Extraction of Lithium by-products from electrolyte salt using acetic acid without emitting toxic gases

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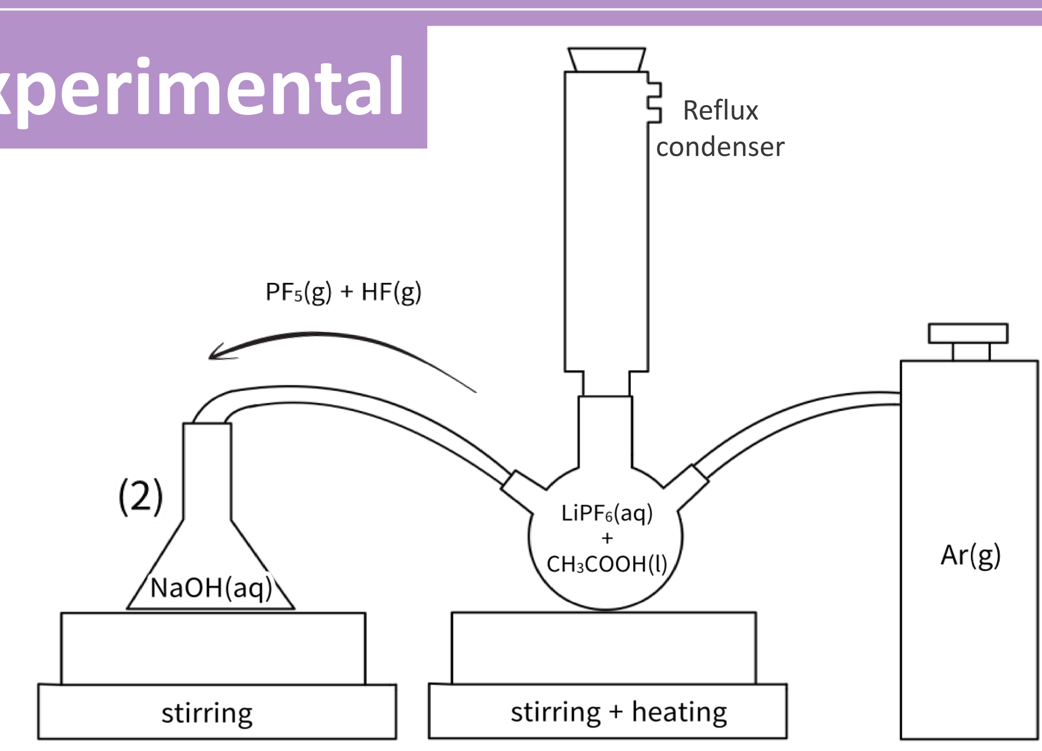
Introduction

- Recycling process of the used-battery is mainly focused on obtaining valuable metals in cathode by using inorganic acid which is harmful to the environment.
- Research on used-electrolyte recycling is insufficient, also few research has been conducted on handling the harmful gas generated through the recycling.
- In our study, we retrieved Li, F from $LiPF_6$, HF to CH_3COOLi, NaF by using acetic acid which is environmental-friendly organic acid.
- Through this process, no harmful gas is emitted and most of Li can be collected.

