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

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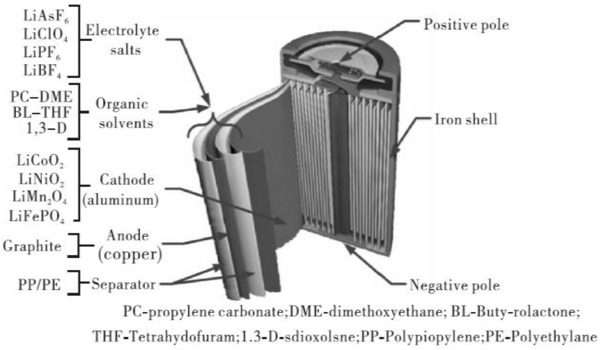
1. Background and Objective

Lithium-ion battery (LIB) is widely used in electronic products and electric vehicles. The production of LIB keeps increasing in recent years. However, its service life is only about 3-5 years. Huge amounts of LIB are being wasted. High-priced metals (Co, Ni, Li) exist in LIB, which are worth recycling. And it also contains volatile organic compounds (VOCs), PVC/PVDF and fluorine, which are harmful during the recycling process. In current technology and related researches, a complete recycle procedure usually includes 4 steps: preparation of waste LIB, material sorting, enrichment of metals, separation and purification of metals. In the second and the third steps, the main methods include high temperature incineration and hydrometallurgy. Though these conventional methods are useful for recycling metals from waste LIB, there are various setbacks. For example, high temperature incineration is energy-consuming and hydrometallurgy requires the use of environmentally harmful solvent. In addition, both methods will release waste gas such as HF and VOCs. [1,2]



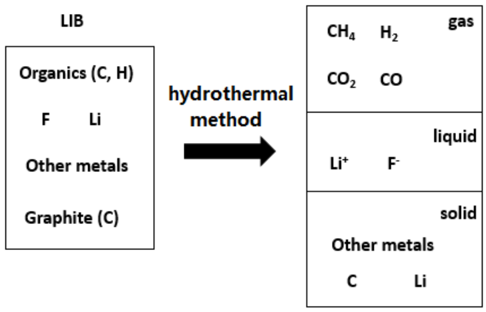


Fig. 1. The structure of lithium-ion battery.[1] **Fig. 2. Expected separation result by SCWO.**

Hydrothermal method is expected to be used in treating waste. For example, supercritical water oxidation (SCWO), utilizing water over 374℃, 22.1 MPa as reaction field, is capable of efficiently treating hazardous and non-hazardous wastes. Organic compounds could be oxidized to CO_2 and H_2O by SCWO [3]. In addition, subcritical water is also able to treat organic waste with lower temperature and pressure [4]. From this, I propose a method of using hydrothermal reaction for the treatment of waste LIB. It is expected that by using hydrothermal method, the organic materials in waste LIB will be completely oxidized to gas phase to effectively separate metals in solid residue or dissolved in liquid phase as ion. The benefits of hydrothermal method include avoiding the use of organic solvents, release of waste gas or production of waste acid and alkali. Furthermore, the required temperature (<450°C) is much lower compared to conventional methods (>600℃), which is energetically more efficient. In addition, some fuel gas (CH_4 and H_2) may also be generated according to supercritical gasification, which could be collected for energy reuse. [5][6]

The aim of this research is to study the compatibility of hydrothermal method for effective treatment of waste LIB. Batch experiment was conducted to study on the effects of hydrothermal reaction on waste LIB where metal recovery, oxidation of organic compounds and gas production were analyzed. Continuous recommendation will be suggested based on the findings in the future.

2. Experiment method

The figure of the whole experiment flow and batch-type reactor (inner volume: 23.303 mL) are shown in Fig. 3 and Fig. 4. For pretreatment, LIB was cut by electric sew to remove the iron shell. Then, a food mixer was used to crush the substance inside into powder and ribbon. 0.3 g pretreated LIB sample (0.2518 g powder and 0.0482 g ribbon) was put into the reactor with H_2O and oxidizing agent (H_2O_2). The reactor was put into salt bath, which could provide sub- and supercritical conditions. Reaction temperature is 250 °C~400 °C. Amount of added H_2O is 4 mL, 6 mL and 8mL. Amount of added H_2O_2 is 0%, 100% and 200% of demand O_2 to oxidize all organic carbon in waste LIB. Reaction time is 30 min, 60 min, 90 min.

