Application News

ICP-AES, GC–MS, EDXRF

Analysis of Electrolyte and Electrode in LIB Degraded by Overcharge and High Temperature

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User Benefits

- ICP-AES enables accurate quantification of cathode material dissolved in electrolytes.
- GC-MS assesses degradation from components in electrolytes with unknown usage.
- EDXRF easily evaluates transition metals, phosphorus, fluorine, and other elements deposited on electrodes.

■ Introduction

When lithium-ion batteries are used in EVs or ESS applications, numerous cells are connected in series and parallel to form modules, and multiple modules are further connected to construct a pack. In such configurations—where many cells are connected in series—the state of charge of individual cells varies, as shown in Figure 1. Moreover, because the cells are densely packed to reduce volume, the ambient temperature experienced by each cell also varies. In this application, we conducted cycle tests under overcharged or high-temperature conditions, disassembled the degraded pouch cells, and analyzed both the electrolytes and the electrodes.

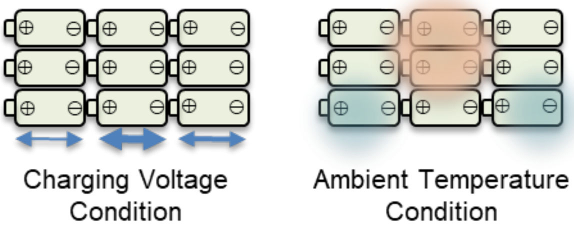


Fig.1 Charging and temperature conditions in a module (conceptual image)

■ Cell prototyping and cycle testing

Using the materials listed in Table 1, pouch cells were assembled and subjected to cycle testing under the conditions shown in Table 2. Figure 2 shows the appearance of the cells for Conditions #2 and #3 at the end of the cycle tests. In the pouch cell tested under Condition #3, swelling caused by gas generated inside the cell was observed.

Table 1 Structure of the pouch cell

Cathode	:	NCM523 / PVDF / Carbon black
Anode	:	Graphite / SBC+CMC / Carbon black
Electrolyte salt	:	$LiPF_6$ (1mol/L)
Electrolyte solvent	:	EC: EMC: DEC (1: 1: 1)
Electrolyte additives	:	VC (1vol.%), FEC (1vol.%)
Separator	:	PP

Table 2 Conditions of the cycle test (0.2C, 100 cycles) and SOH* at end of test

#	Cutoff voltage(V)	Ambient temperature (˚C)	SOH at 100 cycles (%)
1	4.0	40	99.8
2	5.0	40	39.2
3	5.6	40	38.7
4	4.0	50	89.8
5	4.0	60	89.5

(*) SOH (State of Health) indicates battery degradation and is defined as (full-charge capacity / initial full-charge capacity) × 100 (%).

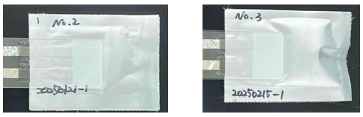


Fig.2 Condition of the pouch cells after cycle testing (left: #2, right: #3)

■ Analysis of electrolyte and electrode

Electrolytes and electrodes were extracted from the batteries degraded through the cycle tests (hereafter referred to as "degraded cells") and analyzed using the instruments shown in Figures 3–5. It is known that electrolytes in degraded cells contain transition metals (Ni, Co, Mn) dissolved from the cathode active material1). In addition, electrolyte solvents are known to generate characteristic degradation products as deterioration progresses2). By analyzing these degradation-related elements and compounds, the degradation state of the battery can be assessed. In this article, we propose a multifaceted evaluation of electrolytes using ICP-AES and GC-MS. On both the cathode and anode, insulating layers known as CEI/SEI form on the electrode surfaces. Under improper charging conditions, excessive formation of these layers can lead to capacity loss. Furthermore, the dissolved metals from the cathode deposit and precipitate on the anode. These deposits can cause internal short circuits, posing risks such as fire hazards. While such electrode conditions are typically evaluated by ICP-AES or XPS to examine elemental content or surface chemical states, this article introduces a simpler evaluation method using EDXRF.

