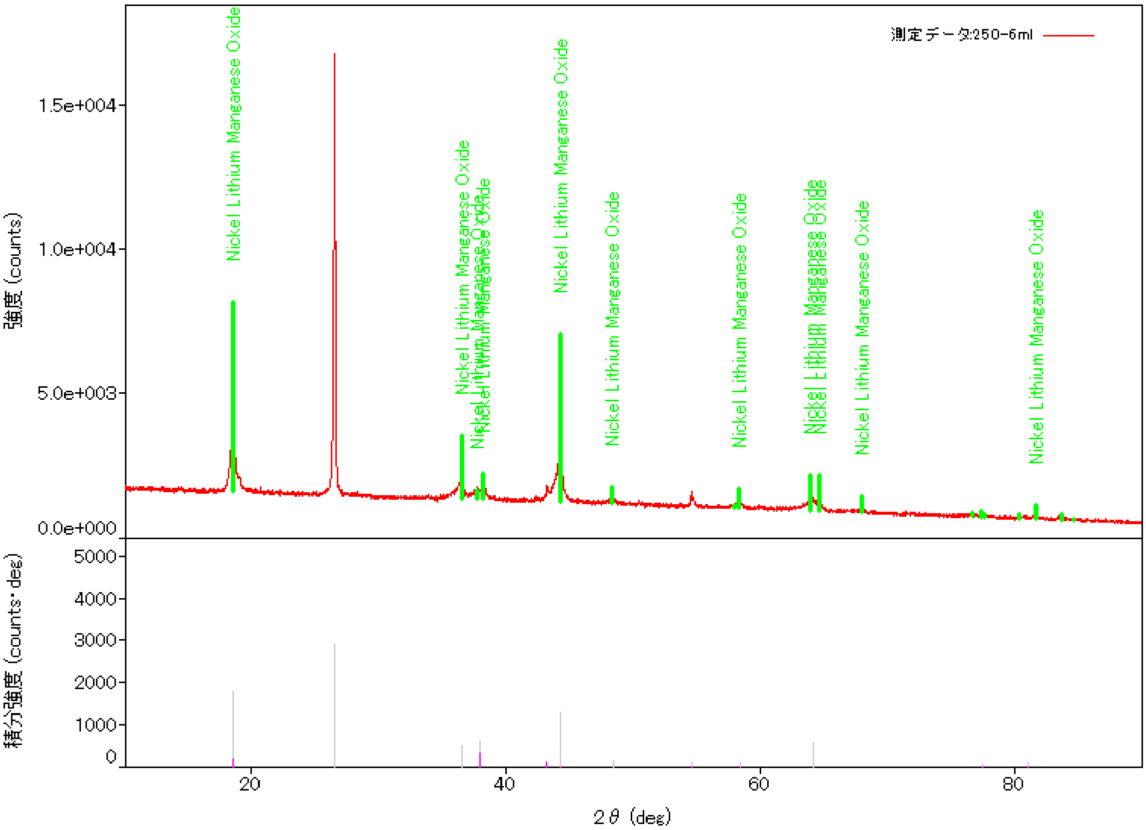

Figure 5-10. Metal peaks in XRD analysis result of solid sample
(6 mL H_2O, 250℃, 0% H_2O_2, 30min)

Table 5-1. Substance analysis result of solid powder samples by XRD

T/°C	H_2O_2/%	Reaction time/min	Solid substance besides graphite
250	0	30	$LiMn_{0.5}Ni_{0.5}O_2$ (61.1%)
300			$Li_{0.75}Ni_{1.25}O_2$ (50.7%), $Co_{1.5}Li_{0.5}O_2$ (17.3%)
350			$Li_{0.68}Ni_{1.32}O_2$ (14.8%)
375			$Co_{0.815}Li_{0.185}O$ (19%), $CoLiO_2$ (3%)
400			NiO (13.2%)
250	100	30	$Li_{1.111}Mn_{0.556}Ni_{0.333}O_2$ (54.9%), $Li_{0.83}Mn_{1.76}O_4$ (11.4%)
300			$Li_{0.6}Mn_{0.5}Ni_{0.5}O_2$ (24.9%), $CoCo_2O_4$ (4.3%)
350			$Li_{0.68}Ni_{1.32}O_2$ (23%)
375			NiO (19.3%), $LiMn_{1.5}Ni_{0.5}O_4$ (5.0%)
400			$NiO_{0.97}$ (36.0%)
250	200	30	$Li_{0.95}Mn_{0.21}Ni_{0.84}O_2$ (22.1%), $LiMn_{1.5}Ni_{0.5}O_4$ (10.1%)
300			$LiMn_{0.5}Ni_{0.5}O_2$ (20.9%), $Li_{1.06}Mn_{1.5}Ni_{0.44}O_4$ (5.0%)
350			$Li_{0.79}Ni_{1.21}O_2$ (44%), $CuMn_{1.496}Ni_{0.504}O_4$ (4.1%)
375			NiO (16%), $Li_{0.91}Mn_{2.09}O_4$ (9.0%)
400			NiO (20.3%), $Li_{0.63}Ni_{1.02}O_2$ (11.9%)
250	100	60	$LiMn_{0.5}Ni_{0.5}O_2$ (45.2%), $LiMn_{1.5}Ni_{0.5}O_4$ (14.3%)
300			$Li_{0.75}Ni_{1.25}O_2$ (27%)
350			$Co_3Li_{1.47}O_{3.72}$ (22.9), diamond (36.0%)
375			NiO (44%), $LiCoO_2$ (18%)
400			NiO (28.8%)
250	100	90	$Li_{0.956}Mn_{2.044}O_4$ (18.9%), $LiMn_{1.5}Ni_{0.5}O_4$ (8.4%)
300			$Li_{0.75}Ni_{1.25}O_2$ (29%)
350			NiO (23%), $Li_{0.68}Ni_{1.32}O_2$ (46%)
375			NiO (54.1%), $Li_{0.49}Ni_{1.01}O_2$ (10.4%)
400			NiO (36.6%)
Original			$Co_{0.2}LiMn_{0.4}Ni_{0.4}O_2$ (57.6%), $Co_{0.4}Mn_{0.6}$ (2.6%)

