XES Chimica

X-ray Emission Spectrometer

Rigaku

POWERING NEW PERSPECTIVES

X-ray Emission Spectrometer

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Toward Another Standard in Chemical State Analysis

X-ray Emission Spectroscopy (XES) is a technique that enables quantitative analysis of the chemical states of elements. By examining spectral chemical shifts and profile variations, it provides information on valence states and compound forms.

Unlike surface- or microarea–restricted techniques, XES offers wide-range bulk analysis with excellent quantitative performance derived from high-intensity measurements. It provides a unique analytical perspective distinct from conventional methods. Moreover, without relying on synchrotron radiation, XES allows precise evaluation of chemical states in a standard laboratory environment.

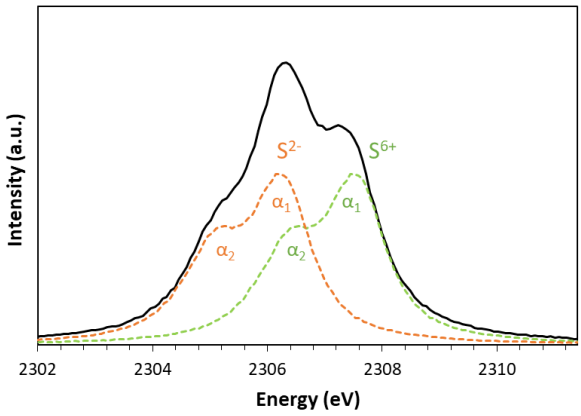
Rigaku's X-ray emission spectrometer XES Chimica is equipped with a newly developed optical system that further enhances reproducibility and reliability. The system incorporates automatic spectroscopic crystal exchange, automated sample exchange, and software for quantitative analysis, combining operability with practicality.

XES Chimica supports a wide variety of applications, including battery materials and catalysts.

Easy, Quantitative Bulk Chemical State Analysis—Anytime, in the Laboratory

Chemical State Analysis via Chemical Shifts

X-ray Emission Spectroscopy (XES) measures fluorescent X-rays with high energy resolution, capturing spectral variations arising from chemical bonding states. By analyzing chemical shifts and profile changes in the acquired spectra, XES enables the determination of valence states, chemical compositions, and compound forms of elements.



S Kα spectrum of sodium sulfite.
The fine structure reflects the −2 and +6 oxidation states of sulfur present in a 1:1 ratio in the compound, as well as the α1 and α2 electronic configurations.

No Synchrotron Required

XES provides information similar to that obtained by X-ray Absorption Spectroscopy (XAS), yet without the need for synchrotron radiation. This allows convenient chemical state analysis in a standard laboratory environment at any time.

Bulk-Averaged Analysis

The analytical range of XES covers an area of approximately 10–20 mm in diameter and a depth of several to several tens of micrometers. Unlike X-ray Photoelectron Spectroscopy (XPS), which is limited to micro-regions at the sample surface, XES acquires bulk-averaged information. This makes XES highly practical and reliable for analyzing surface-active samples and materials with heterogeneous compositions.

