Preparation of Pure LiPF$_6$ Using Fluorine Gas at Room Temperature

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Pure lithium hexafluorophosphate (LiPF$_6$) was successfully prepared at room temperature (23 °C) by introducing fluorine gas into a reactor containing LiF and P at −196 °C. The mass fractions of LiPF$_6$ and LiF in products prepared at 23 °C were 1.00 and 0.00, respectively, by means of XRD-Rietveld analysis. Namely, the prepared LiPF$_6$ was pure enough to be used as an electrolyte salt in lithium ion batteries.

Lithium hexafluorophosphate (LiPF$_6$) is the most common electrolyte salt used in commercial Li-ion cells.[1,2] Many research efforts have been to made to obtain highly pure LiPF$_6$ because even a trace amount of water can deteriorate the performance of the battery significantly. Generally, liquid anhydrous hydrogen fluoride (L-AHF) is used as a medium for the preparation of LiPF$_6$ from LiF and PCl$_5$.[3] LiPF$_6$ must be purified by recrystallization in a dry organic medium to remove the H$_2$O and HF remaining in the products after preparation. Lithium oxyfluorophosphate (LiPO$_x$F$_y$) is also obtained as a by-product during preparation; it is partially dissolved in the HF solution and remains as an impurity in LiPF$_6$.[4] A previous study[5,6] reported a new method for preparing the LiPF$_6$ by reacting LiF and P with F$_2$ gas at 300 °C; this method was noted as the F$_2$ direct method. The LiPF$_6$ prepared using the F$_2$ direct method had much higher purity than that prepared using the L-AHF method. To prevent high exothermicity between P and F$_2$, however, stepwise introduction of F$_2$ gas into the reactor should be carried out. Furthermore, to obtain the LiPF$_6$ in high yield, the reactor must be heated to 300 °C.

By introducing F$_2$ gas into the reactor containing a mixture of LiF and P at −196 °C, in this paper we tried to prepare pure LiPF$_6$ at room temperature (23 °C) controlling the exothermicity between P and F$_2$ gas.

Fluorine gas (99.5%) was purchased from Daikin Industries Ltd. LiF and red phosphorus (P) were commercially provided and guaranteed as 99.9% pure. A mixture (1 g) of LiF and P with a molar ratio of 1:1 was loaded in the reactor (3.4×10^{-6} m^3) and maintained at −196 to 23 °C under 0.3 MPa (F$_2$ pressure at 23 °C) for 1–10 h. The fluorine gas was introduced into the reactor at −196 °C, the boiling point of liquid nitrogen (N$_2$). The fluorination apparatus and reactor were specially designed and made of SUS316L.[7] The product has been already confirmed as a mixed compound of LiPF$_6$ and LiF as nonreactive residue using XRD-Rietveld analysis (Rietan 2000 program[8]). The mass fraction of each compound was determined using the results for scale factor in the output file. The crystal structure of LiPF$_6$ was also examined using XRD-Rietveld analysis. The gaseous products in the reactor were measured by means of FT-IR analysis (Nicolet380SPY).

Figure 1 shows XRD profiles of products obtained through reaction between LiF and P in F$_2$ gas under various reaction conditions. After excess F$_2$ gas was introduced into the reactor at −196 °C, the reaction temperature was increased stepwise up to a maximum of 23 °C. At the temperature of −196 °C, the reaction between the solid mixture of LiF and P and liquid F$_2$ never occurred because of the low temperature. Up to −80 °C, the LiPF$_6$ peak (●) started to appear in the XRD (Figure 1a). When the reaction temperature increased to −20 °C (Figure 1b), the peak intensity of LiPF$_6$ increased sharply with the formation of PF$_5$ gas as shown in the IR spectrum (Figure 1f), while the LiF peaks (○) decreased. The IR spectrum (Figure 1f) indicates the gaseous products formed from the reaction between the mixture of LiF and P and the F$_2$ gas at −20 °C. The small peak of POF$_3$ at 1416 cm^{-1} (Figure 1f) may originate from oxygen adsorbed on the IR cell wall. Clearly, in the dry gas, PF$_5$ is the only gas phase product detected by FT-IR analysis. All IR data are summarized in Table 1. Furthermore, the reactor was warmed to room temperature (23 °C) and allowed to stand for 1 and 10 h. Pure LiPF$_6$ was successfully prepared at 23 °C after reaction for 10 h. Compared to the typical peak position of LiPF$_6$ by JCPDS in Figure 1e, only diffraction peaks attributable to LiPF$_6$ were observed in the XRD pattern of Figure 1d. Rietveld refinement of XRD data also showed that the mass fractions of LiPF$_6$ and LiF contained in the product (Figure 1d) were 1.00 and 0.00, respectively as shown in Table 2.

Reaction processes at each step estimated from XRD and IR spectra (Figure 1), and the mass fractions of mixed compounds are summarized in Table 2. Concerning the reaction between LiF and P in excess F$_2$, the PF$_5$ gas is first created by the reaction between P and F$_2$ at −80 °C. The solid–gas reaction between LiF and PF$_5$ gas then produces effectively LiPF$_6$ with increasing temperature and reaction time. Particularly, the LiPF$_6$ obtained at 23 °C after reaction for 10 h was pure enough to be used as an electrolyte salt in lithium-ion batteries. When LiF was reacted with preprepared PF$_5$ gas from P and F$_2$ at 23 °C, however, highly pure LiPF$_6$ was not obtained in this reaction. To acquire LiPF$_6$ with high purity, it was necessary to increase the reaction temperature above 150 °C.