Fig.3 ICP-AES (Model: ICPE-9820)

Fig.4 GC-MS (Model: GCMS-QP2050 + AOC™-30i)

Fig.5 EDXRF (Model: EDX-8100)

■ Electrolyte analysis results (ICP-AES)

Table 3 shows the ICP-AES analysis results of transition metals in electrolytes. Because the electrolyte samples were measured after dilution, Table 3 lists both the measured values of the diluted solutions and the corresponding concentrations in original electrolytes. The analytical conditions are described later in Table 7.

Figure 6 compares the concentrations of Ni, Mn, and Co in electrolytes under different cutoff voltages (#1, #2, #3), while Figure 7 presents comparisons under different ambient temperatures (#1, #4, #5). For the cutoff voltage conditions, the detected amounts of transition metals increased as the conditions became more severe. In contrast, under the different ambient temperature conditions, the detected amounts were below 1 ppm in all cases.

Table 3 ICP-AES analysis results of transition metals in electrolytes

Element		Ni	Mn	Co
Wavelength (nm)		231.604	257.610	238.892
Instrument Quantitation Limit[*1] (10σ) (mg/L)		0.004	0.0002	0.001
Measured value of diluted solutions (mg/L)	#1	0.004	0.00024	N.D. [*2]
	#2	1.18	0.0237	0.264
	#3	0.913	0.197	0.215
	#4	0.014	0.00191	0.0025
	#5	0.004	0.00022	N.D.
Concentration in electrolytes[*3] (mg/kg)	#1	0.30	0.016	N.D.
	#2	179	3.59	40.0
	#3	380	82.1	89.6
	#4	0.72	0.098	0.13
	#5	0.25	0.015	N.D.

*1 Instrument quantitation limit = 10 × σ (standard deviation of the blank solution) × calibration curve slope.
*2 N.D.: below the quantitation limit.
*3 Concentration in electrolytes = measured value of diluted solutions × dilution factor. Refer to Table 7 for dilution factors.

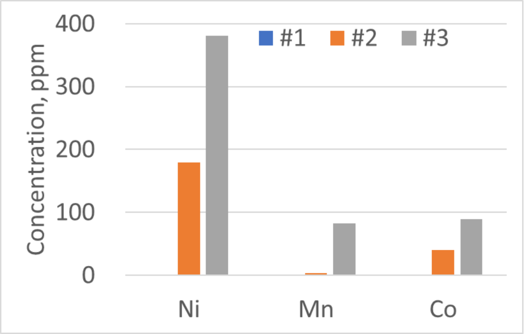


Fig.6 Comparison of Ni, Mn, and Co concentrations in electrolytes (by cutoff voltage)

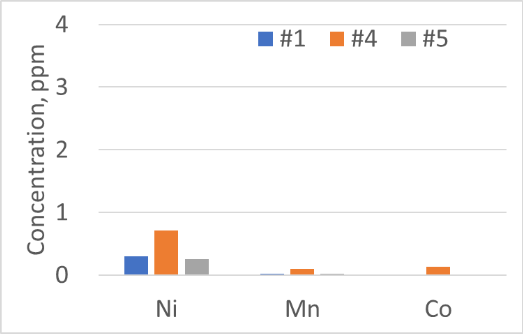


Fig.7 Comparison of Ni, Mn, and Co concentrations in electrolytes (by ambient temperature)

■ Electrolyte analysis results (GC-MS)

Table 4 lists electrolyte degradation products[2),3)]. Figure 8 shows example chromatograms of EDMP and DEDOHC detected under Condition #3. The peak area values of Compounds A–I obtained in SIM mode are summarized in Table 5. The analysis conditions are described later in Table 8.

Figures 9 and 10 compare the peak areas of each compound for different cutoff voltages and different ambient temperatures, respectively. For the cutoff voltage conditions, the detected amounts of all compounds increased markedly, and for the ambient temperature conditions, compounds G, H, and I also showed an increasing trend.