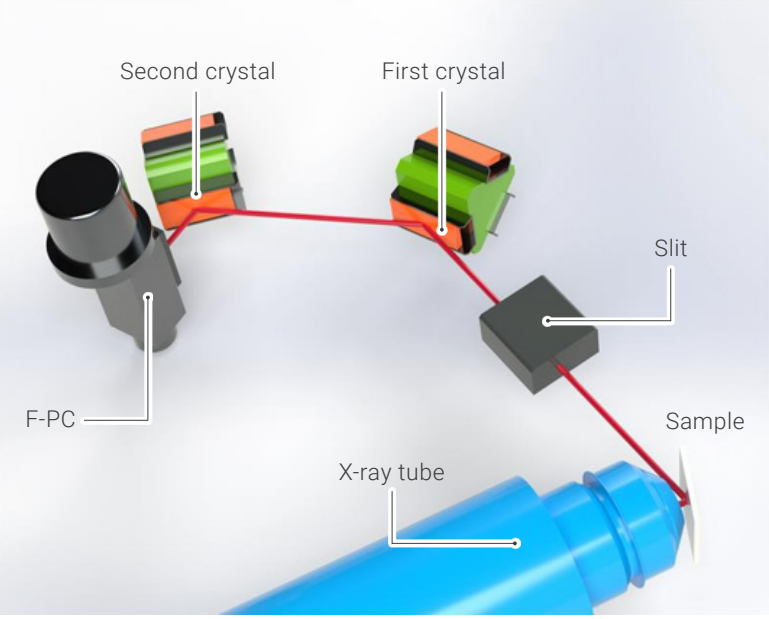
Highly Quantitative

Due to its high signal intensity, XES is particularly suitable for quantitative analysis. By fitting the obtained spectra, quantitative evaluation of chemical states can be readily performed.

	XES (X-ray Emission Spectroscopy)	XAS (X-ray Absorption Spectroscopy)	XPS (X-ray Photoelectron Spectroscopy)
Measurement Principle	Emission spectrum from outer-shell to inner-shell orbitals	Absorption spectrum from core orbitals to unoccupied orbitals	Kinetic energy of photoelectrons emitted from solid surfaces
Analysis Area (Depth / Diameter)	Bulk (μm/mm)	Bulk (μm/mm)	Surface / Microarea (nm/μm)
Measurement Environment	Vacuum	Atmosphere	High vacuum
Applicable Elements	Light (e.g., Si, S) to heavy elements	Transition to heavy elements	Light to heavy elements
Features	Quantitative chemical state analysis, bulk-averaged information	Chemical state and structural information	Surface chemical state analysis

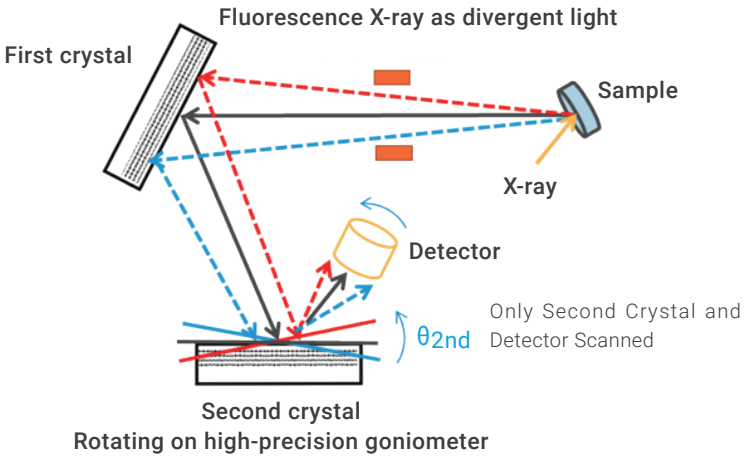
Instrument Design for High Precision and High Efficiency

Newly Developed Double-Crystal Spectroscopic Optics: Achieving High Resolution and Superior Reproducibility



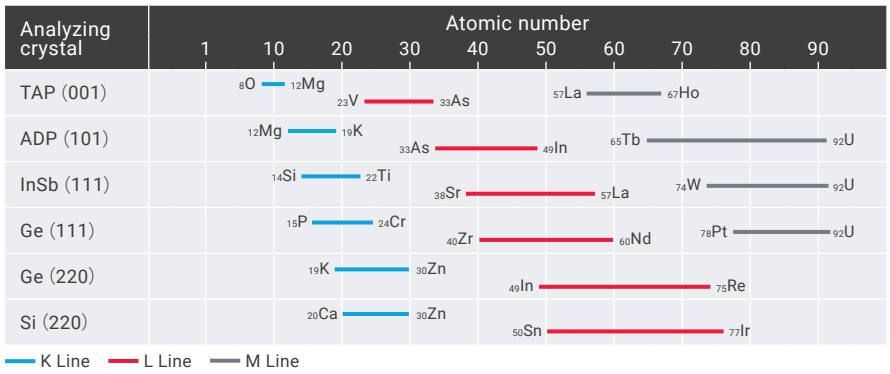
Narrow-Range Type Double-Crystal Spectrometer