After the reaction and cooling down, the valve was opened and gas was introduced into the gas sampling system. Liquid sample and solid sample were separated by filtration later.

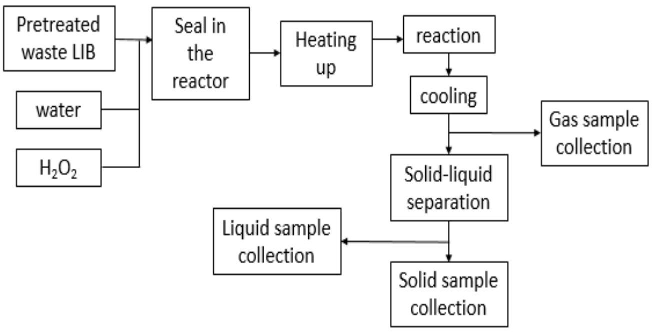


Fig. 3. Experiment flow.

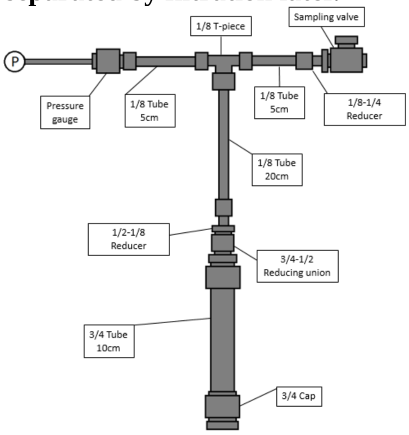


Fig. 4. Figure of the reactor.

3. Analysis method

To analyze the initial metal contents in waste LIB before hydrothermal reaction, metal dissolution is necessary. 5 mL HNO_3 and 3 mL H_2SO_4 were added into 0.5 g waste LIB sample and heated for 5 h. Then, the metal containing solution was analyzed by ICP-MS.

Total C, H in waste LIB were analyzed by CHN coder and F was analyzed by Combustion-IC method in Microanalytical Lab in Hongo Campus.

After hydrothermal reaction, gas sample (H_2, CO, CO_2, CH_4, O_2) was analyzed by gas chromatography (GC-TCD). F in liquid was analyzed by ion chromatography (IC). Organic carbon in liquid phase was analyzed by TOC analyzer. Metals in liquid phase (Li, Co, Ni, Cu, Mn) were analyzed by ICP-MS while metals in solid phase were analyzed by XRD in X-Ray Analysis Laboratory of the Institute for Solid State Physics.

4. Results and discussion

4.1 Behavior of organic compounds

Fig. 5 shows the carbon gasification efficiency and Fig. 6 shows the carbon separation rate (carbon in gas and liquid phase). In hydrothermal reaction, the utilization of H_2O_2 could help oxidize more organic carbon in waste LIB sample and separate it from metals in solid phase. In lower temperature, longer reaction time could promote CGE and carbon separation rate a little but in higher temperature, it makes negative effects. The highest carbon separation rate (57.86%) appears under 350°C with 200% H_2O_2, 30 min. In addition, under 250°C with longer reaction time (60 & 90 min) and 100% H_2O_2, carbon separation rate (51.70% & 50.24%) is also attractive. So, both higher temperature with more H_2O_2 and lower temperature with longer reaction time are positive to decompose organic compounds and to separate them from metals in solid phase, which is expected in the research. But much higher temperature

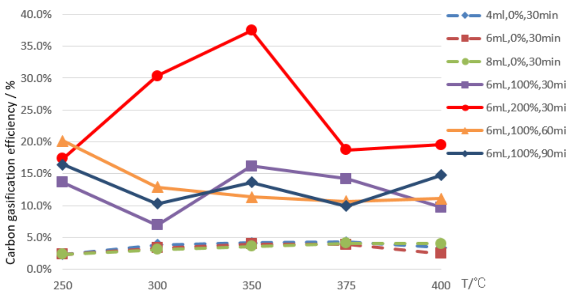


Fig. 5. Carbon gasification efficiency.

and much longer reaction time might be negative, transferring organic compounds to solid phase while the composition of this part of carbon is unknown.