Table 4 Electrolyte degradation products list identified by GC-MS

Symbol	Compounds (abb.)	Quantitative ion (*m/z*)	Qualitative ion (*m/z*)
A	Dimethyl phosphorofluoridate (DMFP)	90	80
B	Ethyl methyl phosphorofluoridate (EMPF)	115	127, 97
C	Diethyl phosphorofluoridate (DEPF)	101	129, 113
D	Ethyl dimethyl phosphate (EDMP)	127	110, 109
E	Diethyl methyl phosphate (DEMP)	141	113, 95
F	Triethyl phosphate (TEP)	155	127, 99
G	Dimethyl-2,5-dioxahexane dicarboxylate (DMDOHC)	102	91, 59
H	Ethylmethyl-2,5-dioxahexane dicarboxylate (EMDOHC)	116	91, 89
I	Diethyl-2,5-dioxahexane dicarboxylate (DEDOHC)	103	90, 89

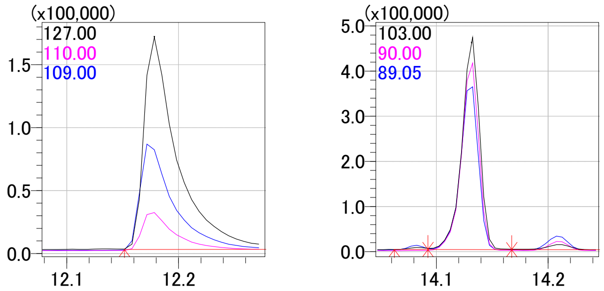


Fig.8 Chromatograms of compounds detected from Condition #3 by SIM-mode (right: EDMP, left: DEDOHC)

Table 5 Peak area values for each compounds

Symbol	#1	#2	#3	#4	#5
A	-	21,221	125,609	-	-
B	-	261,555	1,804,650	-	-
C	-	371,846	4,745,557	-	-
D	-	38,925	352,338	-	-
E	-	6,784	249,905	-	-
F	-	30,207	612,945	-	-
G	-	17,494	26,039	331	592
H	2,351	231,407	363,546	3.209	7,179
I	5,168	364,041	503,875	6,885	14,370

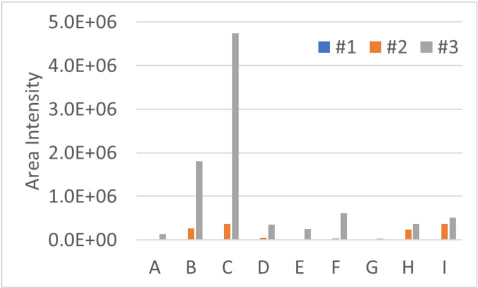


Fig.9 Comparisons of peak area values of compounds in electrolytes (by cutoff voltage)

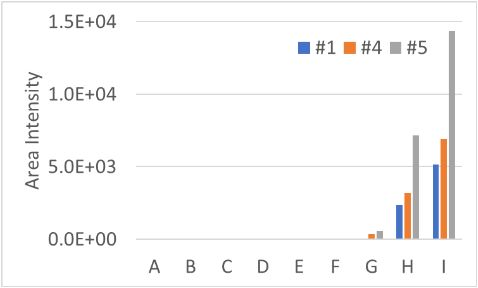


Fig.10 Comparisons of peak area values of compounds in electrolytes (by ambient temperature)

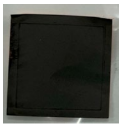
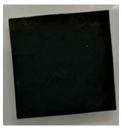
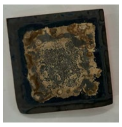
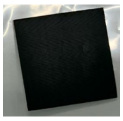
■ Electrode analysis results (EDXRF)

Table 6 shows the appearance of the extracted electrode surfaces. Representative samples (#1, #2, and #4) are shown here.

Visually, the sample for different cutoff voltages (#2) exhibited greater changes than the sample for different ambient temperatures (#4). In addition, comparison of the cathode and anode in sample #2 indicated that the anode showed more pronounced changes.

Elemental analysis of these electrode surfaces was performed using EDXRF. Because EDXRF allows direct analysis of solid samples, the extracted electrodes could be analyzed without any pretreatment.

Table 6 Appearance of electrodes after cycle testing

#	Cathode	Anode
1		
2		
4		

Figures 11–14 show the analysis results for the different cutoff voltage conditions. Analysis conditions are provided later in Table 9.

Figure 11 presents overlaid EDXRF profiles of Ni, Mn, and Co in the cathode, and Figure 12 compares their elemental amounts, shown as ratios relative to sample #1.