Fluorescent X-rays emitted from the sample are collected as divergent radiation, reflected by the first crystal at a fixed angle, and then spectrally dispersed by precisely synchronized rotation of the second crystal. This enables acquisition of high-resolution spectra. With a design that minimizes the number of moving components, the system achieves excellent reproducibility despite employing a sequential scanning method.



Automatic Exchange Mechanism for Analyzer Crystals: Optimized for Each Target

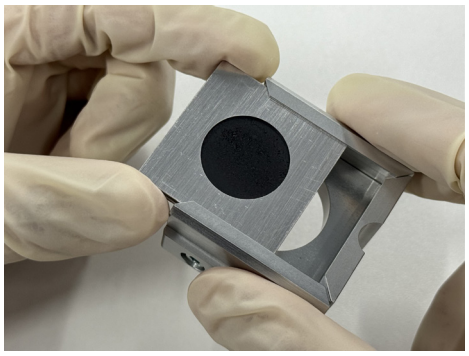
Up to three types of analyzer crystals can be mounted, enabling analysis across a wide elemental range from atomic number 8 (oxygen) to 92 (uranium). The system is equipped with an automatic crystal exchange mechanism, which switches to the optimal crystal according to the target element. It also supports soft X-ray analysis, such as O Kα and Fe Lα lines.



Automatic Sample Exchange Mechanism: Supporting Continuous Measurement and Automatic Calibration

The six-sample turret enables automated sample exchange for sequential measurements. The turret can also be replaced with a single-sample holder, providing flexibility to accommodate a wide range of applications.

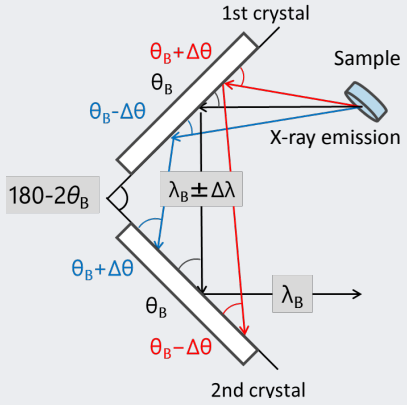
Sample holders: for six-sample turret (left) and for single-sample holder (right)



Electrodes and pellet samples are mounted by placing them between a mask and a backing plate, and then sliding the assembly into the holder.

Principle of Double-Crystal Spectroscopy

Double-crystal spectroscopy is based on the principle of Bragg reflection. In a (++) configuration (anti-parallel arrangement) of two identical crystals, the diffracted X-rays of wavelength λ_B, corresponding to the Bragg angle θ_B determined by the angle between the two crystals ($180° - 2\theta_B$), can be spectrally resolved with high resolution.

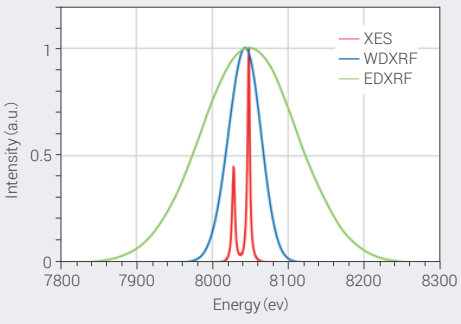


Bragg's law

$n\lambda = 2d \sin\theta$

λ : Wavelength of X-rays
θ : Glancing angle of X-rays
d : Lattice spacing of analyzing crystal
n : Integer

