

Application News

High Performance Liquid Chromatography

No.L417

Analysis of the Decomposition Products of Lithium Hexafluorophosphate in the Electrolytic Solution of Lithium-Ion Rechargeable Batteries by Column-Switching Ion Chromatography

Lithium hexafluorophosphate, which serves as the electrolytic solution in lithium-ion rechargeable batteries, is hydrolyzed by the small amounts of water contained in the electrolytic solution. Since fluoride ions formed as a result of the hydrolytic decomposition can affect battery performance, analysis of the decomposition products is necessary as part of the

■ Analysis of Standard Solution

Two decomposition products of lithium hexafluorophosphate, the fluoride ion (F⁻) and monofluorophosphate ion (PO₃F⁻) were selected as analytes.

Fig. 1 shows a flow diagram of the column switching system constructed for analysis. Since the hexafluorophosphate ion contained in the electrolytic solution is retained in the analytical column more strongly than the decomposition products, a single analysis for all components takes a relatively long time. In the dual-column system, the sample is first introduced in the 10 mm-long column (1) for a rough or qualitative separation, where only the peak consisting of the decomposition products is sent to column (2) (analytical column) for a more complete separation. After the decomposition products are sent to column (2), pump 2 elutes the hexafluorophosphate ion to waste and washes the column in preparation for the next sample.

Fig. 2 shows the results of analysis of 10.87 g/L (20 to 1 dilution of 1.5 mol/L LiPF₆) hexafluorophosphate ion spiked with 10 mg/L fluoride ion and 100 mg/L monofluorophosphate ion. The analytical conditions are shown in Table 1.

Table 1 Analytical Conditions

Column	: (1) Shim-pack IC-SA2 (G) (10 mm L. × 4.6 mm I.D.) (2) Shim-pack IC-SA2 (250 mm L. × 4.0 mm I.D.)
Mobile Phase	: 12 mmol/L NaHCO ₃ , 0.6 mmol/L Na ₂ CO ₃ in Water
Flow Rate	: 1.0 mL/min (Pump1, Pump 2)
Injection Vol.	: 10 μL
Column Temp.	: 30 °C
Detection	: CDD-10A _{SP} (Suppressor)

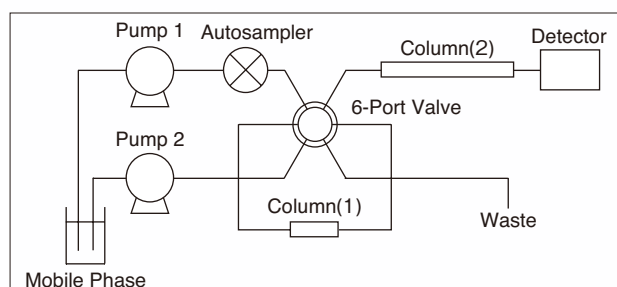


Fig. 1 Flow Diagram

quality control process.

Here, we introduce an analysis of the decomposition products of lithium hexafluorophosphate used as the electrolytic solution in lithium-ion rechargeable batteries, in which we constructed a column-switching system using the Shimadzu Prominence HIC-SP ion chromatography system.

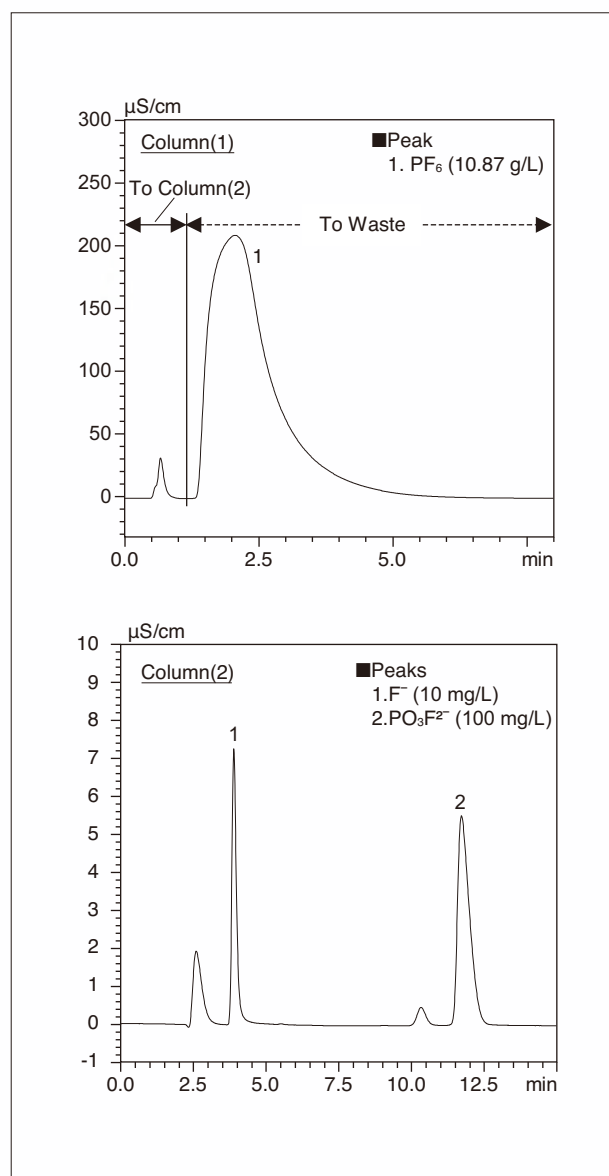


Fig. 2 Chromatogram of Standard Solution

■ Linearity

Fig. 3 shows the calibration curves generated using standard solutions of 0.1 to 10 mg/L F^- , and 1 to 100 mg/L PO_3F , respectively. Excellent linearity was obtained for both, with R^2 values greater than 0.999.

