Preparation of Lithium Hexafluorophosphate from LiF and P in Fluorine Atmosphere

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Pure lithium hexafluorophosphate ($LiPF_6$) has been successfully prepared by the reaction between the elemental fluorine and the equi-molar mixture of LiF and P (F_2 direct method). The product was pure enough to be used as an electrolyte salt of lithium secondary battery. Especially, the stepwise introducing of fluorine gas into a reaction system was effective to prepare $LiPF_6$ in a high yield. The results of Rietveld refinement of XRD data revealed that the structure of $LiPF_6$ was trigonal ($R\bar{3}, Z = 3, a_0 = 0.4932(2)$, $c_0 = 1.2641(5)$ nm, cell volume; $2.663(2) \times 10^{-28}$ m^3). The cell constants of $LiPF_6$ prepared by the F_2 direct method were almost the same as those of $LiPF_6$ prepared by the reaction between LiF and PF_5 in a liquid anhydrous hydrogen fluoride (L-AHF method).

The most popular electrolyte salt used in the Li-ion battery is lithium hexafluorophosphate ($LiPF_6$) which has good solubility in various solvents, such as PC (propylene carbonate).[1] A lot of efforts has been done to obtain highly pure $LiPF_6$ because even the trace amount of water can critically deteriorate the battery performance. Generally liquid anhydrous hydrogen fluoride (L-AHF) is used as a media for the preparation reaction of $LiPF_6$ between LiF and PF_5.[2,3] Acetonitrile can also be used as a media for the preparation reaction. In both cases, $LiPF_6$ must be purified by recrystallization in a dry organic media to remove H_2O and HF remained in the products after the preparation reaction. Lithium oxyfluorophosphate ($LiPO_xF_y$) must also be produced as a by-product which is partially dissolved into HF solution and remains as an impurity in $LiPF_6$.[4] The trace amount of water in AHF has been tried to be removed by using F_2 gas.[5] In order to decrease the amount of HF remained in the product, the process is proceeded by the way of forming the adduct, $Li(CH_3CN)_4PF_6$, with highly dried acetonitrile. It is, however, very difficult to remove them sufficiently. In this study, the preparation method of $LiPF_6$ by the reaction of the mixture of LiF and P(red phosphorus) with elemental fluorine was developed (F_2 direct method). Fluorine gas (99.5% pure) was supplied from Daikin Industries, Ltd. LiF and red phosphorus were commercially provided and was guaranteed as 99.9% pure. $LiPF_6$ has been successfully prepared by the reaction between the mixture of LiF and P in an equi-molar ratio and F_2 gas at 300 °C under 0.4 MPa (F_2 pressure) within 5 min. The amounts of LiF, P, and F_2 were 1.3×10^{-3}, 1.3×10^{-3}, and 3.9×10^{-3} mol, respectively in this case. The volume of reactor made of nickel is 1.57×10^{-5} m^3. It was found that stepwise introducing of F_2 into the reactor was effective to obtain $LiPF_6$ in a high yield. F_2 of p/n (n, steps) was introduced for each step where p corresponds to its stoichiometric amount to complete the reaction.

Figure 1 shows the results of XRD pattern of the sample prepared at 300 °C at various steps, n. The peaks corresponding to LiF appeared at 39° and 45° in Figure 1a. That means the reaction between LiF and P in F_2 gas has not been completed under this condition. Increasing the steps, n, these peaks diminished and finally no peak corresponding to LiF was detected for $n = 4$ (Figure 1d). The procedure of the stepwise introduction of fluorine gas may be more important to carry out the reaction efficiently and homogeneously than the other factors such as temperature, F_2 pressure and reaction time in this case. There must be a certain equibrium which conducts this phenomenon during the reaction. It has been known that $LiPF_6$ dissociates into LiF and PF_5 at a temperature higher than 220 °C. But here, $LiPF_6$ was efficiently been prepared at 300 °C. F_2 might prevent $LiPF_6$ and PF_5 from dissociation and hydrolysis, respectively or play an important role to promote the reaction of $LiF + PF_5 = LiPF_6$.