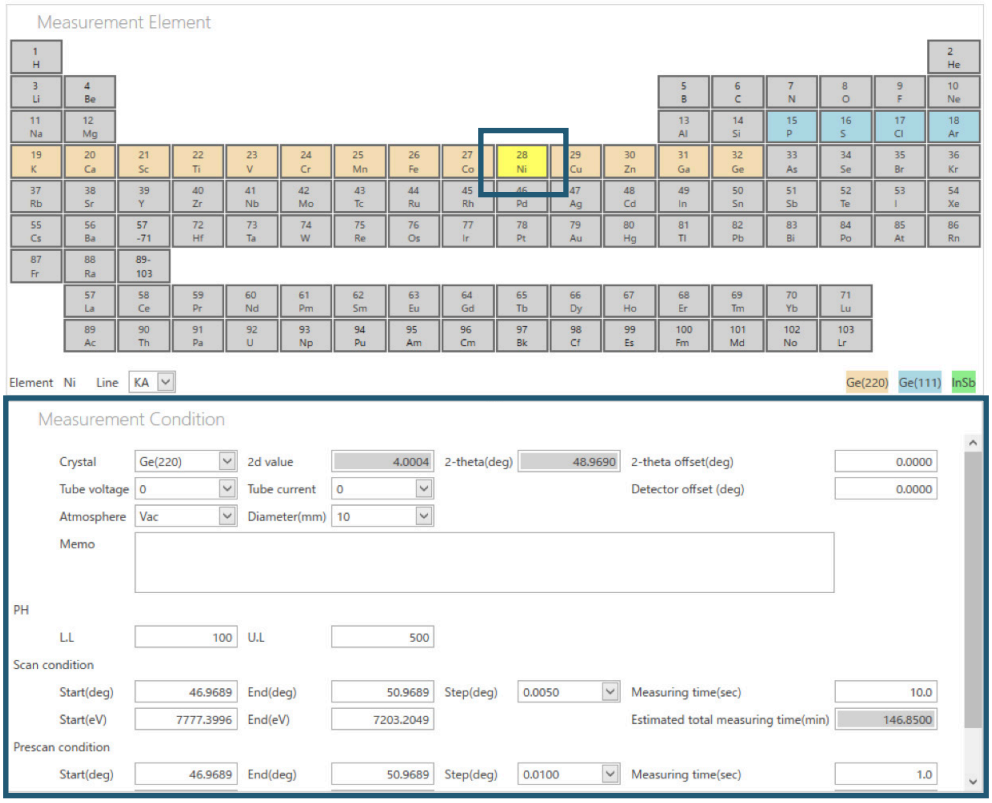
Cu Kα spectra of Cu metal



Integrated Software Supports Measurement and Analysis

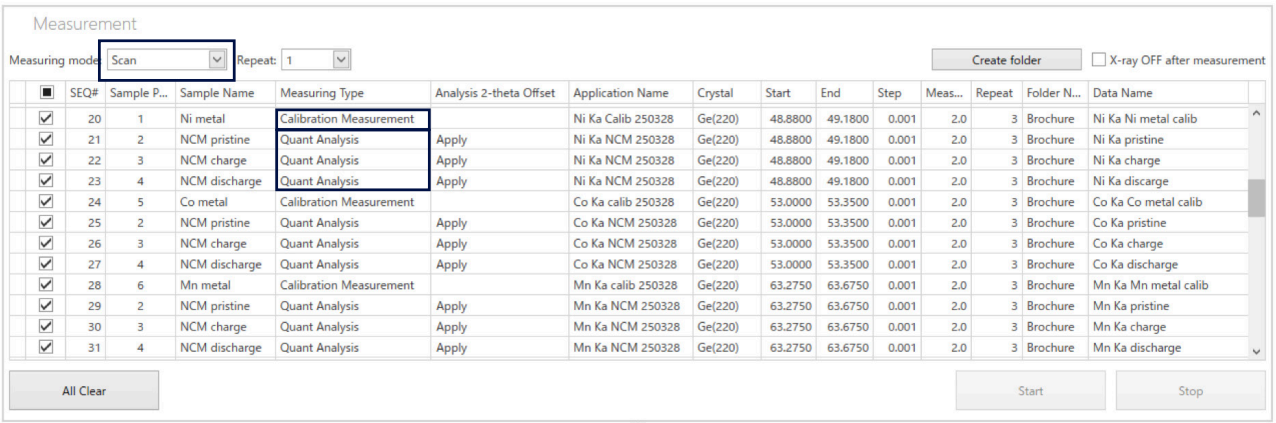
Measurement Condition Setting Assistance