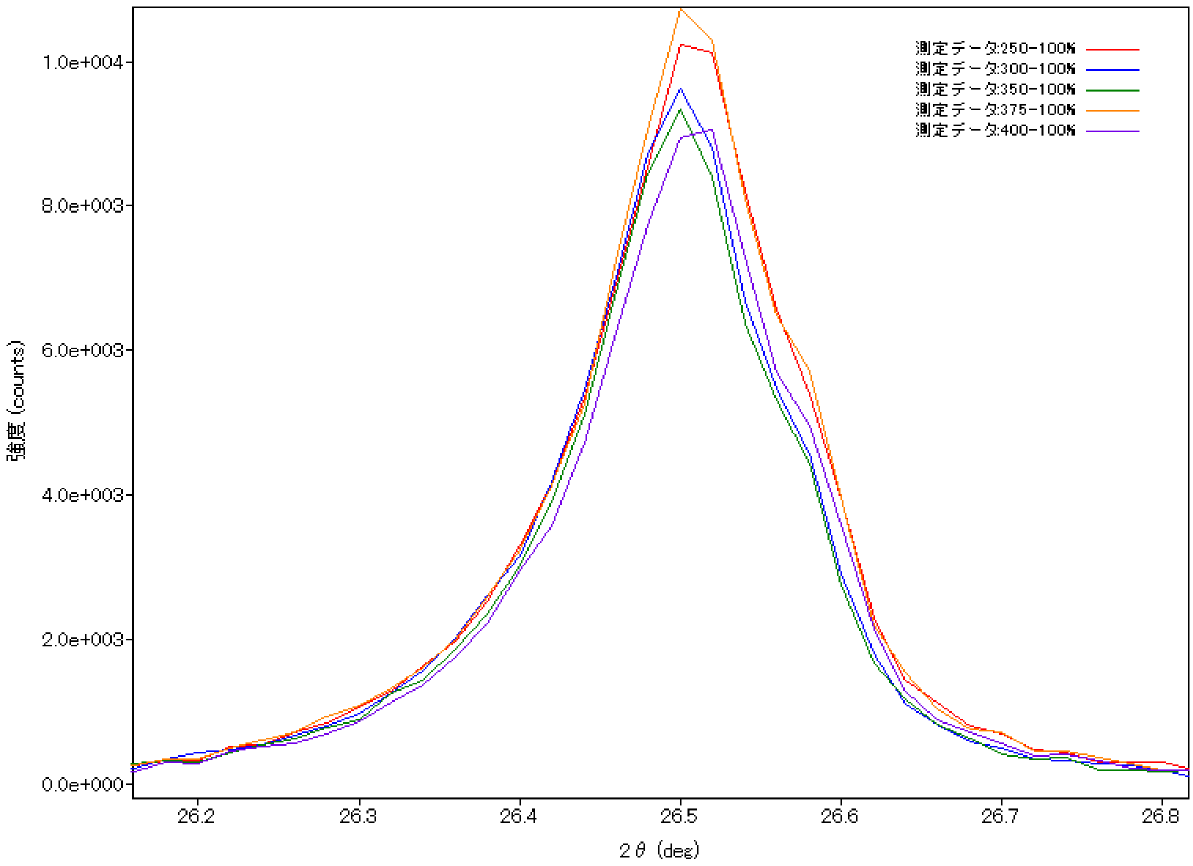

Figure 5-11. Graphite peaks of powder samples after reaction with 100% H_2O_2, 30min

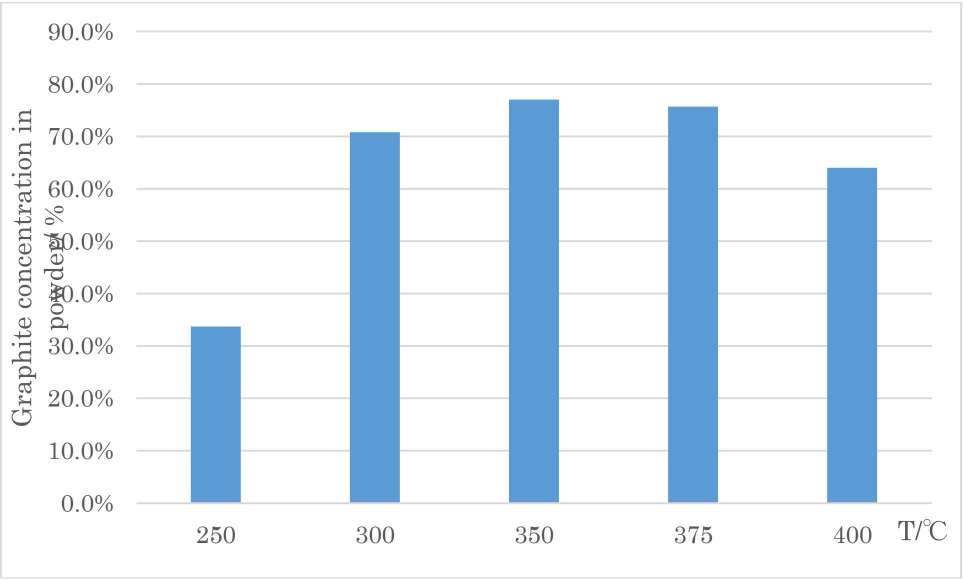

Figure 5-12. Graphite concentration analyzed by RIR method

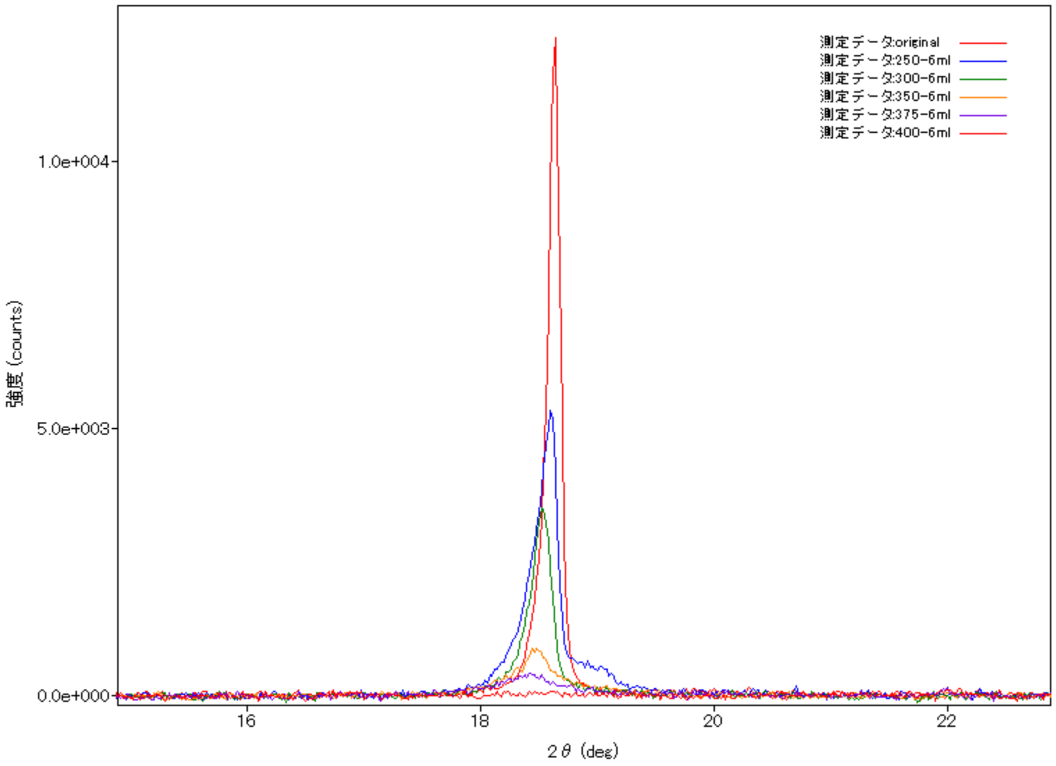

Figure 5-13. Metal peaks around 20 degree of powder samples with 0% H_2O_2, 30min