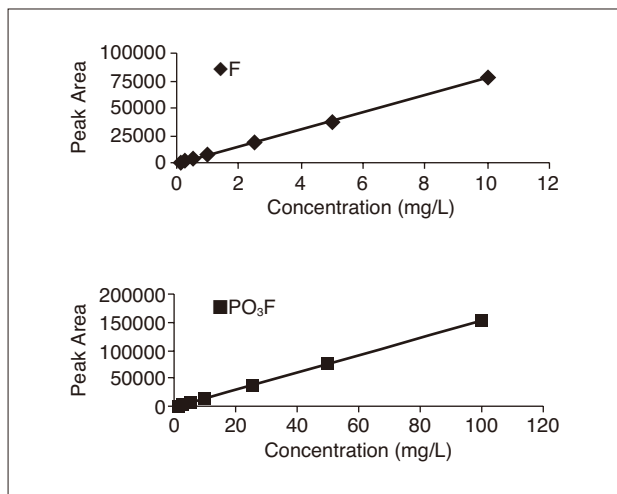


Fig. 3 Linearity

■ Repeatability

Table 2 shows the relative standard deviation ($n = 6$) obtained for retention times and peak areas in analysis of the standard solutions (F^- 1 mg/L, PO_3F 10 mg/L). Excellent repeatability of retention time and peak area were obtained for both.

Table 2 Repeatability of Retention Time and Peak Area

	F		PO_3F	
	Retention Time	Peak Area	Retention Time	Peak Area
1st	3.93	7573	12.19	14987
2nd	3.93	7329	12.17	14471
3rd	3.93	7482	12.18	14764
4th	3.92	7434	12.17	14700
5th	3.92	7480	12.14	14630
6th	3.92	7523	12.13	14809
%RSD	0.05	1.12	0.20	1.18

■ Analysis of Electrolytic Solution for Lithium-Ion Rechargeable Battery

Fig. 4 and Fig. 5 show the results of analysis of the electrolytic solution of a commercially available lithium-ion rechargeable battery. Fig. 4 is the chromatogram obtained using a new sample, and Fig. 5 is that obtained after leaving the new sample exposed to the air for 24 hours. Each sample was analyzed after diluting 20 to 1 with pure water, and filtering through a membrane filter.

*Regarding the difluorophosphate ion (PO_2F_2), only peak identification was conducted because a stable standard substance could not be obtained.

In addition, it could not be ascertained whether the fluoride ion, difluorophosphate ion and monofluorophosphate ion were present from the start in the electrolytic solution, or if they were formed instead at the time of dilution.

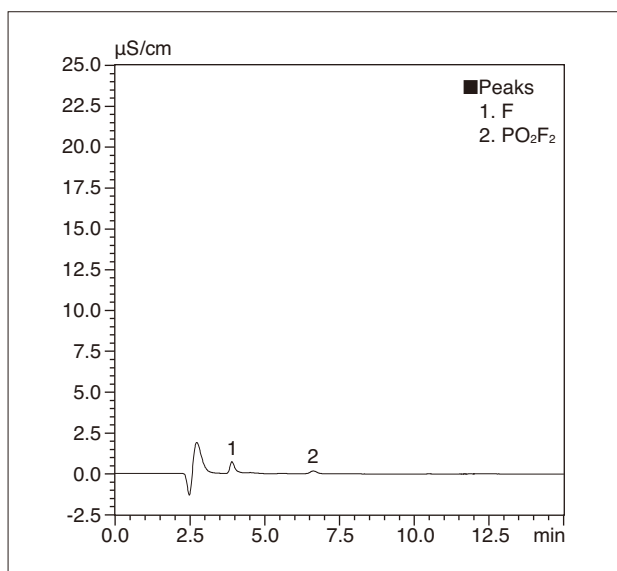


Fig. 4 Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (New)

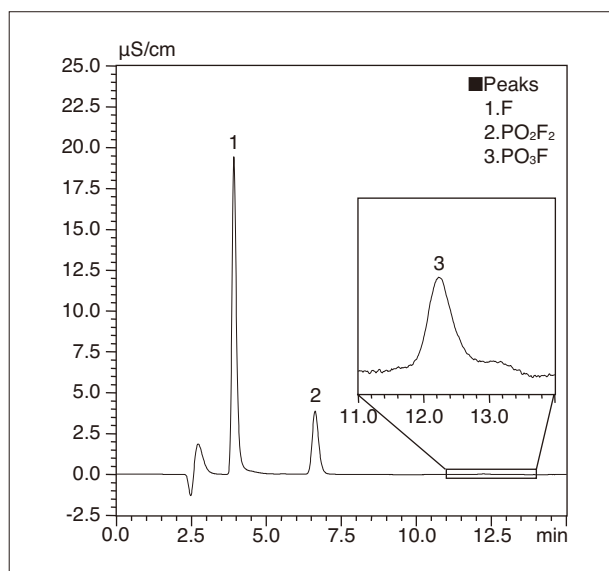


Fig. 5 Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (After 24 Hours)