We have reported that LiPF$_6$ can be prepared through reaction between LiF and P in F$_2$ gas even at a temperature of −80 °C. Increasing the temperature to −20 °C, the intensity of the LiPF$_6$ peak increased drastically with the formation of PF$_5$ gas. Pure LiPF$_6$ products could be successfully prepared at room temperature (23 °C) in 10 h. XRD-Rietveld refinement showed that the mass fractions of LiPF$_6$ and LiF in products prepared at 23 °C were 1.00 and 0.00, respectively. Namely, the LiPF$_6$ obtained at 23 °C was pure enough to be used as an electrolyte salt in lithium-ion batteries.
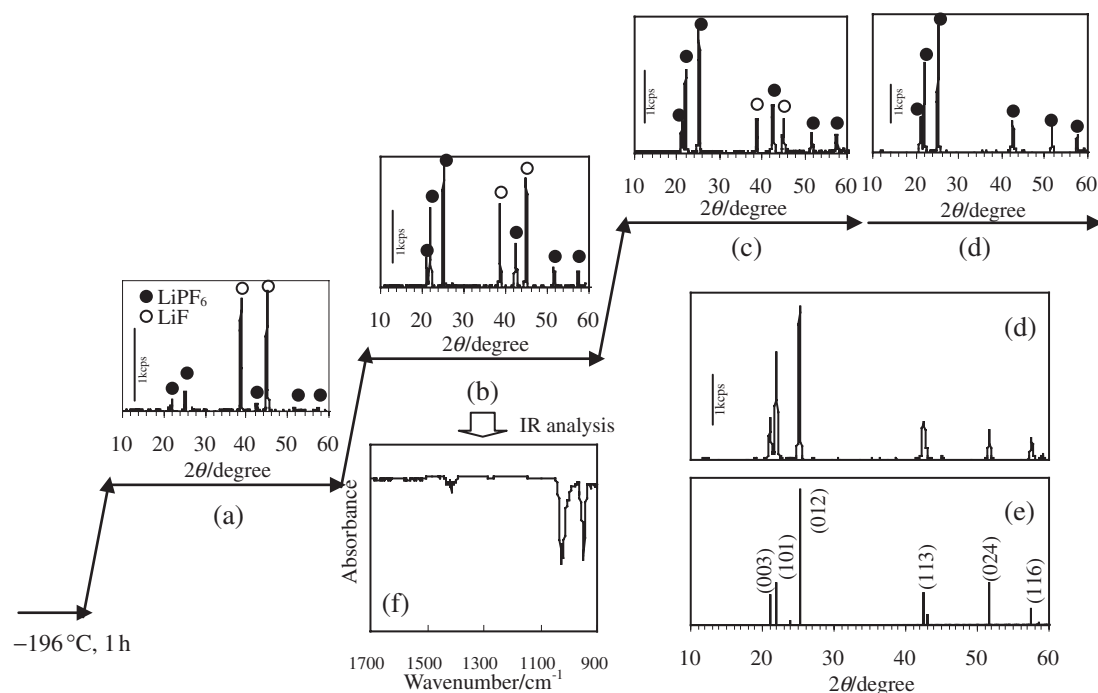
Figure 1. XRD patterns of products obtained at various reaction conditions [(a): −80 °C, 1 h; (b): −20 °C, 1 h; (c): 23 °C, 1 h; (d): 23 °C, 10 h] and IR spectra (f) of gaseous products obtained at −20 °C. And comparison of (d) XRD profile of $LiPF_6$ and (e) the typical peak position of $LiPF_6$ by JCPDS.

Table 1. IR frequency assignments of gaseous products obtained in the reactor at −20 °C as shown in Figure 1f

Vibrational frequencies/cm^{-1}	Assignment
1018	PF_5 (PF stretching mode)
945	PF_5 (PF stretching mode)
1416	POF_3 (P=O stretching mode)

Table 2. Reaction processes and products obtained at each reaction conditions

Reaction processes at reaction conditions		Mass fractions of products^a	
Conditions	Process	$LiPF_6$	LiF
−196 °C, 1 h	$LiF(s) + P(s) + F_2(l)$	0.00	1.00
−80 °C, 1 h	$LiF(s) + PF_5(l \text{ or } g) + F_2(g) + LiPF_6(s)$	0.08	0.92
−20 °C, 1 h	$LiF(s) + PF_5(g) + F_2(g) + LiPF_6(s)$	0.52	0.48
23 °C, 1 h	$LiF(s) + PF_5(g) + F_2(g) + LiPF_6(s)$	0.84	0.16
23 °C, 10 h	$LiPF_6(s) + F_2(g)$	1.00	0.00

^{a}Mass fractions of products were evaluated from XRD-Retveld results in Figure 1.

Consequently, our work presents a new synthesis method of pure $LiPF_6$ using fluorine gas at room temperature.

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