Experimental



▶ Reaction Mechanism

1) $LiPF_6(aq.) + CH_3COOH(l) \rightarrow HF(g) + CH_3COOLi(aq.) + PF_5(g)$

2) $HF(g) + NaOH(aq.) \rightarrow NaF(s) + H_2O(l)$

$CH_3COOH(l) + NaOH(aq.) \rightarrow CH_3COONa(aq.) + H_2O(l)$

$PF_5(g) + 4H_2O(l) \rightarrow H_3PO_4(aq.) + 5HF(g)$

$H_3PO_4(aq.) + 2NaOH(aq.) \rightarrow Na_2HPO_4(aq.) + 2H_2O(l)$

▶ Reaction Condition

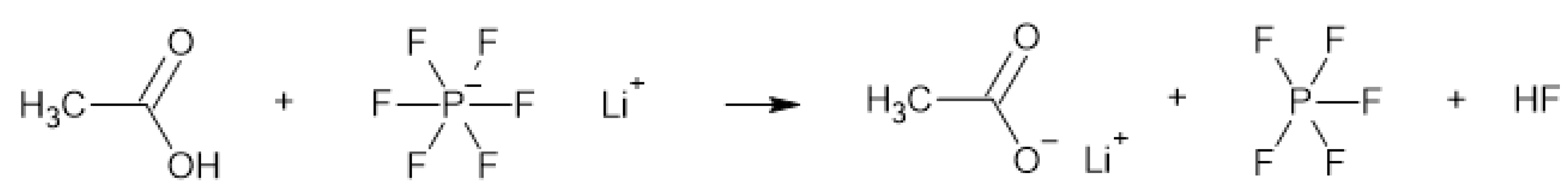
Reaction time : 3 hour

Reaction temperature : 80 ℃, 100 ℃

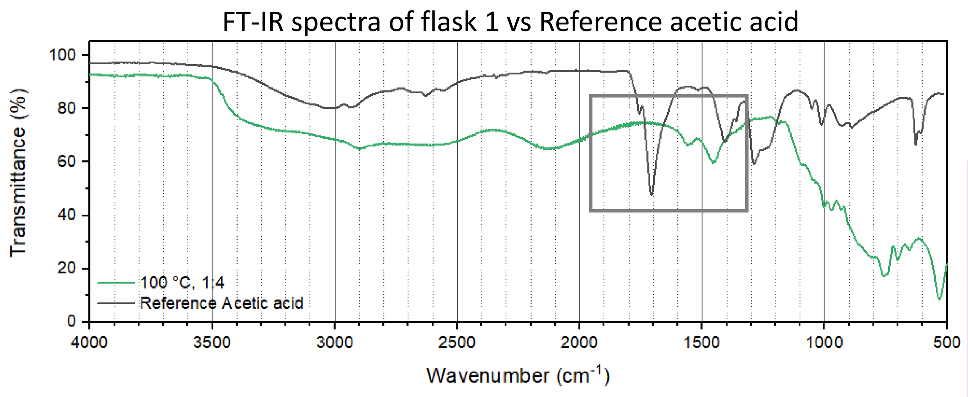
Reaction molar ratio : $LiPF_6 : CH_3COOH = 1:2, 1:4$

Results & Discussion

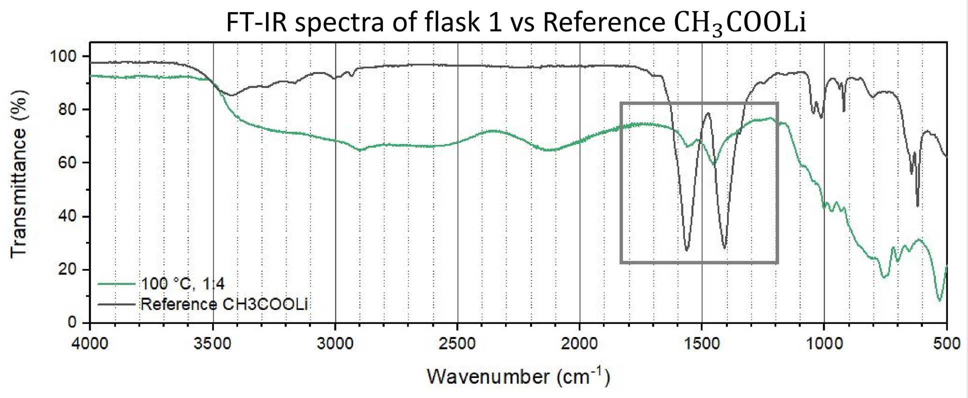
▶ Flask (1)



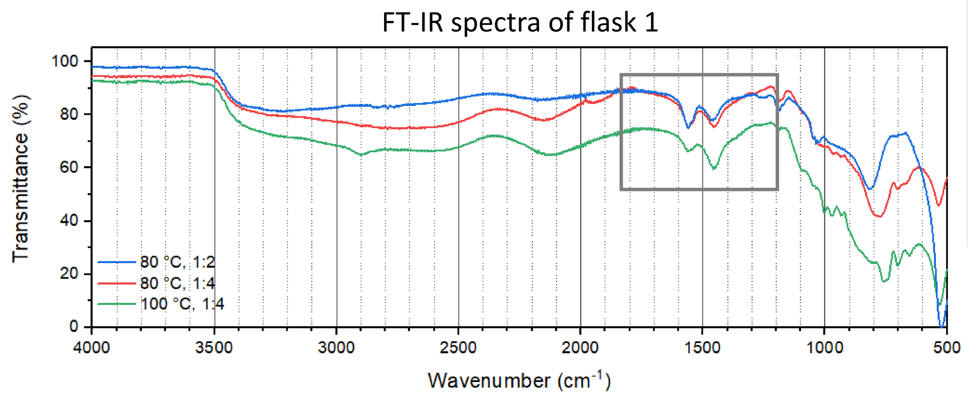
FT-IR spectra of flask 1 vs Reference acetic acid