At the same time, H_2 and CH_4 also generated after the reaction. However, with the use of H_2O_2 and longer reaction time, hydrogen gasification efficiency decreased as shown in Fig.7. So, the condition promoting organic carbon separation is not good for hydrogen gasification. Although H_2 and CH_4 could promote economic benefits as fuel gas, it is not the main target in this research. So, considering the treatment results of organic compounds, the optimum experimental condition to treat organic compounds is 350℃ with 200% H_2O_2, 30min.

However, even in the best condition, the carbon separation rate is still far from 100% because of the incomplete utilization of O_2 from H_2O_2 probably. To get better treatment result, better experiment device may be necessary.

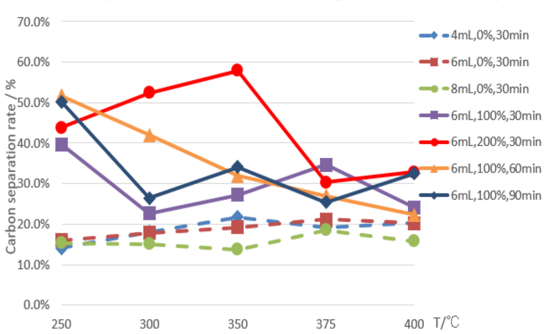


Fig. 6. Carbon separation rate.

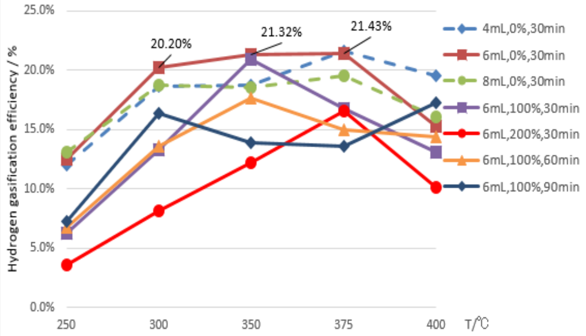


Fig. 7. Hydrogen gasification efficiency.

4.2 Behavior of fluorine

Fig. 8 shows fluorine recovery rate in liquid after hydrothermal reaction. High fluorine recovery rate in liquid phase means the decomposition of PVDF (solid) in waste LIB sample and 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 that fluorine in waste LIB sample could be easily recovered into liquid phase under high temperature (400°C). The use of H_2O_2 seems able to accelerate the decomposition of PVDF, increasing fluorine recovery rate in lower temperature (below 350°C).

However, based on the sudden decrease of F recovery rate under 350°C with H_2O_2, high temperature and H_2O_2 might lead to fluorine corrosion of the reactor, forming fluorine-containing solid and causing security risk. Thus, the corrosion mechanism and product should be researched further to guarantee the safety both in experiments and real application.

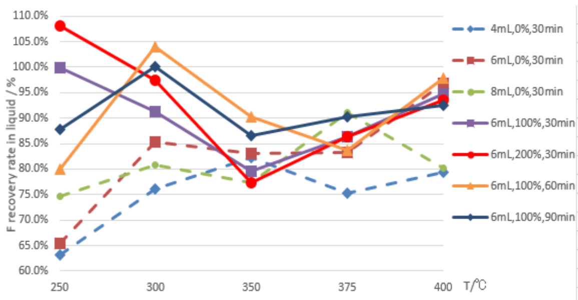


Fig. 8. Fluorine recovery rate in liquid.

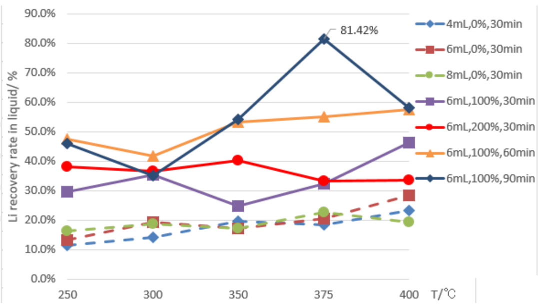


Fig. 9. Li recovery rate in liquid.

