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Preparation of $LiPF_6$ using ClF_3 below room temperature

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ABSTRACT

A reaction among LiF, P (red phosphorous), and ClF_3 was conducted to prepare $LiPF_6$ at −20 to 100 °C. First, P reacts with ClF_3 to form PF_5. Then PF_5 reacts with LiF to form $LiPF_6$. The reaction preparing $LiPF_6$ from LiF, P, and ClF_3 can take place at less than 0 °C, although the reaction using F_2 instead of ClF_3 did not proceed well at such a lower reaction temperature. The $LiPF_6$ preparation reaction can be promoted by increasing the reaction temperature. However, if the reaction temperature increases, some side reaction and/or decomposition reaction take place. The optimal conditions to obtain highly pure $LiPF_6$ in this study were 0 °C reaction temperature and 5 h reaction time for the composition of LiF:P:ClF_3 = 1:1:2 (mol) as the starting mixture.

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1. Introduction

Lithium hexafluorophosphate ($LiPF_6$) is the most popular supporting salt for electrolyte solutions in lithium secondary batteries now. The solubility of $LiPF_6$ into the organic solvents used for lithium ion batteries is higher than that of other compounds such as $LiBF_4$ and $LiClO_4$ [1]. Therefore, the electrolyte solution containing $LiPF_6$ exhibits high electric conductivity. In addition, $LiPF_6$ is stable against the redox reaction in the lithium ion battery [2]. The electrolyte solution containing $LiPF_6$, however, contains HF as an impurity. In fact, HF contamination degrades the performance of lithium ion batteries [2,3]. Therefore, numerous efforts have been undertaken to develop a process by which highly pure $LiPF_6$ is obtainable. Several methods are used in industry. For example, LiF is dissolved into liquid anhydrous hydrogen fluoride (L-AHF) and PF_5 gas is supplied into this system [4]. $LiPF_6$ is generated and precipitated as a crystal. Alternatively, LiF and PCl_3 are reacted in L-AHF to obtain the $LiPF_6$ crystal [5]. Generally AHF is used as the medium for these methods (AHF method). However, HF can remain in the products produced using these methods. Although the amount of HF in the product is extremely small, its presence causes deliquescence of the products because HF gives hygroscopicity to the product and promotes the hydrolysis of $LiPF_6$ to form LiPOxFy and HF. The preparation of $LiPF_6$ without AHF can be addressed to solve this problem. Among them, the reaction among LiF, P, and F_2 is the simplest AHF-free method to prepare $LiPF_6$. A previous study demonstrated a new process to prepared $LiPF_6$ in which the mixture of LiF and P is heated in F_2 gas at 300 °C (F_2 method). Highly pure $LiPF_6$ was obtained using this F_2 method: purer than that obtained using L-AHF method. However, with F_2 method, it is difficult to control the reaction because the exothermal reaction between P and F_2 proceeds vigorously. To maintain the temperature of the reaction system, for example, F_2 gas must be introduced into the system very slowly [6].

In this study, ClF_3 was used instead of F_2 in the reaction system among LiF, P, and F_2 to assess the possibility of preparing $LiPF_6$ at a reaction temperature below room temperature.

2. Results and discussion

The FT-IR profile of the gas product after the reaction among LiF, P, and ClF_3 in the molar ratio of 1:1:2 is shown in Fig. 1. The reaction temperature and time were 25 °C and 5 h, respectively. From comparison of the profiles of ClF_3 and the product gas, peaks appeared at 1026 cm^{-1} (strong), 941 cm^{-1} (strong), and 532 cm^{-1} (weak) after the reaction. These peaks correspond to those of PF_5 gas [7–10]. Excess ClF_3 for P remained in the reactor after the reaction was also observed at 833 cm^{-1} (strong) in the profile for the product. Red phosphorous was converted to PF_5 completely. No PF_3 remained after the reaction because no peak was observed at 860 cm^{-1} (strong) and 892 cm^{-1} (strong). Using T% values at 833 cm^{-1} for ClF_3, the absorbance of ClF_3 (A_{ClF3}) was calculated from the T% value and the ratio of A_{ClF3} for pure ClF_3 to that for ClF_3 after the reaction was calculated. Results show that 83% of ClF_3