FT-IR spectra of flask 1 vs Reference CH_3COOLi



FT-IR spectra of flask 1



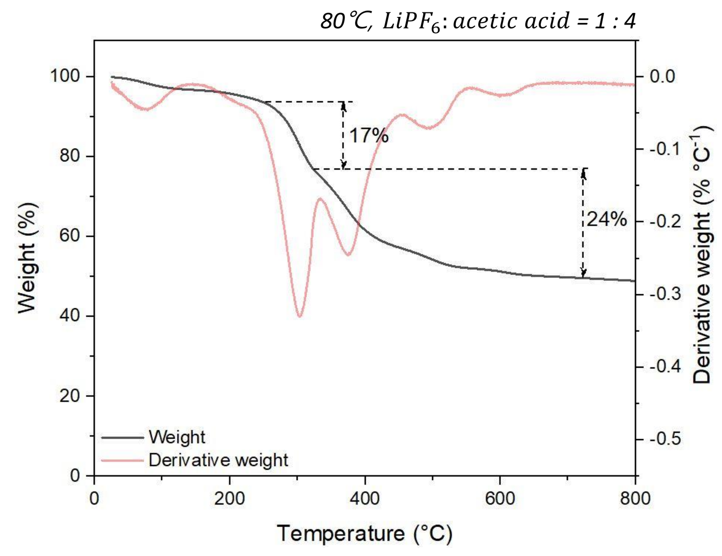
▶ FT-IR Analysis

Table.1 FT-IR data of flask 1

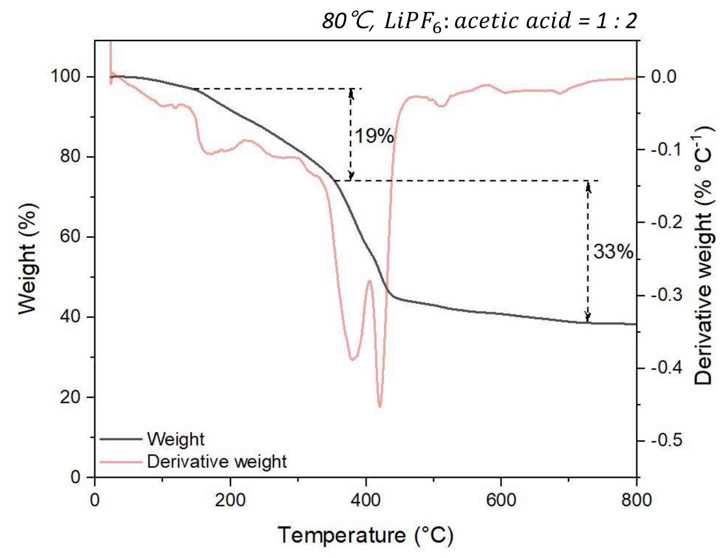
Acetic acid (cm^{-1})	Experimental (cm^{-1})
1759	1564
1709	1460

- Upon addition of Li salt, a new peak is expected to appear at lower wavenumbers because of the $C=O \cdots Li^+$ interaction.[1]
  $\therefore LiPF_6(aq.) + CH_3COOH(l)$
  $\rightarrow HF(g) + CH_3COOLi(aq.) + PF_5(g)$
- Even if the reaction conditions change, the same substances can be seen from the experiments.

80℃, $LiPF_6$: acetic acid = 1 : 4



80℃, $LiPF_6$: acetic acid = 1 : 2



▶ TGA Analysis

[Theory]

- 200~300 ℃ : $2CH_3COOLi \cdot nH_2O\ (100\%) \rightarrow 2CH_3COOLi\ (100 \times \frac{66}{66+18n}\%) + 2nH_2O\ (100 \times \frac{18n}{66+18n}\%)$
- 300~500 ℃: $2CH_3COOLi\ \left(100 \times \frac{66}{66+18n}\%\right) \rightarrow Li_2CO_3\ \left(100 \times \frac{66}{66+18n} \times \frac{74}{132}\%\right) + C_3H_6O\ \left(100 \times \frac{66}{66+18n} \times \frac{58}{132}\%\right)$

[80℃, $LiPF_6$: acetic acid = 1: 4]