Even without specialized knowledge, users can simply select the elements to be measured and the system performs the analysis automatically.



Multi-Sample Measurement Function

Continuous measurement of multiple samples improves measurement efficiency. The system supports automatic calibration and automatic quantification, with calibration results automatically applied to quantitative analysis. By switching between scan and pre-scan modes, users can smoothly perform everything from measurement condition verification to full measurements.



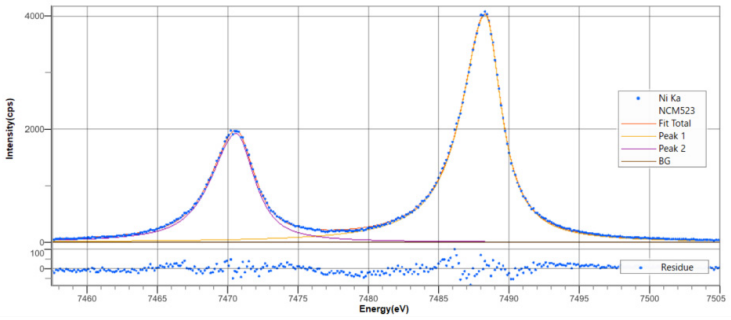
	SEQ#	Sample P...	Sample Name	Measuring Type	Analysis 2-theta Offset	Application Name	Crystal	Start	End	Step	Meas...	Repeat	Folder N...	Data Name
☑	20	1	Ni metal	Calibration Measurement		Ni Ka Calib 250328	Ge(220)	48.8800	49.1800	0.001	2.0	3	Brochure	Ni Ka Ni metal calib
☑	21	2	NCM pristine	Quant Analysis	Apply	Ni Ka NCM 250328	Ge(220)	48.8800	49.1800	0.001	2.0	3	Brochure	Ni Ka pristine
☑	22	3	NCM charge	Quant Analysis	Apply	Ni Ka NCM 250328	Ge(220)	48.8800	49.1800	0.001	2.0	3	Brochure	Ni Ka charge
☑	23	4	NCM discharge	Quant Analysis	Apply	Ni Ka NCM 250328	Ge(220)	48.8800	49.1800	0.001	2.0	3	Brochure	Ni Ka discarge
☑	24	5	Co metal	Calibration Measurement		Co Ka calib 250328	Ge(220)	53.0000	53.3500	0.001	2.0	3	Brochure	Co Ka Co metal calib
☑	25	2	NCM pristine	Quant Analysis	Apply	Co Ka NCM 250328	Ge(220)	53.0000	53.3500	0.001	2.0	3	Brochure	Co Ka pristine
☑	26	3	NCM charge	Quant Analysis	Apply	Co Ka NCM 250328	Ge(220)	53.0000	53.3500	0.001	2.0	3	Brochure	Co Ka charge
☑	27	4	NCM discharge	Quant Analysis	Apply	Co Ka NCM 250328	Ge(220)	53.0000	53.3500	0.001	2.0	3	Brochure	Co Ka discharge
☑	28	6	Mn metal	Calibration Measurement		Mn Ka calib 250328	Ge(220)	63.2750	63.6750	0.001	2.0	3	Brochure	Mn Ka Mn metal calib
☑	29	2	NCM pristine	Quant Analysis	Apply	Mn Ka NCM 250328	Ge(220)	63.2750	63.6750	0.001	2.0	3	Brochure	Mn Ka pristine
☑	30	3	NCM charge	Quant Analysis	Apply	Mn Ka NCM 250328	Ge(220)	63.2750	63.6750	0.001	2.0	3	Brochure	Mn Ka charge
☑	31	4	NCM discharge	Quant Analysis	Apply	Mn Ka NCM 250328	Ge(220)	63.2750	63.6750	0.001	2.0	3	Brochure	Mn Ka discharge