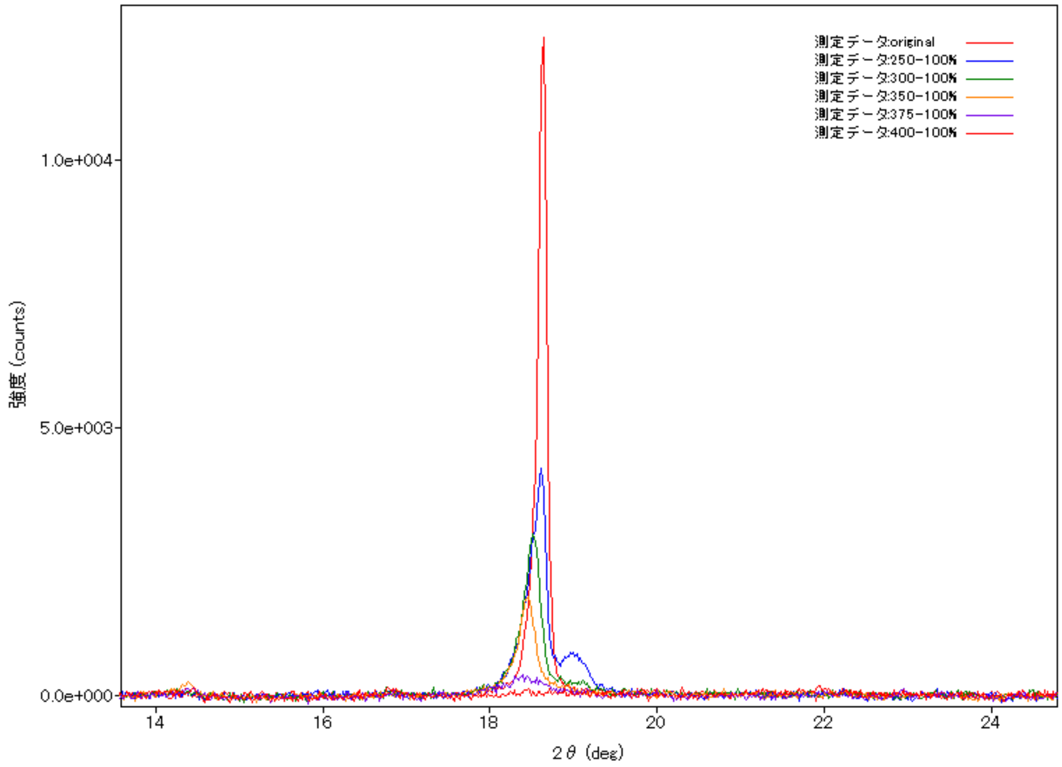

Figure 5-14. Metal peaks around 20 degree of powder samples with 100% H_2O_2, 30min

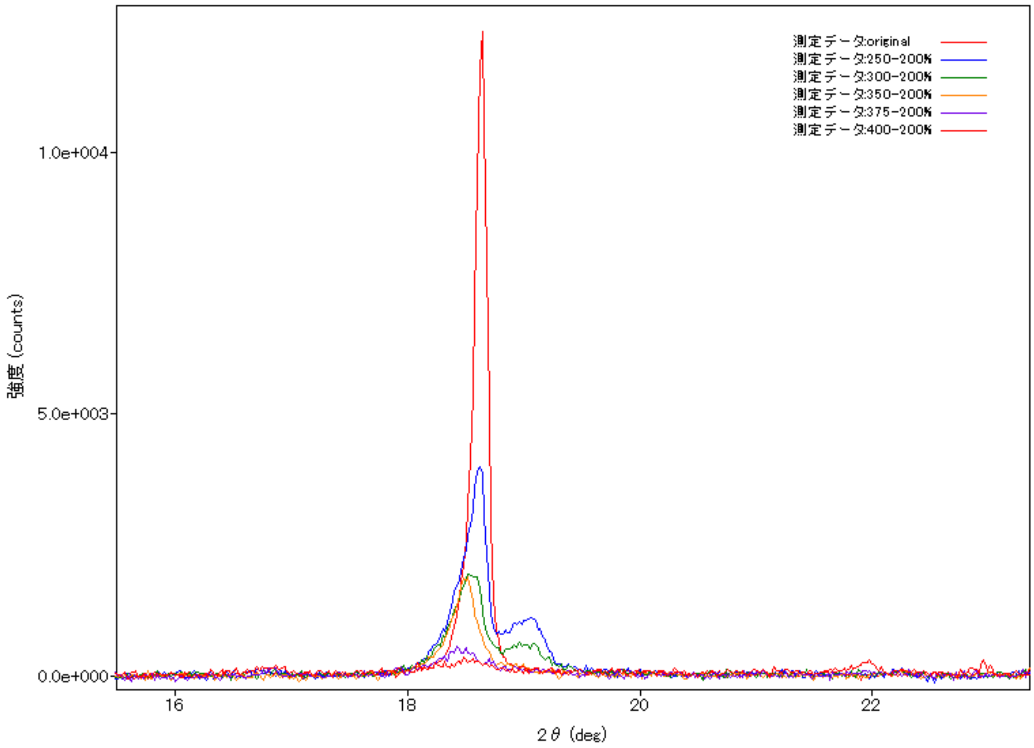

Figure 5-15. Metal peaks around 20 degree of powder samples with 200% H_2O_2, 30min

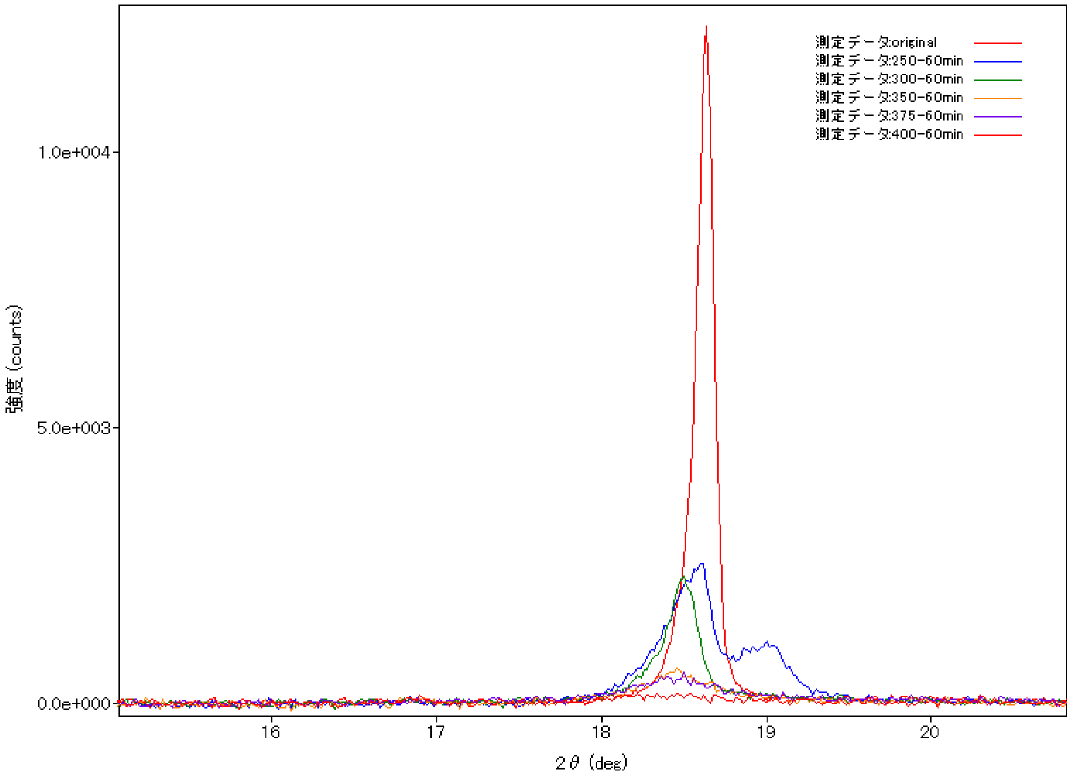

Figure 5-16. Metal peaks around 20 degree of powder samples with 100% H_2O_2, 60min