- $CH_3COOLi \cdot 1.14H_2O\ (90\%) \rightarrow CH_3COOLi\ (73\%) + 1.14H_2O\ (17\%)$
- $2CH_3COOLi\ (73\%) \rightarrow Li_2CO_3\ (49\%) + C_3H_6O\ (24\%)$

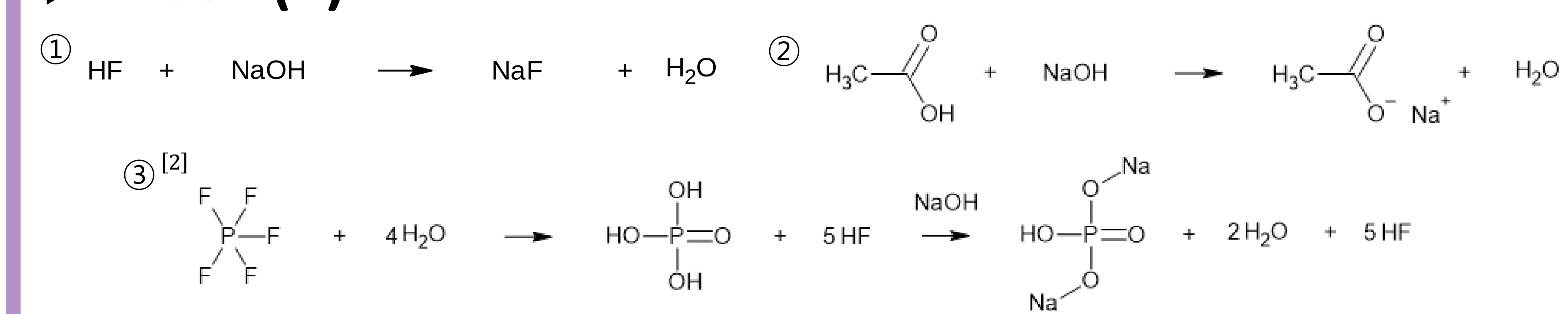
[80℃, $LiPF_6$: acetic acid = 1: 2]

- $CH_3COOLi \cdot 1.22H_2O\ (94\%) \rightarrow CH_3COOLi\ (75\%) + 0.92H_2O\ (19\%)$
- $2CH_3COOLi\ (75\%) \rightarrow Li_2CO_3\ (40\%) + C_3H_6O\ (33\%)$

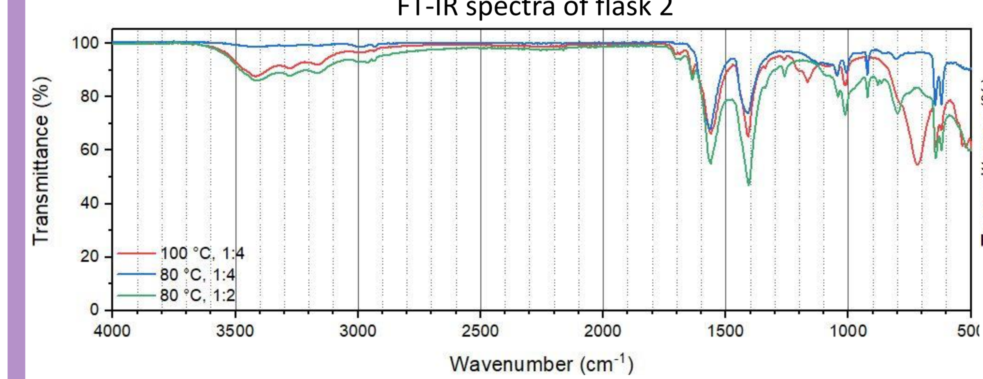
=> The number of H_2O attached to CH_3COOLi changed with the reaction ratio of $LiPF_6$ and CH_3COOH.

- Lithium acetate is very useful in DNA analysis and is used as a buffer for gel electrophoresis of DNA and RNA.
- Lithium carbonate is an important industrial material. Its main use is a precursor for compounds used in lithium-ion batteries. Cathode and electrolyte are made with lithium carbonate