Spectrum Fitting and Quantitative Analysis

The dedicated GUI allows smooth and detailed data analysis. It supports energy calibration, Voigt function fitting, and linear combination fitting, enabling immediate extraction of important information from spectral analysis results.

Valence Analysis via Chemical Shifts

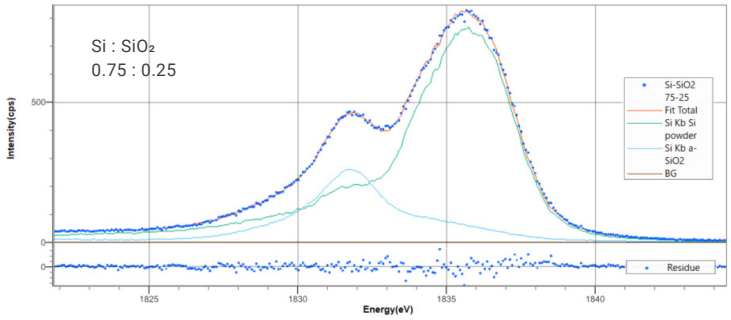
The average valence of a sample can be determined from the calibration curve relating peak energy to valence.



Peak No.	1	2
Use	☑	☑
Parameter Value	Result	Result
Peak Energy (eV)	7478.3877	7460.7304
Half Width (eV)	3.3945	3.6457
Asymmetry Index	1.4790	1.3631
Lorentz Ratio	0.9955	0.8708
Integral Intensity (eV*cps)	20494.3947	9750.3840
Intensity Ratio (%)	67.7618%	32.2382%

Component Analysis Using Linear Combination Fitting

The proportions of constituent components are estimated using standard reference spectra.



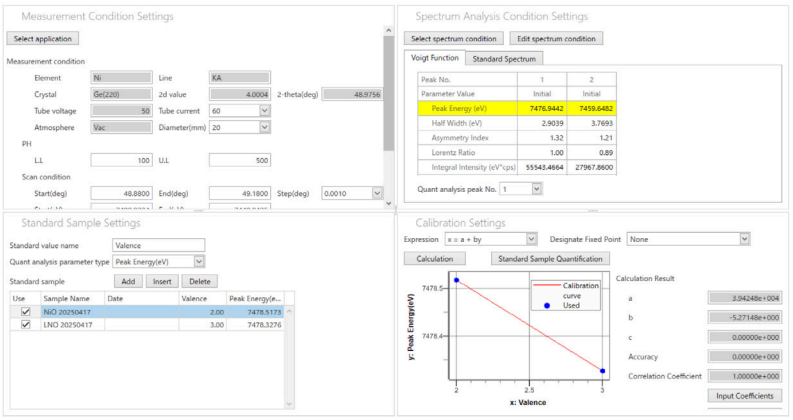
Wave No.	1	2
Use	☑	☑
Wave Name	Si Kb Si powd	Si Kb a-SiO2
Parameter Value	Result	Result
Integral Intensity (eV*cps)	3933.8932	1198.0800
Intensity Ratio (%)	76.6546%	23.3454%

Automated Quantification System

Pre-configured quantitative applications, including measurement conditions, analysis parameters, and calibration curves allow automatic quantification of analytical results such as valence states and compositional ratios.