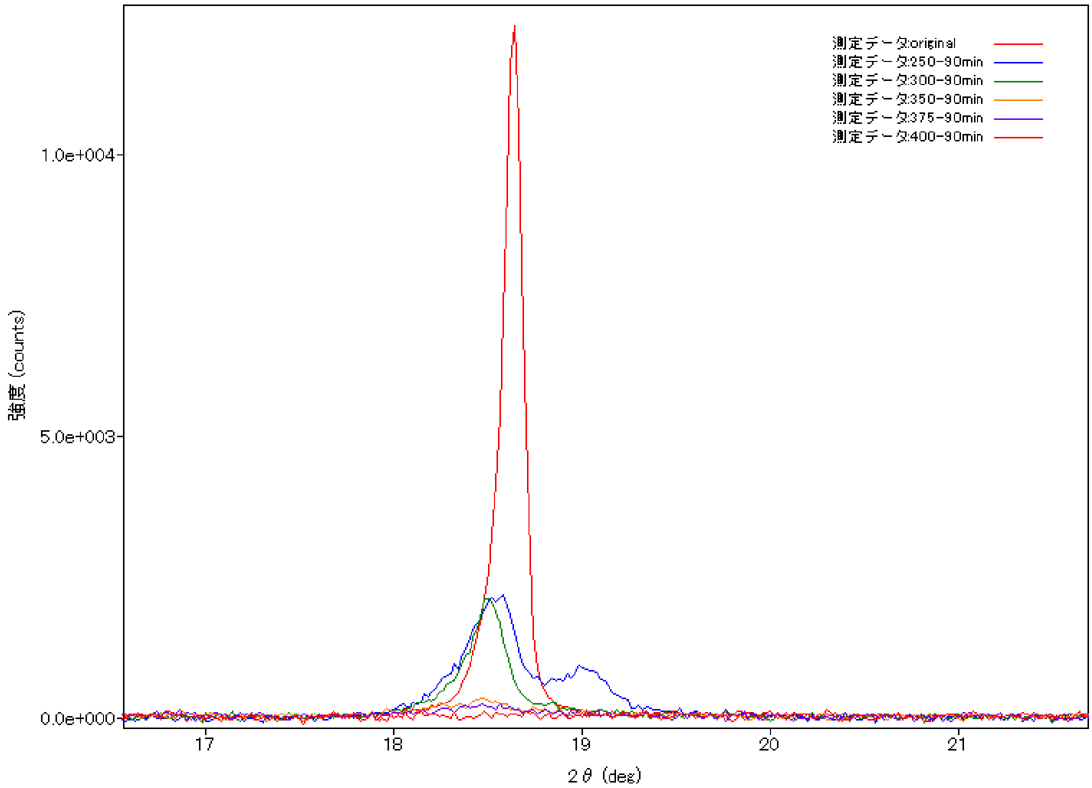

Figure 5-17. Metal peaks around 20 degree of powder samples with 100% H_2O_2, 90min

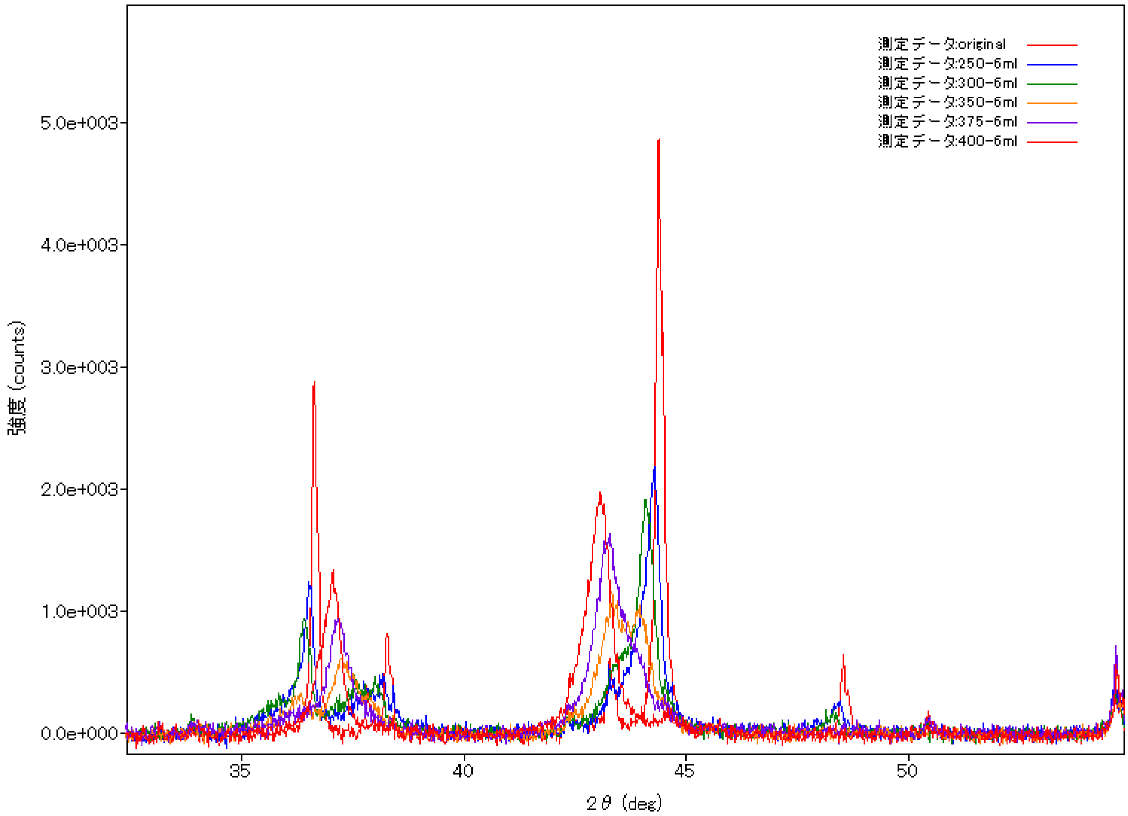

Figure 5-18. Metal peaks around 40 degree of powder samples with 0% H_2O_2, 30min

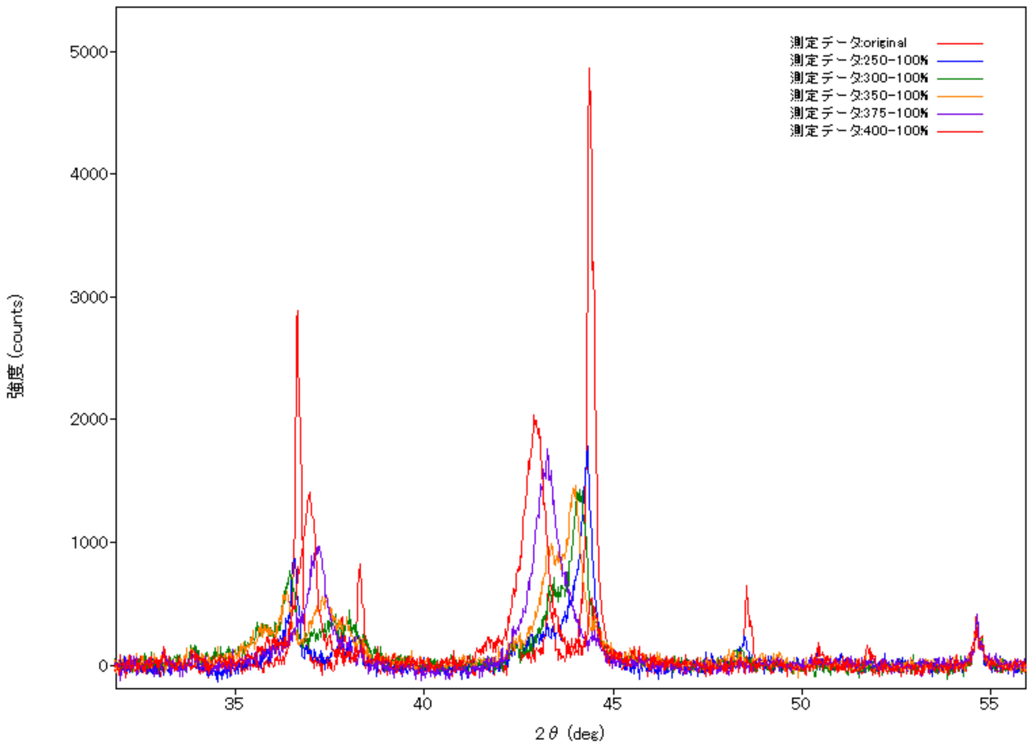

Figure 5-19. Metal peaks around 40 degree of powder samples with 100% H_2O_2, 30min