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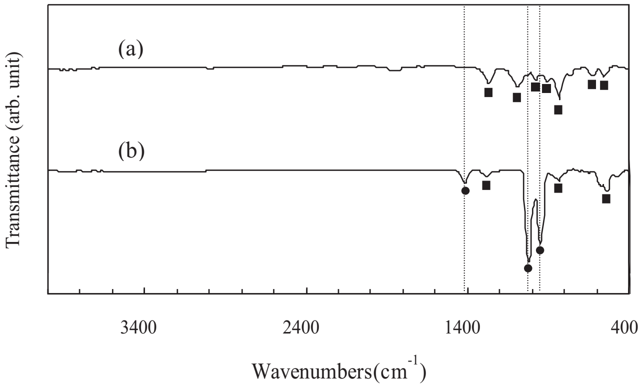

Fig. 1. IR spectra of (a) raw ClF_3 gas and (b) gas product prepared after reaction at RT, 5 h (■, ClF_3; ●, PF_5).

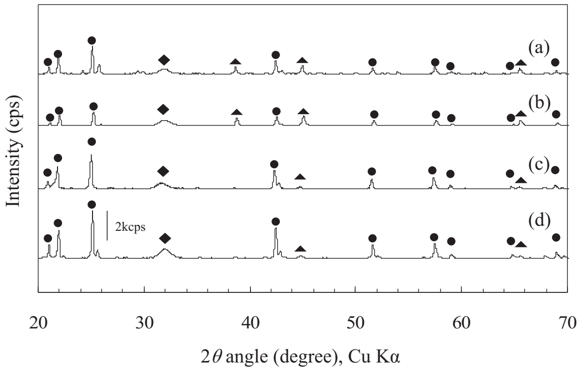

Fig. 2. XRD profiles of $LiPF_6$ prepared under various conditions: (a) 25 °C, 1 h; (b) 0 °C, 1 h; (c) 25 °C, 5 h; (d) 0 °C, 5 h (●, $LiPF_6$; ▲, LiF; ◆, cover film).

loaded to the reactor reacted with P. This ratio corresponds to the molar ratio of P and ClF_3 to 1:1.7 (P:F:Cl = 1:5:2). PF_5 and Cl_2 must be produced stoichiometrically. Finally, a white solid product was obtained. Therefore, red phosphorous remained in the solid product, which is consistent with the calculation for PF_5 formation described above.

Fig. 2 presents XRD profiles of the solid product of the reaction of LiF, P, and F_2 at 25 °C or 0 °C in 1 or 5 h. Some peaks correspond to $LiPF_6$ (solid circle) and LiF (solid triangle) in Fig. 2. Peaks attributable to $LiPF_6$ strongly appeared, meaning that the major product must be $LiPF_6$ with a small amount of LiF included in it. Completely, PF_5 should be generated from the reaction between P and ClF_3 first. Then PF_5 is expected to react with LiF in the presence of ClF_3 to produce $LiPF_6$. The white solid product was not powder anymore. It was condensed just as snow hardens into ice. The intensity ratios of the peaks attributable to $LiPF_6$ (24.9°) and LiF (44.5°) in Fig. 2, $I_{LiPF6/LiF}$ are presented in Table 1.