Figures 13 and 14 summarize the anode results. Because Ni, Mn, Co, and F were not detected in the anode of sample #1, their values are compared relative to the cathode of sample #1, while P is compared relative to the anode of sample #1.

Figures 12 and 14 show that transition-metal quantities changed in line with the ICP-AES electrolyte analysis, indicating dissolution from the cathode and deposition in the anode. Fluorine decreased in the cathode and increased in the anode, whereas phosphorus increased in both electrodes.

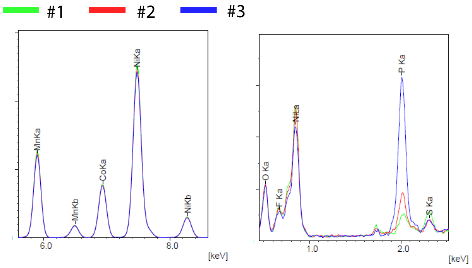


Fig.11 Overlaid elemental profiles in the cathode (by cutoff voltage)

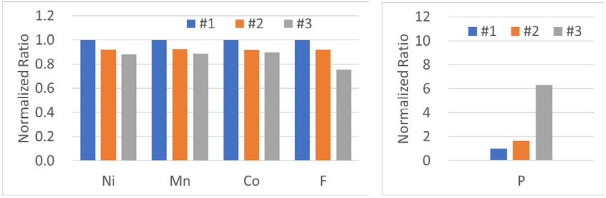


Fig.12 Comparison of cathode elemental amounts (by cutoff voltage) (Ratios relative to the #1 cathode)

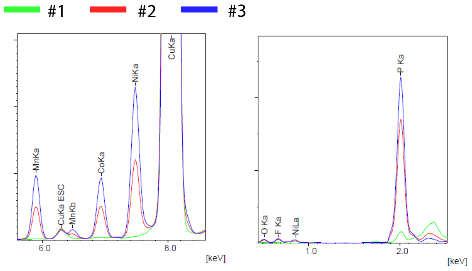


Fig.13 Overlaid elemental profiles in the anode (by cutoff voltage)

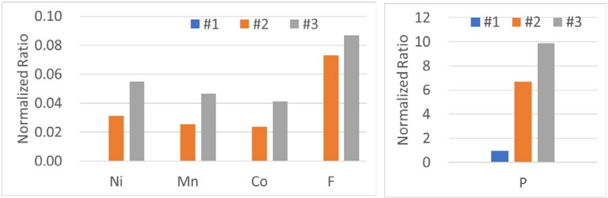


Fig.14 Comparison of anode elemental amounts (by cutoff voltage) (Ni/Mn/Co/F relative to the #1 cathode; P relative to the #1 anode)

Figures 15 and 16 present the comparison of elemental amounts for the different ambient temperatures. As in Figures 12 and 14, the values are shown as ratios with each elemental amount in sample #1 set to 1. No changes in transition metals were observed in the cathode, and none were detected in the anode under any condition.

In contrast, phosphorus showed an increasing trend with higher ambient temperature, although the change was smaller compared with samples #2 and #3.

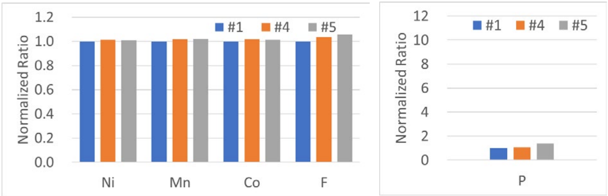


Fig.15 Comparison of cathode elemental amounts (by ambient temperature) (Ratios relative to the #1 cathode)

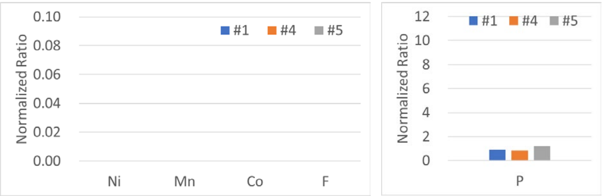


Fig.16 Comparison of anode elemental amounts (by ambient temperature) (Ni/Mn/Co/F relative to the #1 cathode; P relative to the #1 anode)

■ Summary

Analysis of the electrolytes from degraded batteries using ICP-AES and GC-MS revealed dissolution of transition metals as well as the formation of degradation products. Furthermore, EDXRF analysis of the electrodes enabled straightforward detection of changes in elemental composition, including transition metals, fluorine, and phosphorus. These analytical techniques allow for a multifaceted evaluation of battery degradation.