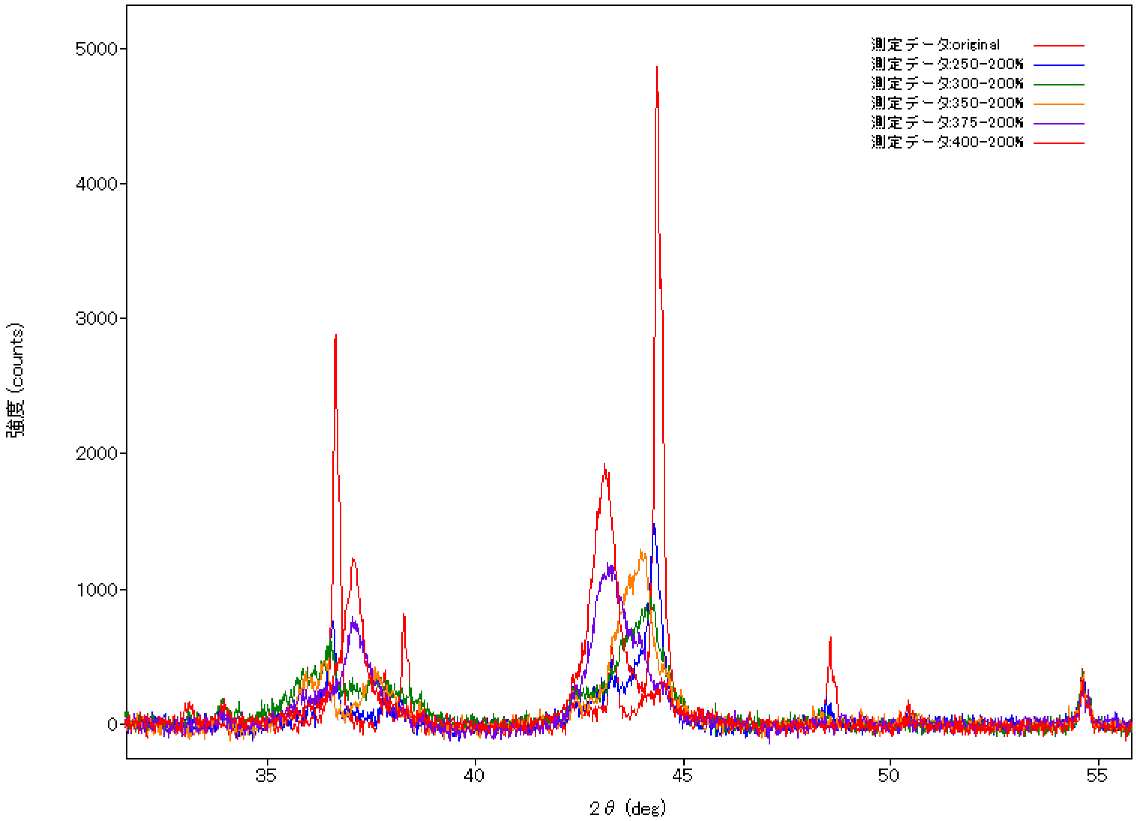

Figure 5-20. Metal peaks around 40 degree of powder samples with 200% H_2O_2, 30min

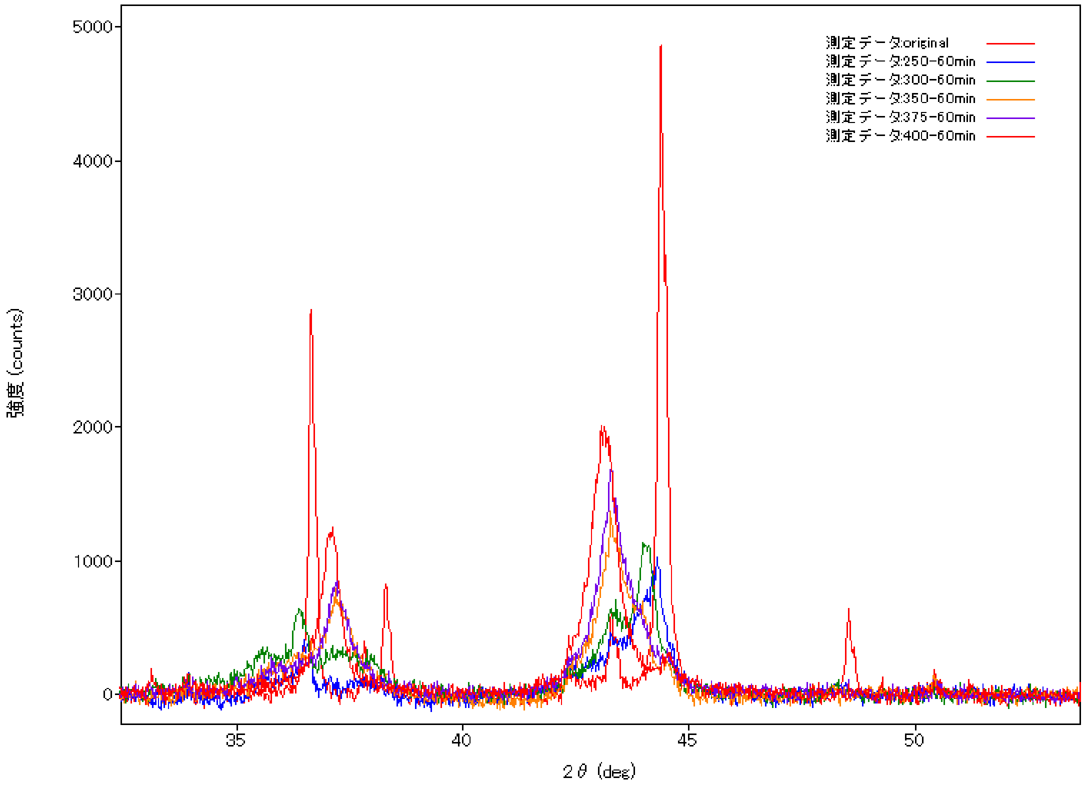

Figure 5-21. Metal peaks around 40 degree of powder samples with 100% H_2O_2, 60min