Measurement → Automated spectral analysis → Automatic quantification → Result

Quantification application



Result

Analysis result

Voight function	Standard spectrum
Valence	3.000
Energy shift (eV)	0.000

Lithium-ion Battery Applications

In recent years, the adoption of electric vehicles (EVs) and stationary energy storage systems (ESS) has been accelerating to achieve carbon neutrality, leading to a significant increase in the demand for lithium-ion batteries (LiBs). To meet diverse requirements such as performance, cost, and cycle life, research on optimizing electrode materials and exploring advanced alternative materials is actively underway. Consequently, a variety of analytical techniques, including spectral analysis and in-operando cell testing, have become essential tools for evaluating material properties.

In battery material development, understanding electrochemical reaction mechanisms and analyzing electrode material degradation are critical challenges. XES is an effective method for quantitatively assessing these chemical state changes. XES analysis has been applied to a wide range of battery materials, including:

- NCM (Lithium Nickel Cobalt Manganese Oxide) cathodes
- LFP (Lithium Iron Phosphate) cathodes
- Silicon-based anodes
- Lithium–sulfur batteries
- LPS sulfide-based solid electrolytes

Controlled-atmosphere Chamber (Optional)

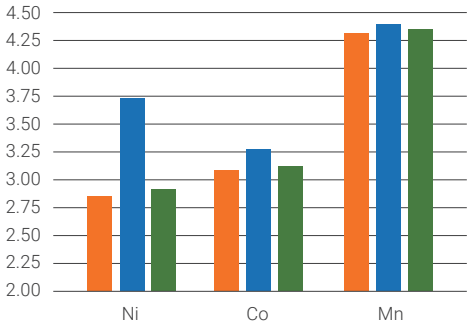
Samples can be placed inside a controlled-atmosphere chamber. By flowing dry air or argon gas, samples that are difficult to handle in ambient air can be measured smoothly and safely.

Chemical State Analysis of Ni, Co, and Mn in NCM Cathodes

Ni Co Mn

Lithium Nickel Cobalt Manganese Oxide ($LiNi_{1-x-y}Co_xMn_yO_2$, hereafter NCM) is widely used as a cathode material for lithium-ion batteries (LiBs) in electric vehicles (EVs) due to its high energy density, high nominal voltage, and excellent Coulombic efficiency. Material properties such as composition and particle size significantly affect battery performance, including capacity, cycle life, safety, and cost. Understanding the behavior of nickel (Ni), cobalt (Co), and manganese (Mn) during charge–discharge cycles is particularly important, as their redox activity directly impacts battery performance.

Although XAS using synchrotron radiation is commonly used, XES also enables quantitative evaluation of chemical state changes. We analyzed the chemical states of Ni, Co, and Mn in $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) cathodes in the pristine, charged, and discharged states. Based on the peak energies of each element's $K\alpha_1$ line, the valence of Ni increased from +2.9 to +3.8 during charging, contributing approximately +0.9 valence equivalent relative to the charge capacity. Co and Mn showed only minor changes during charging, and all elements largely returned to their original states upon discharge.



Valence states of Ni, Co, and Mn in NCM523 electrodes were quantified for the pristine, initial charge, and discharge states.

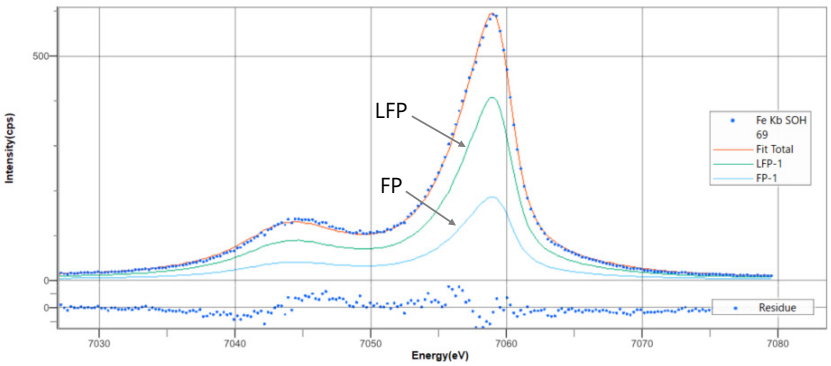
With XES Chimica, using the automated quantification system allows you to immediately assess changes in valence after measurement, without the need for time-consuming analysis.