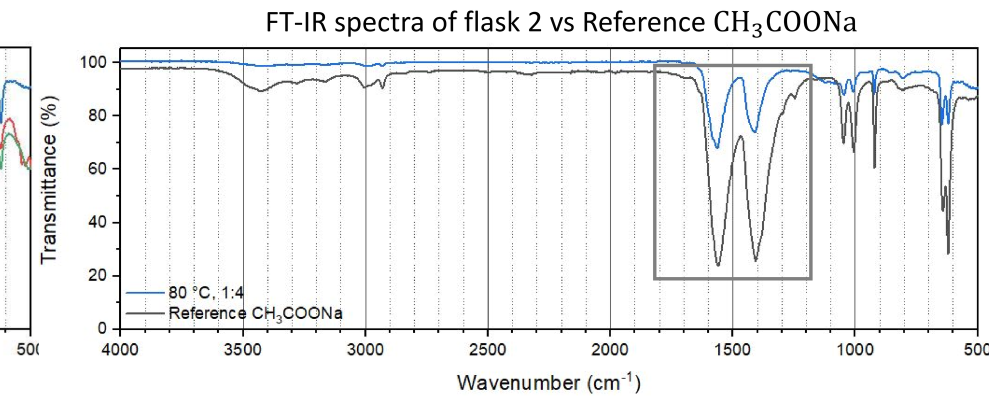
▶ Flask (2)



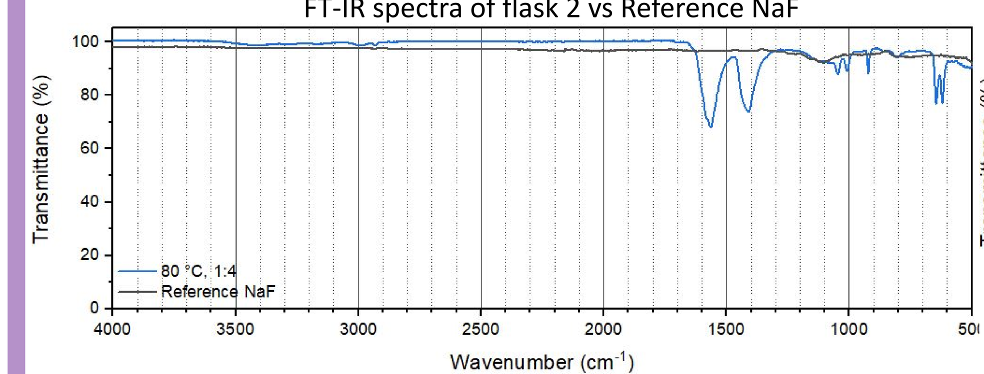
FT-IR spectra of flask 2



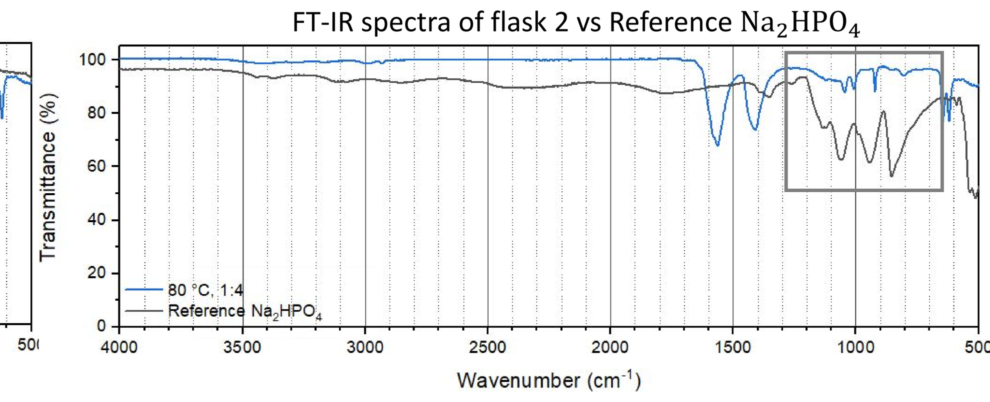
FT-IR spectra of flask 2 vs Reference CH_3COONa