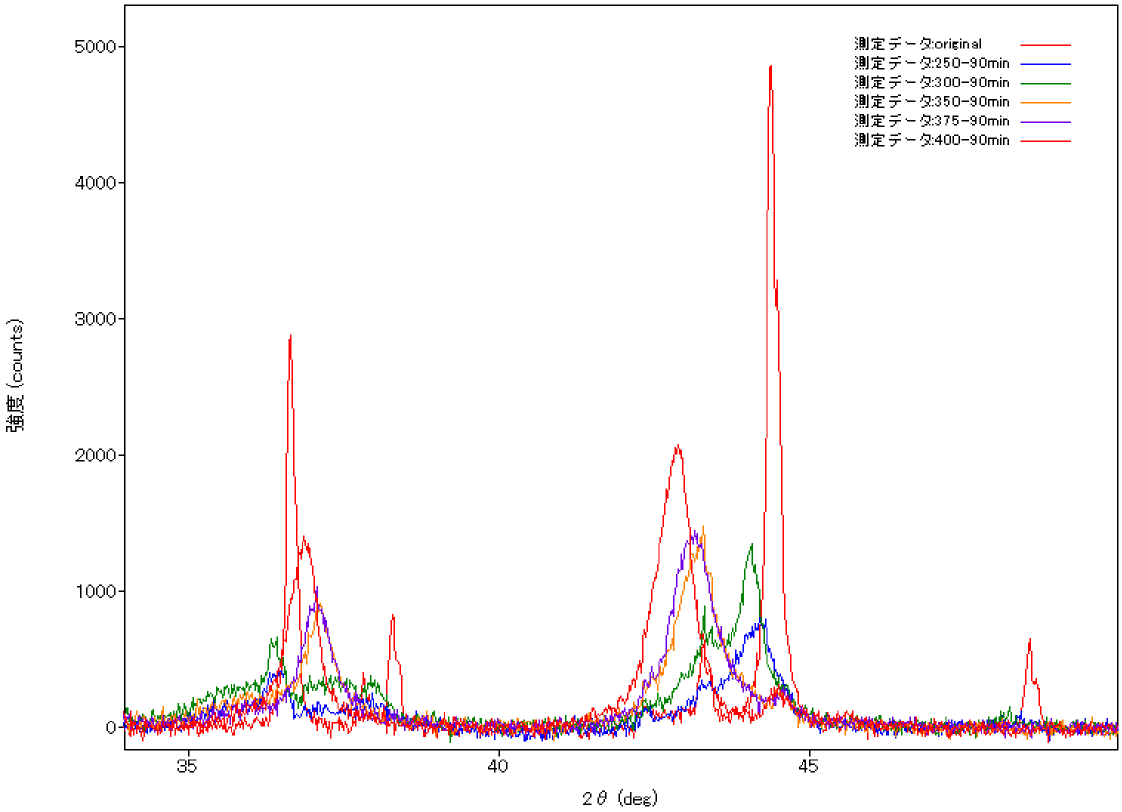

Figure 5-22. Metal peaks around 40 degree of powder samples with 100% H_2O_2, 90min