The larger value of $I_{LiPF6/LiF}$ indicates a larger yield of $LiPF_6$. When the reaction time was set at 1 h, $I_{LiPF6/LiF}$ of the product at 25 °C was more than two times larger than that at 0 °C. However, for 5 h reaction time, both $I_{LiPF6/LiF}$ values for 0 and 25 °C increased greatly compared to that of 1 h reaction. There was less than 10% difference between $I_{LiPF6/LiF}$ values for 0 and 25 °C for 5 h reaction. Therefore, 5 h is apparently sufficient for the progress of the $LiPF_6$ formation process even if the reaction is conducted at 0 °C. Based on these results, the reaction time was determined as 5 h. A higher reaction temperature was investigated to improve the $LiPF_6$ formation rate. XRD profiles of the products prepared at 0 °C, 25 °C, 50 °C and 100 °C are depicted in Fig. 3. Considering that $I_{LiPF6/LiF}$ values for 50 °C and 100 °C were 23.51 and 13.49 respectively, the yield of $LiPF_6$ increased to the reaction temperature of 50 °C and decreased over 50 °C. Apparently, 5 h is sufficient to complete the reaction to form $LiPF_6$ at temperatures higher than 0 °C. Some decomposition process might occur at higher temperatures such as 100 °C. Because the dissociation of $LiPF_6$ into LiF and PF_5 occurs at temperatures higher than 150 °C [11], the decomposition at less than 100 °C observed here was not attributable to the dissociation of $LiPF_6$. Some small peaks are apparent in Fig. 3(d), but these peaks did not appear in Fig. 3(a)–(c). The reaction between $LiPF_6$ and impurities, O_2 and H_2O for example, can be promoted by increasing the reaction temperature. Therefore, the preparation at −20 °C was conducted to infer the decomposition of the product. The XRD profiles of the products prepared at −20 °C in 5 h are shown in Fig. 4.

Table 1
Intensity ratio of the peaks because of $LiPF_6$ (24.9°) and LiF (44.5°) for the products under various preparation conditions.

Conditions (reaction temperature, time)	Intensity ratio ($I_{LiPF6/LiF}$)
25 °C, 1 h	2.76
0 °C, 1 h	1.21
25 °C, 5 h	18.12
0 °C, 5 h	17.32

The profiles of products prepared at −20 °C in 5 h resemble those obtained at 0 or 25 °C. The peak intensities in Fig. 4, however, were extremely small compared to those in Fig. 3. The ratio, $I_{LiPF6/LiF}$ of the product prepared at −20 °C was 14.76, which was consistent with the values of the products prepared at other temperatures. Briefly, the amount of the product was extremely small in case of the reaction at −20 °C, whereas the yield for the reaction at −20 °C was similar to that at 0, 25 and 50 °C. If the LiF solid sample simply reacts with PF_5 to form $LiPF_6$, this phenomenon would not be explained well. LiF might have some interaction with ClF_3 (e.g., a $LiClF_4$-like arrangement is possible on the LiF surface) and this might influence the reaction. However, no peak was distinguished that corresponds to $LiClF_4$. The peak attributable to LiF was extremely small in Fig. 4. This yield-related result might be simply attributable to the product crystallinity. The reaction process must be clarified after more quantitative research particularly addressing the behavior of LiF during the reaction. It is noteworthy that the reaction at a temperature lower than −20 °C was not efficient for industrial mass production. Optimal conditions to obtain pure $LiPF_6$ here were the reaction temperature of 0–50 °C and reaction time of 5 h.

Fig. 5 shows XRD profiles of $LiPF_6$ prepared using F_2 gas or ClF_3 gas. The reaction temperature and time were 25 °C and 5 h. As

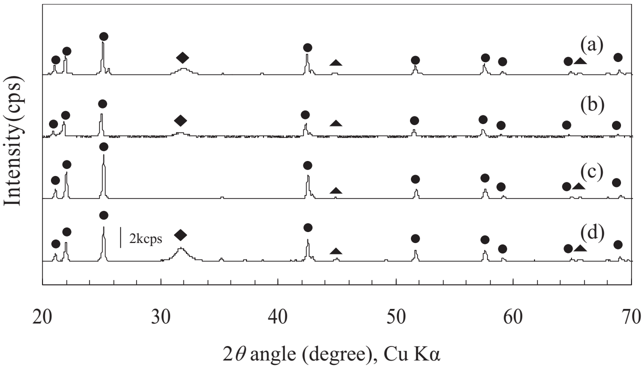

Fig. 3. XRD profiles of $LiPF_6$ prepared under various conditions: (a) 0 °C, 5 h; (b) 25 °C, 5 h; (c) 50 °C, 5 h; (d) 100 °C, 5 h (●, $LiPF_6$; ▲, LiF; ◆, cover film).

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