FT-IR spectra of flask 2 vs Reference NaF



FT-IR spectra of flask 2 vs Reference Na_2HPO_4



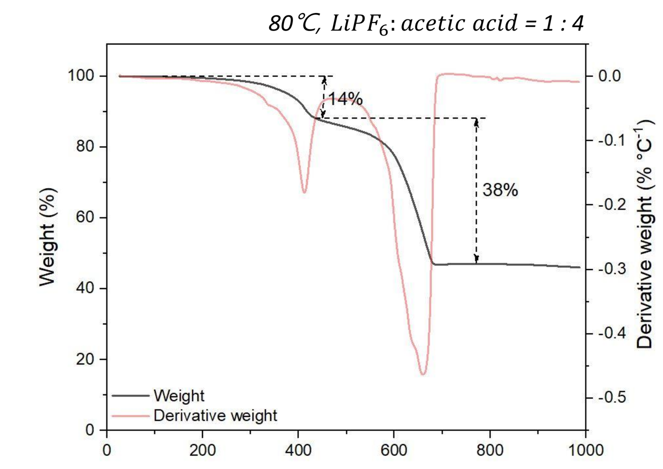
▶ FT-IR Analysis

Table.2 FT-IR data of flask 2

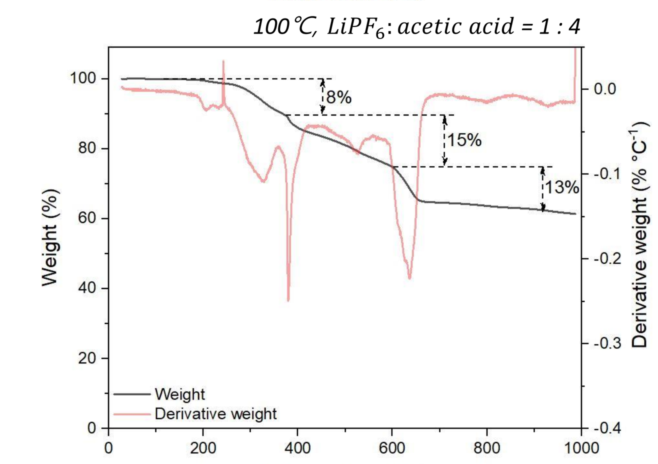
Prediction	Reference(cm^{-1})	Experimental(cm^{-1})	Verification	Note
CH_3COONa	1561	1560	O	$C=O \cdots Na$ interaction
	1410	1406	O	
NaF	No strong peak	-	-	TGA analysis
Na_2HPO_4	856	924	X	HPO_4^{2-} [3]
	942	1013	X	
	1057	1045	X	

- NaF existence can't be checked by FT-IR -> Needs another method to verify its structure.
- Need a detailed plan for reaction condition of $LiPF_6 : CH_3COOH = 1:1$ -> Check PF_5 behavior.

80℃, $LiPF_6$: acetic acid = 1 : 4



100℃, $LiPF_6$: acetic acid = 1 : 4



▶ TGA Analysis

[80℃, $LiPF_6$: acetic acid = 1: 4]

- $2CH_3COONa\ (40\%) \rightarrow Na_2CO_3\ (26\%) + (CH_3)_2CO\ (14\%)$
- $Na_2CO_3\ (26\%) \rightarrow Na_2O\ (15\%) + CO_2\ (11\%)$
- Approximately 20% of weight loss can't be defined.

[100℃, $LiPF_6$: acetic acid = 1: 4]

- $CH_3COONa \cdot H_2O\ (56\%) \rightarrow CH_3COONa\ (48\%) + H_2O\ (8\%)$
- $2CH_3COONa\ (48\%) \rightarrow Na_2CO_3\ (33\%) + (CH_3)_2CO\ (15\%)$
- $Na_2CO_3\ (33\%) \rightarrow Na_2O\ (20\%) + CO_2\ (13\%)$

∴ Approximately 40% NaF, theory ≈ experiment

- It is inevitable that PF_5 is formed through the reaction between $LiPF_6$ and CH_3COOH, but we couldn't find out the trace of PF_5 through FT-IR analysis.
- Utilization of by-products
  - Sodium fluoride for cavity prevention and toothpaste.
  - Sodium acetate for carbon source for culturing bacteria by ethanol precipitation.

Conclusions

- This study examined an environmental-friendly treatment method of lithium and harmful gas in electrolytes recycling process.
- Through this process, Li of $LiPF_6$ was obtained in the form of CH_3COOLi and F of HF was obtained in the form of NaF.
- Li_2CO_3 and Na_2O can be obtained by thermal processing of CH_3COOLi and CH_3COONa.

References

[1] Kento KimuraJoh, MotomatsuYoichi, TominagaYoichi Tominaga. "Correlation Between Solvation Structure and Ion-Conductive Behavior of Concentrated Poly(ethylene carbonate)-Based Electrolytes", The Journal of Physical Chemistry C 120(23)

[2] 홍연숙. 비수 전해액 및 이를 포함하는 리튬 이차 전지. 10-2014-0098925,2013/01/31

[3] Saba Daneshgar, Arianna Callegari(2018), "Impact of pH and Ionic Molar Ratios on Phosphorous Forms Precipitation and Recovery from Different Wastewater Sludges", The journal of Resources.