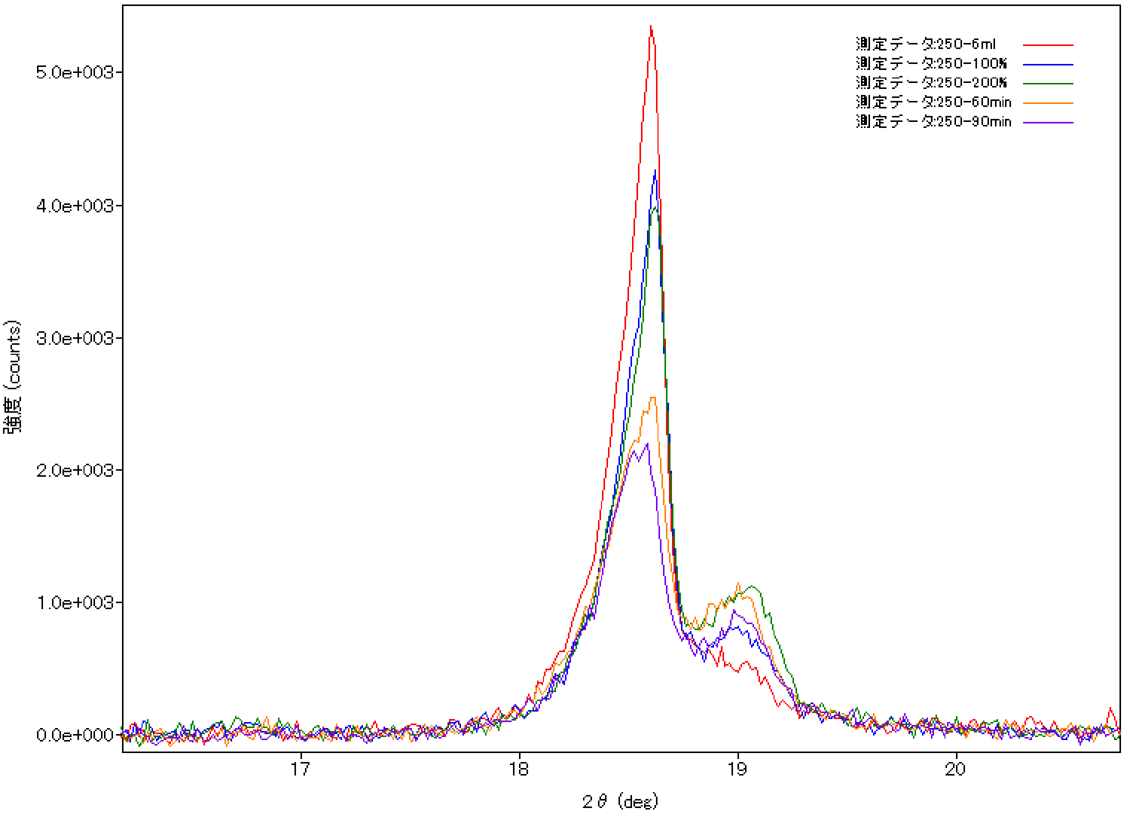

Figure 5-23. Metal peaks around 20 degree of powder samples under 250℃

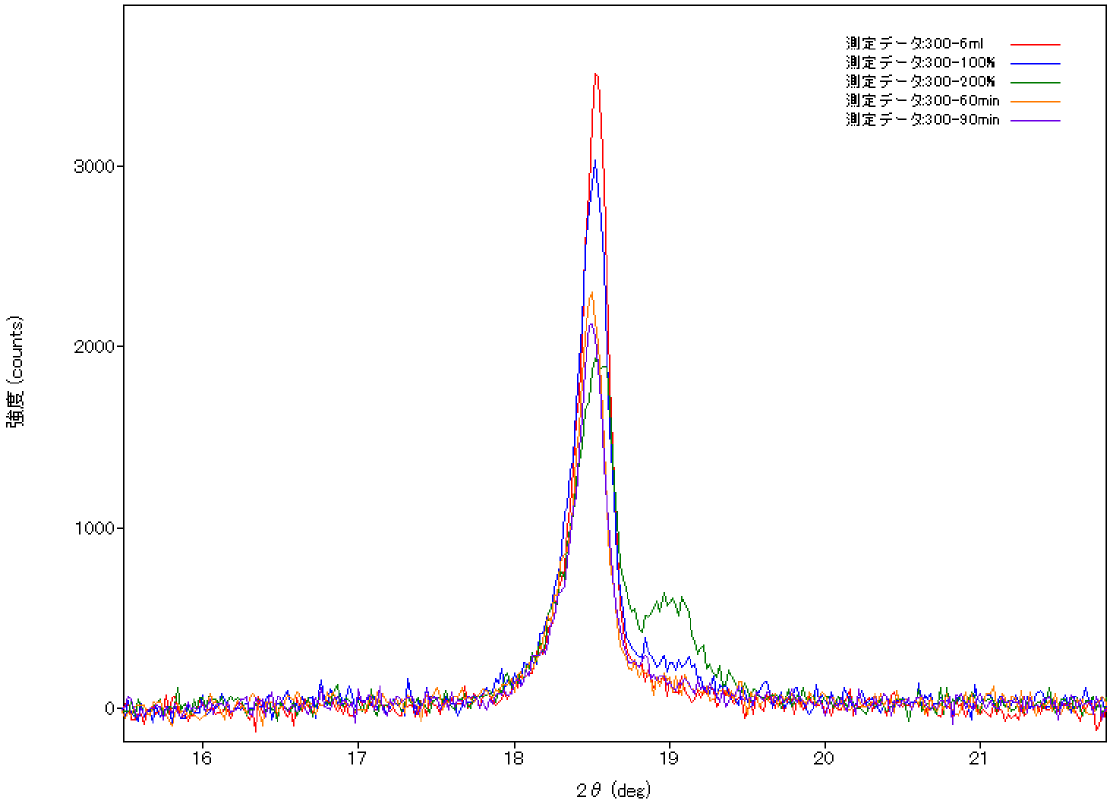

Figure 5-24. Metal peaks around 20 degree of powder samples under 300℃

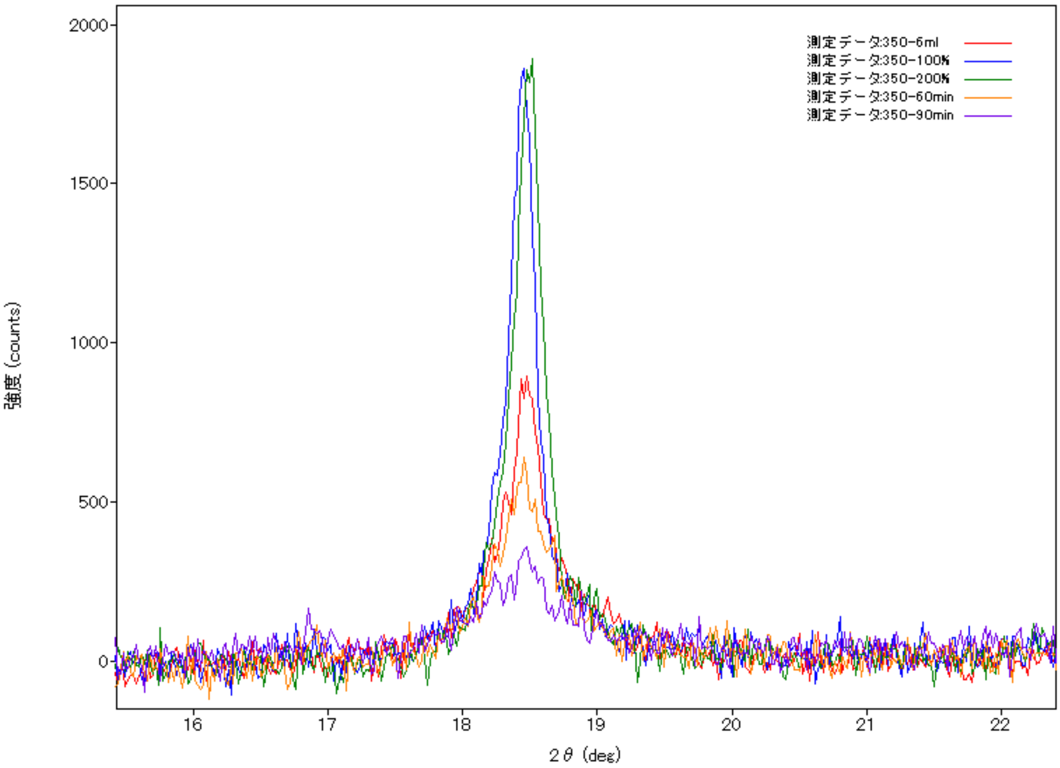

Figure 5-25. Metal peaks around 20 degree of powder samples under 350℃

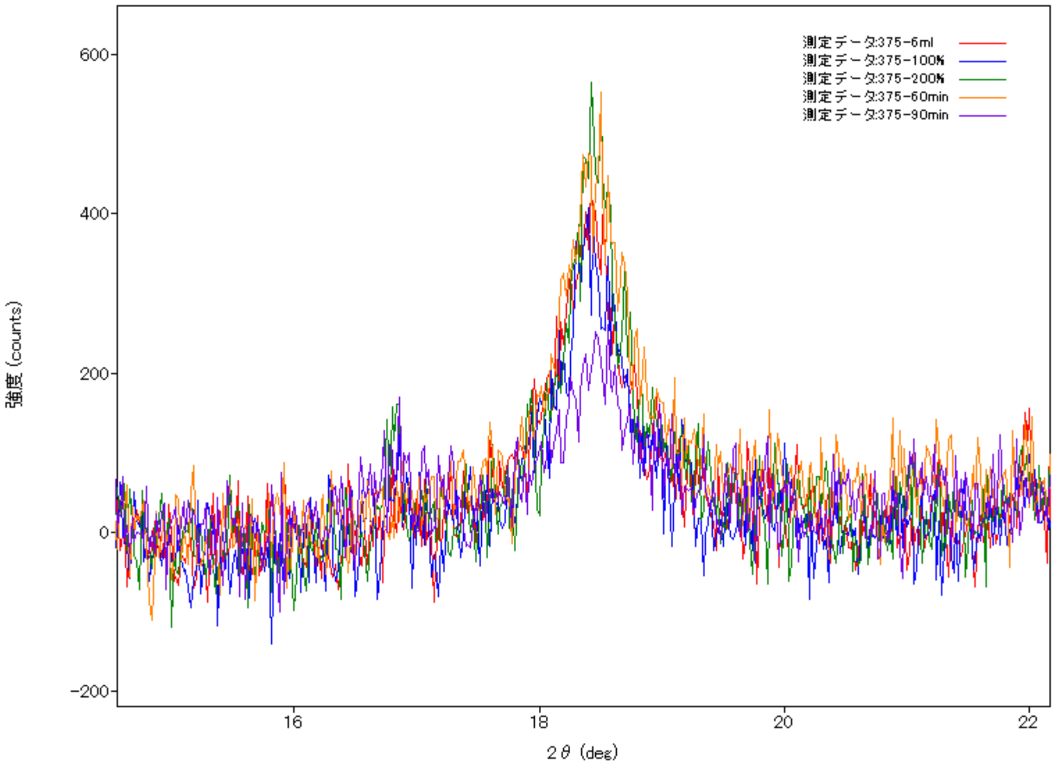

Figure 5-26. Metal peaks around 20 degree of powder samples under 375℃

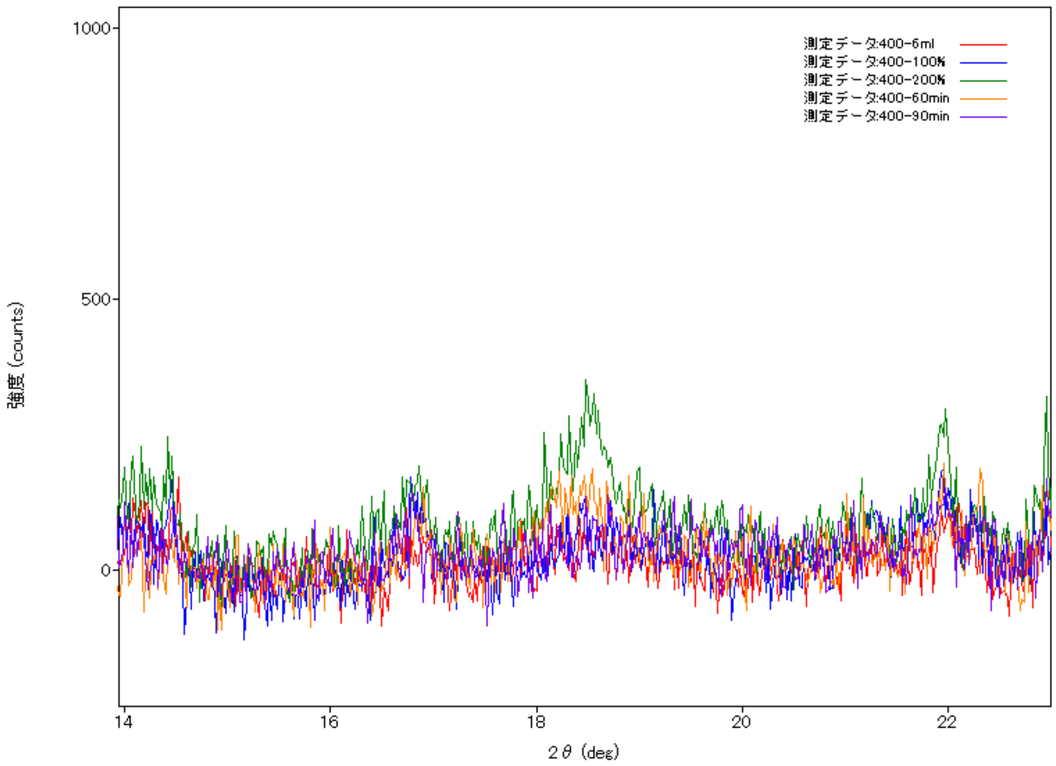

Figure 5-27. Metal peaks around 20 degree of powder samples under 400℃

5.3 Summary and discussion

In this chapter, effects of hydrothermal reaction on metals in waste LIB sample are discussed.

Only Li is dissolved into liquid phase after the reaction. Higher temperature, longer reaction time and the use of H_2O_2 are all positive to dissolve more Li into liquid. The highest Li recovery rate in liquid is 81.42%, appearing under 375℃, 100% H_2O_2, 90min. High Li recovery rate into liquid phase is better for next recycle treatment of Li in real application and helpful to separate Li from other metals, reducing the cost of separation.

To research about the other target metals (Co, Mn, Ni and Cu), XRD is used to analyze the solid powder sample separated from larger particles. But the quantitative analysis of RIR method of XRD is not accurate because of interference of peaks. The qualitative analysis through observing metal peaks indicates that higher temperature, longer reaction time and utilization of H_2O_2 are effective to decrease metal concentration in powder sample. When temperature is over 375℃, a main metal peak in XRD analysis result almost disappeared. The other two metal peaks reduce to around half after reaction. They still exist but one of them shifts in XRD results, indicating some change of metals.

XRD analysis result also proves that as reaction temperature rises, the metal composition also changes. In 400℃, the final products containing metals in powder sample are all NiO in different experimental conditions while Mn, Li, Co disappear.

So, in solid powder sample, a part of metals (Mn, Li, Co) disappeared, might have been forming larger particles, which could be seen as the enrichment of metals and is positive for the whole recycle process. Another part of metals (Ni) remains in powder but some reaction happened. The final reaction product containing metals is NiO.

The possible reaction of the metals in solid phase might be:

$$Co_{0.2}LiMn_{0.4}Ni_{0.4}O_2 \rightarrow NiO + Li_xCo_yMn_zO_a + Li^-_{(aq)}$$

NiO exists in powder while $Li_xCo_yMn_zO_a$ exists in larger particles. Of course, a part of Li exist in liquid phase as ion.

But it needs more experiments to confirm this speculation as well as the composition of larger particles because this conclusion is based on mass balance calculation. For example, both powder and larger particles should be dissolved by acid for ICP-MS to know the metal compositions, calculating the behavior of metals.

6. Conclusions and recommendation

6.1 Conclusion

In this research, hydrothermal experiments are conducted to research about whether hydrothermal method is suitable to treat waste Li-ion batteries, removing organic compounds and separating metal materials.

Chapter 3 discussed behavior of organic compounds. It indicates that in condition of 350℃ with 200% H_2O_2, 30min, 57.86% of organic carbon is separated from metals in solid phase and 28.78% of organic carbon is oxidized to CO_2. This is the best treatment result of organic compounds but is still far from the initial target, 100% removal. The possible reason might be the incomplete utilization of O_2 provided from added H_2O_2. If the rest O_2 after reaction could be completely consumed, more organic carbon should be oxidized to CO_2 and removed. At the same time, the generation of H_2 is also found.

