

Application News

No.L429

High Performance Liquid Chromatography

Analysis of the Decomposition Products of Lithium Hexafluorophosphate in the Electrolytic Solution of Lithium-Ion Rechargeable Batteries by Column-Switching Ion Chromatography (Part 2)

Lithium hexafluorophosphate is commonly used as the electrolytic solution in lithium-ion rechargeable batteries. It is hydrolyzed by the small amounts of water contained in the electrolytic solution to produce fluoride and other ions. In Application News L417, we presented an example of

analysis of electrolytic solution which had deteriorated due to exposure to air, using a column-switching ion chromatography system. Here, we introduce an analysis of an electrolytic solution that had been subjected to accelerated deterioration during testing.

■ 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 (PF₆) in the electrolytic solution is retained in the analytical column more strongly than the decomposition products, a single analysis for all components would be very time consuming. In the column switching system, initial

separation of the analyte substances from PF₆ is conducted by column (1), and only the analytes from the decomposition are sent to column (2). Then the valves are switched so that while the analytes in column (2) are being separated, the high-concentration PF₆ retained on column (1) is discharged to waste.

This system permits a greatly shortened analysis time for 1 cycle.

Fig. 2 shows the results of analysis of the standard solution (F: 1 mg/L, PO₃F: 10 mg/L), and Table 1 shows the analytical conditions.

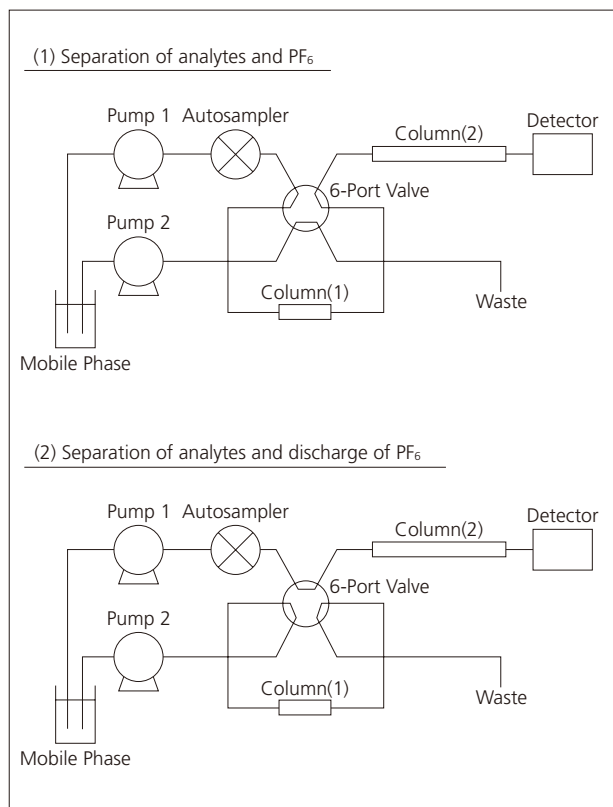


Fig. 1 Flow Diagram

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 (Pump 1, Pump 2)
Injection Vol.	: 10 μL
Column Temp.	: 30 °C
Detection	: CDD-10A _{SP} (Suppressor)

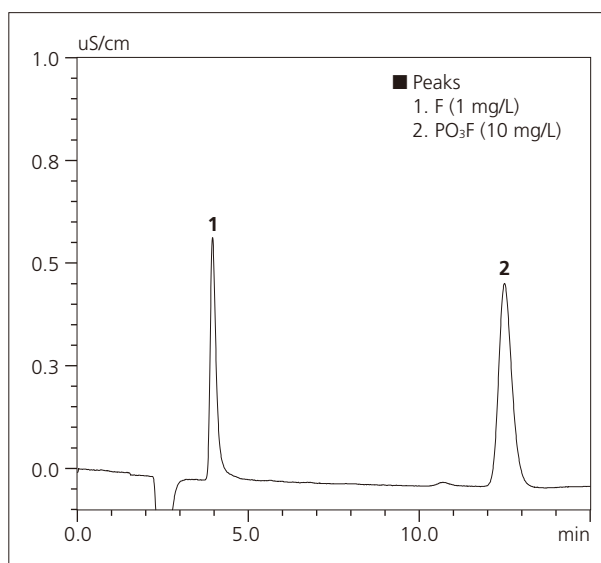


Fig. 2 Chromatogram of a Standard Solution

■ Analysis of Electrolytic Solution for Lithium-Ion Rechargeable Battery

Fig. 3 shows the accelerated deterioration conditions used for testing of the rechargeable battery. Fig. 4 shows the cycle characteristics during the accelerated deterioration process.

Fig. 5 and Fig. 6 show examples of results of analysis of electrolytic solutions for lithium-ion rechargeable batteries. The chromatogram of Fig. 5 was obtained from analysis of unused, new electrolytic solution, while that of Fig. 6 was obtained from analysis of electrolytic solution removed from a battery that was subjected to the accelerated deterioration process described above. Each sample was diluted with purified water by a factor of 100 to 1, filtered through a membrane filter, and then analyzed.