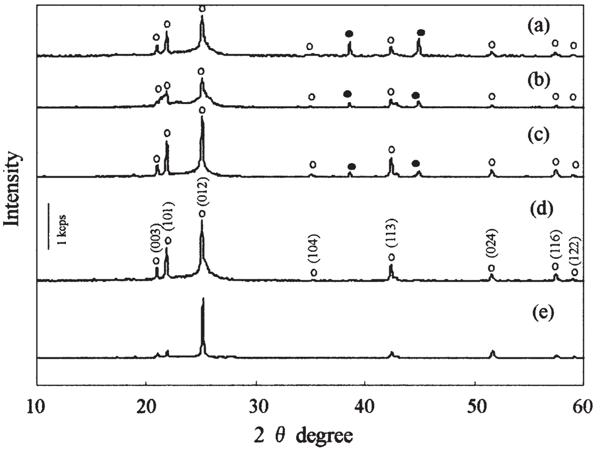

Figure 1. XRD patterns of the products obtained at various steps, n. n means the number of steps in which $(3.9 \times 10^{-3})/n$ mol F_2 was introduced into the reactor (1.57×10^{-5} m^3) for each step. The reaction temperature and time were 573 K and 5 min, respectivery. ((a), $n = 1$; (b), $n = 2$; (c), $n = 3$; (d), $n = 4$; (e), the product prepared by L-AHF) ○ and ● mean the peaks due to $LiPF_6$ and LiF, respectively.

Rietveld refinement of XRD data for $LiPF_6$ was shown in Figure 2. The refinement were carried out by referring the literature.[6–9] R_F and S value for $LiPF_6$ prepared by direct method ($n = 4$, at 300 °C) were 7.94 and 2.09, respectively. Because the product is so hygroscopic that some impurities such as $LiPO_xF_y$ must remained in it, the quality of XRD data was not so high to proceed the further refinement. While the refinement has not been sufficiently finished, several parameters can be available to be used for discussion. They were summarized in Table 1. The Rietveld refinement of XRD data of $LiPF_6$ prepared in liquid AHF (L-AHF method) were carried out in the same manner as that for $LiPF_6$ prepared by direct method and the results were also summarized in Table 1. It may be suggested that $LiPF_6$ prepared by L-AHF method has slightly larger values of c_o and cell volume. It is, however, reasonable that the lattice pa-

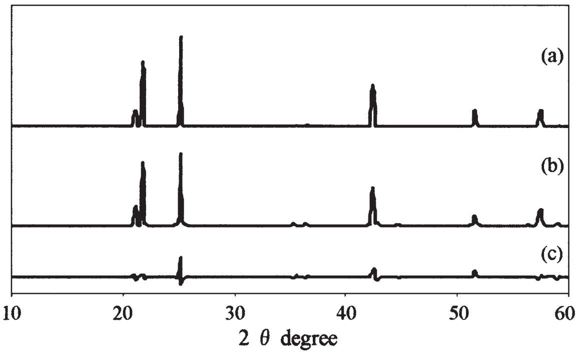

Figure 2. XRD profile of $LiPF_6$ prepared by F_2 direct method and the result of Rietveld refinement ((a) observed, (b) calculated, (c) difference).

Table 1. Lattice parameters of $LiPF_6$ prepared by L-AHF method and F_2 direct method

Method	L-AHF	F_2 direct
Space group	$R\bar{3}$ (no. 148)	$R\bar{3}$ (no. 148)
Cell parameter		
a_0(nm)	0.4933(1)	0.4932(2)
c_0(nm)	1.2657(2)	1.2641(5)
Z	3	3
Cell volume ($\times 10^{-28}$ m^3)	2.668(1)	2.663(2)
Density ($\times 10^3$ kg m^{-3})	2.836	2.841
Bond length (nm)		
F (18*f*) - P (3*b*)	0.161(4) 6×	0.160(3) 6×

rameters of $LiPF_6$ prepared by F_2 direct method have no significant difference from those by L-AHF method in this case unless the quality of XRD data will be improved. These lattice parameters coincide with those of the single crystal in the literature.[9] Essentially the same product was obtained by both methods. But the moisture sensitivities of both $LiPF_6$ were largely different from that of one another. $LiPF_6$ prepared by L-AHF method was decomposed easier than that prepared by F_2 direct method. A trace quantity of HF which remains on the surface of the product and adsorbed on it very tight may cause this phenomenon. $LiPF_6$ prepared by F_2 direct method has an advantage for the stability against hydrolysis compared to that prepared by L-AHF method.