Chapter 4 discussed behavior of hazardous fluorine. It is found that fluorine in electrolyte salts of waste LIB sample could be easily dissolved into liquid phase. The use of H_2O_2 could help accelerate decomposition of PVDF, another fluorine source, and shift this part of fluorine into liquid. The fluorine recovery rate could easily reach 95% under 250℃, 300℃, 400℃ with the use of H_2O_2 but under 350℃ and 375℃, a part of fluorine might react with the materials of reactor, forming solid product. Although nothing dangerous happened during the experiments, it is still necessary to fully understand the corrosion mechanism of fluorine to make sure of security.

Chapter 5 discussed behavior of target metals (Li, Co, Ni, Mn, Cu). Only Li was dissolved into liquid phase. Under 375℃ with 100% H_2O_2, 90min, most Li (81.42%) is dissolved into liquid phase, positive for the next recycle treatment of Li in real application and helpful to separate Li from other metals, reducing the cost of separation.

In solid sample, high temperature, longer reaction time and H_2O_2 make a part of metals form larger particles, which could be seen as the enrichment process of metals and is positive for the whole recycle process. Another part of metals remains in powder (<180μm) but some reaction happened. The final metal product in powder might be NiO but it needs more experiments to confirm as well as the composition of the larger particles.

As a conclusion, hydrothermal method is not suitable to treat waste LIB now because of two main problems:

① Incomplete utilization of O_2 makes the treatment result of organic compounds far from expected.

② Unclearness of the fluorine corrosion to the reactor makes security risk.

Besides, the composition of organic carbon transferred into solid phase, mechanism of the generation of H_2, composition of metal products in larger solid particles and powder are all not clear. The potential explosion of H_2 is also a security risk.

But the separation and enrichment of metals and the generation of H_2 are positive results, deserving further research. In addition, the finding of fluorine corrosion could be seen as a new significant topic for researches about fluorine-containing waste treatment by hydrothermal method.

6.2 Recommendations

To solve the problems mentioned in 6.1, there are some recommendations:

To make full use of O_2 to oxidize organic compounds, another kind of heat device (such as electric furnace) should be used to cover the whole reactor and avoid the loss of heat, ensuring the actual pressure could reach the target pressure and checking in this situation, much more O_2 could participate in the oxidation.

Do experiments to make out the reaction of fluorine and SUS316. Find out the mechanism and analyze the product. This is also meaningful to other fluorine-containing waste treat research by hydrothermal method.

Analyze the organic compounds in liquid sample after reaction.

Conduct experiments with only electrolyte solvent in LIB and only electrode materials in LIB to find out the mechanism of the generation of H_2.

Keep the reactor after reaction far away from heat or fire in case of the H_2 explosion risk

To analyze the final metal products in solid sample, experiments using the same metal materials in LIB could be conducted. Without the interference of graphite and organic solvent, the XRD analysis result might be much clearer and more reliable.

If these problems are all solved and the treatment results are good enough, flow type reactor should be used to see whether it is feasible to be used in real application.

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