In real-world battery operation, fluctuations in charging conditions and ambient temperature introduce variability in degradation states. By assessing degradation mechanisms individually, as demonstrated in this report, it is possible to obtain insights that contribute not only to improving intrinsic battery performance but also to optimizing implementation methods and control conditions.

<References>

1) Xuanting Wu, et al., “A functional slurry additive for robust interphase and stabilized high-voltage nickel-rich cathodes in lithium-ion batteries,” Chemical Engineering Journal, 509 (2025) 161446

2) Waldemar Weber, et al., “Ion and gas chromatography mass spectrometry investigations of organophosphates in lithium ion battery electrolytes by electrochemical aging at elevated cathode potentials,” Journal of Power Sources, 306 (2016) 193-199

3) Martin Grützke, Waldemar Weber, Martin Winter and Sascha Nowak, “Structure determination of organic aging products in lithium-ion battery electrolytes with gas chromatography chemical ionization mass spectrometry (GC-CI-MS)”, RSC Adv., 6 (2016), 57253

<Related Applications>

1. Analysis of Elemental Impurities in Lithium-Ion Secondary Battery Electrolytes Using the ICPE-9800 Series, Application News No. 01-00702-en
2. GC/MS Analysis of Fluorophosphates as Decomposition Products in Lithium Battery Electrolyte, Application News No. 05-SCA-280-105-EN

Table 7 ICP-AES Analytical Conditions

[Configuration]	
Instrument	: ICPE-9820
Nebulizer	: Nebulizer, PFA1S
Chamber	: Cyclonic Chamber for Hydrofluoric Acid
Extension Pipe	: Made of Quartz
Torch	: Organic Solvent Torch
Drain	: Hydrofluoric Acid Resistant Drain
Auto Sampler	: AS-10
[Analysis Conditions]	
RF Power	: 1.40 kW
Plasma Gas Flowrate	: 20.0 L/min
Auxiliary Gas Flowrate	: 0.70 L/min
Carrier Gas Flowrate	: 0.75 L/min
View Direction	: Axial
[Sample Pretreatment]	
Dilution Solvent	: Ethanol : Pure Water = 1 : 1
Dilution Factor*	: #1 : 68.2 #2 : 151 #3 : 416 #4 : 51.5 #5 : 68.8
Internal Standard	: Germanium (Ge) 10 ppm

* The dilution factor varies depending on the amount of electrolytes collected.

Table 8 GC-MS Analytical Conditions

[Configuration]	
GC-MS Model	: GCMS-QP2050
Autoinjector	: AOC-30i
[GC]	
Column	: SH-I-5MS (P/N 221-75940-30) (30 m × 0.25 mm I.D., 0.25 μm)
Inj. Temp.	: 250 ˚C
Inj. Mode	: Split
Split Ratio	: 10
Carrier Gas	: He, constant linear velocity (36 cm/s)
Column Temp.	: 40 ˚C (3 min) → 3 ˚C/min → 60 ˚C→ 30 ˚C/min → 210 ˚C (20 min) → 10 ˚C/min → 280 ˚C (5 min)
[MS]	
Ion Source Temp.	: 230 ˚C
Interface Temp.	: 280 ˚C
Pumping speed	: 255 L/s
Acquisition Mode	: SIM
SIM monitoring *m/z*	: Refer to Table 4

Table 9 EDXRF Analytical Conditions

Instrument	: EDX-8100
Elements	: $_{6}$C-$_{92}$U
Analysis group	: Qualitative / quantitative analysis
Detector	: SDD
X-ray tube	: Rh target
Tube Voltage	: 15 [kV] (C-S) (Cl-V), 50 [kV] (Cr-U)
Tube current	: Auto [µA]
Collimator	: 10 [mmφ]
Primary filter	: Non (C-S), #2 (Cl-V), #3 (Cr-U)
Atmosphere	: Vacuum
Integral time	: 60 [s] x 3 (C-S), (Cl-V), (Cr-U)
Dead time	: Max. 30 [%]

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