Figure 3 shows a result of NMR spectra of 0.15 M $LiPF_6$ in DMSO solution. The doublet peak appeared at −69 ppm which corresponds to PF_6^- in ^{19}F NMR spectrum of $LiPF_6$. The signal due to impurities, such as $PO_2F_2^-$ and HF were very week in content ratios against PF_6^- as 1/600 and 18/600, respectively. No signal except for PF_6^- signal was observed in the ^{31}P NMR analysis.[10,11] It can be said that the $LiPF_6$ prepared by F_2 direct method has much high purity.

Figure 4 shows the plots of equivalent conductivity, Λ vs. $c^{1/2}$ where c is concentration of $LiPF_6$ in PC. There was no difference between the equivalent conductivities of both $LiPF_6$ over 5.0×10^{-2} (mol dm^{-3})$^{1/2}$. On the other hand, Λ of $LiPF_6$ prepared by F_2 direct method at 1.0×10^{-4} was about half of that by L-AHF method. $LiPF_6$ behaves as a weak electrolyte in this case. Because the dissociation constant changes largely at the low concentration in case of weak electrolyte, the difference between two samples may be closed up. HF also behaves as an weak electrolyte. $LiPF_6$ prepared by L-AHF method must contain larger amount of HF than that prepared by F_2 direct method. This might cause the difference of Λ at the low concentration. Consequently $LiPF_6$ prepared by F_2 direct method developed in this study is pure enough to be used as an electrolyte salt for lithium secondary battery.

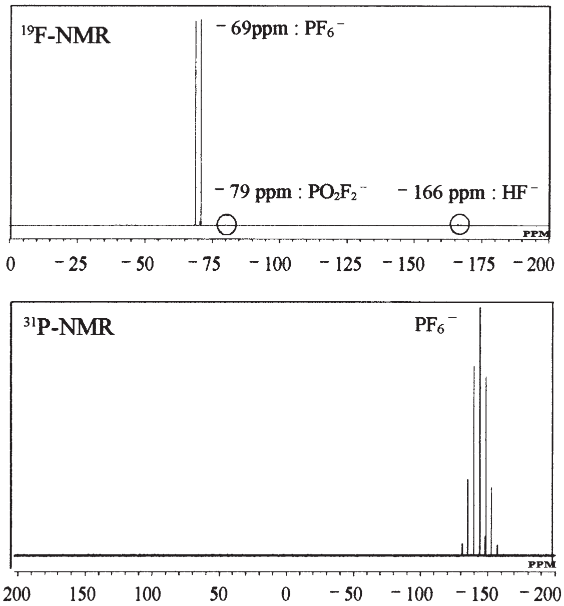

Figure 3. Top: ^{19}F NMR spectrum of 0.15 M $LiPF_6$ in DMSO; bottom: ^{31}P NMR spectrum of 0.15 M $LiPF_6$ in DMSO.

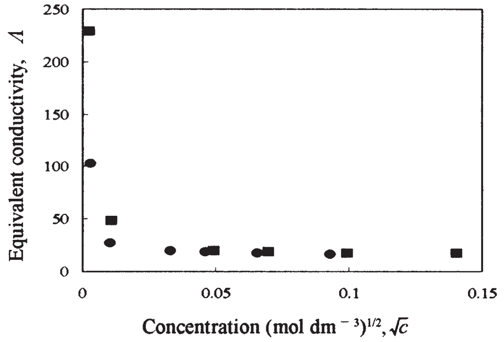

Figure 4. Plots between concentration and equivalent conductivity in $LiPF_6$/PC prepared by L-AHF method (■) and F_2 direct method (●).

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