Note: 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 new electrolytic solution, or if they were formed instead at the time of dilution. Even without quantitation of these ions, the presence of fluoride and difluorophosphate increases dramatically after the accelerated degradation test that simulates battery use.

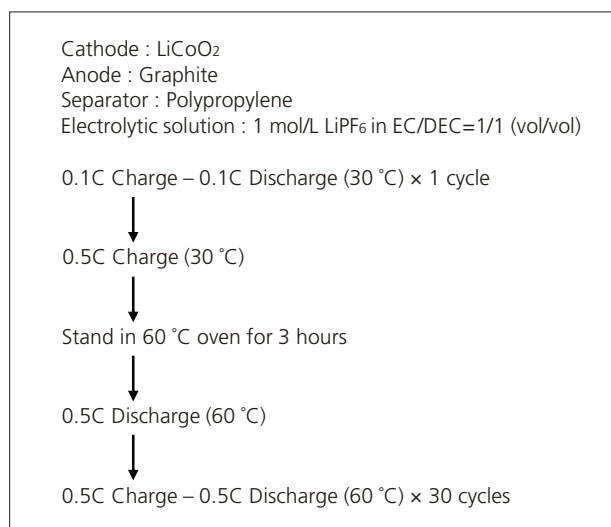


Fig. 3 Conditions of Accelerated Deterioration Test

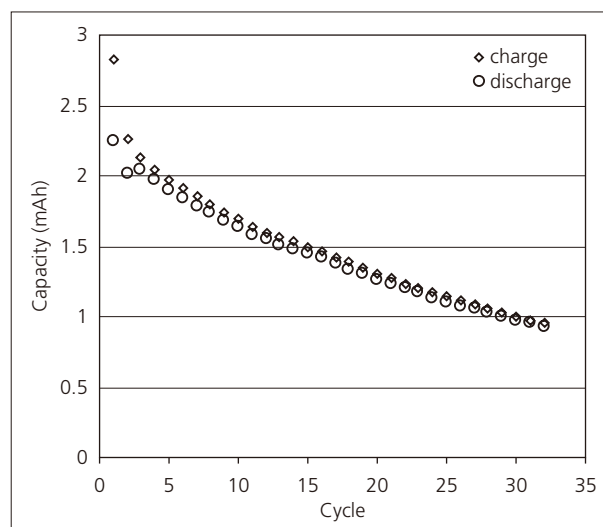


Fig. 4 Cycle Characteristics in Accelerated Deterioration Test

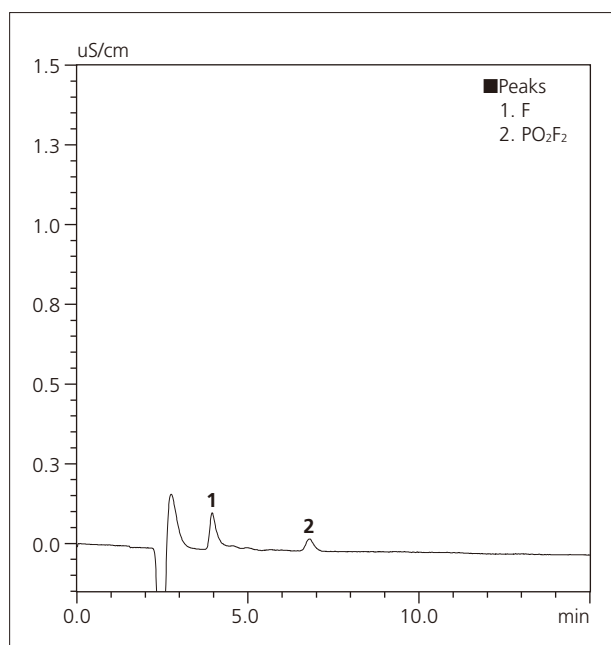


Fig. 5 Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (New)

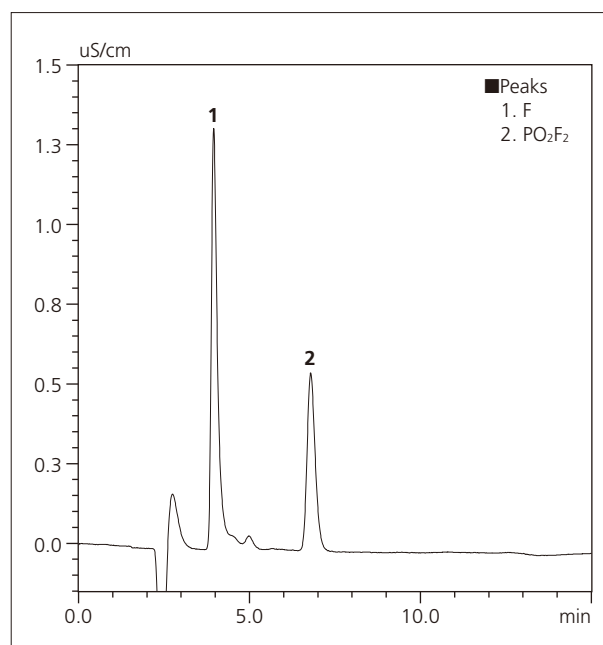


Fig. 6 Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (Deteriorated)