4.3 Behavior of metals

According to ICP-MS analysis result of dissolved metal ion, only Li was dissolved into liquid. Fig. 9 presents the Li recovery rate in liquid after hydrothermal reaction. It is found that 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°C, 100%H_2O_2, 90min. According to some reference [7], high Li recovery rate in 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. The qualitative analysis through observing metal peaks indicates higher temperature, longer reaction time and use of H_2O_2 are effective to decrease metal concentration in powder sample. When temperature is over 375℃, a main metal peak (around 20 degree)in XRD analysis result almost disappeared. The other two metal peaks (around 40 degree) reduce to around half after reaction. They still exist but one peak moved in XRD results, indicating some change and reaction of metals. As for the disappeared part of metals, they might form larger particles which was separated from powder for XRD analysis. This could be seen as the enrichment of metals and is positive for the whole recycle process.

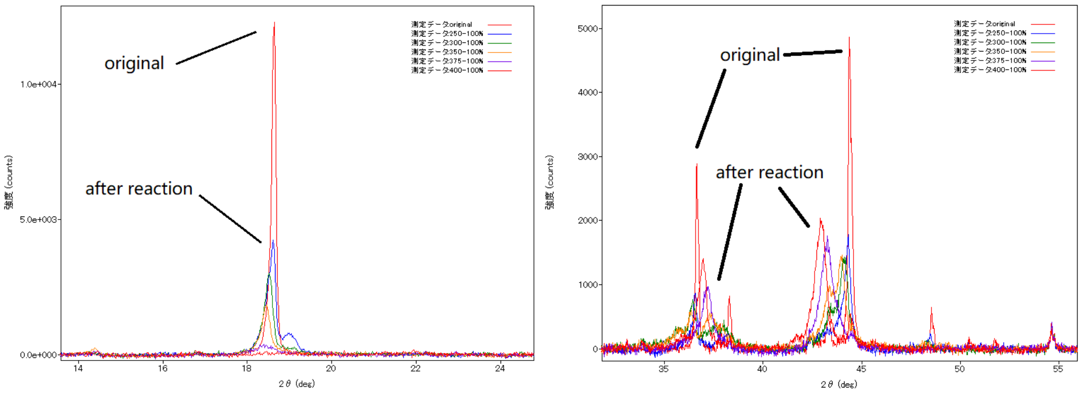


Fig. 10. Metal peaks around 20 and 40 degree of powder samples with 100% H_2O_2, 30min.

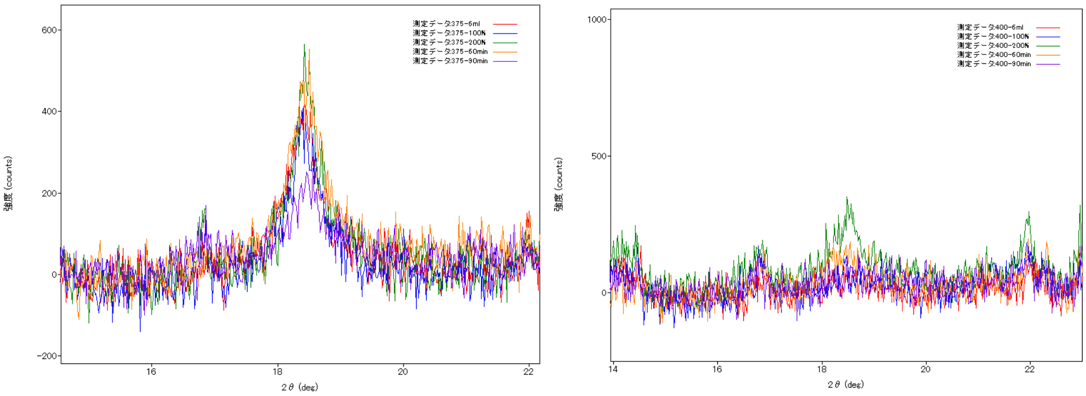


Fig. 10. Metal peaks around 20 degree of powder samples under 375 ℃ and 400 ℃.

5. Conclusions

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 target.

(2) Unclear of the fluorine corrosion to the reactor makes security risk.

But the enrichment of metals and the generation of H_2 are positive results, deserving further research.

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