Chemical State Analysis of Fe in LFP Cathodes

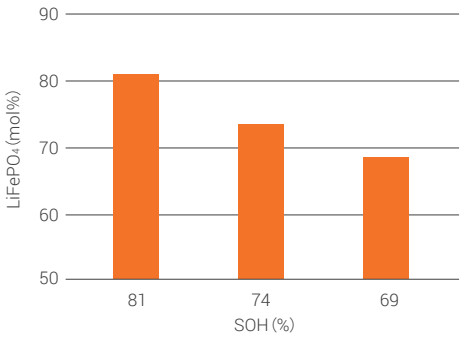
Fe

Lithium Iron Phosphate ($LiFePO_4$, LFP) has attracted attention as an inexpensive and safe cathode material, and its use is rapidly expanding. Due to its expected long cycle life, initiatives for reusing end-of-life batteries are also increasing. Accurate assessment of degradation and chemical changes in used batteries is essential to enable effective reuse.

We discharged and disassembled used, large-format LFP batteries and evaluated the chemical state of Fe in the cathodes. Using the Fe Kβ X-ray emission spectra and standard spectra of $LiFePO_4$ (LFP) and $FePO_4$ (FP), linear combination fitting was performed to determine the proportion of each component. The results showed that, across 15 sampling points per sample, the proportion of LFP decreased with decreasing State of Health (SOH) prior to disassembly. This indicates a loss of lithium within the cathode associated with battery degradation.



Linear combination fitting (LCF) results of Fe Kβ spectra using standard spectra of LFP and FP (sample: SOH 69%).



Correlation between pre-disassembly SOH and LFP fraction obtained from LCF results was plotted.

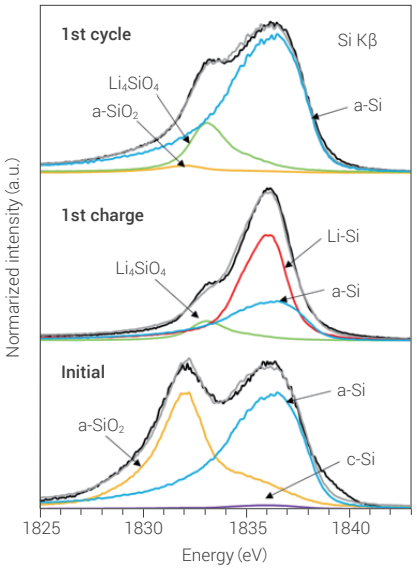
With XES Chimica, the analysis area spans 10–20 mm, making it suitable for in-plane averaged analysis of electrodes.

Quantification of Li/Si Ratio and Composition Analysis of Silicates in Si-based Anodes

Si

Si-based anodes are expected to be applied in automotive lithium-ion batteries (LiBs) due to their high theoretical capacity. However, large volume changes associated with alloying with lithium cause cycle degradation, which remains a major challenge. XES, characterized by high quantitative capability, is proposed as an effective method for analyzing Si states to study electrode reactions and degradation mechanisms.

Si Kβ XES spectra acquired during the first charge–discharge cycle of a SiO–C composite anode are shown. Standard spectra of crystalline Si (c-Si), amorphous Si (a-Si), $Li_{3.75}Si$ (Li–Si), SiO_2, and Li_4SiO_4 were used for linear combination fitting (LCF). The results indicate that, in the pristine state, Si is primarily composed of a-Si and SiO_2; during charging, Li–Si and Li_4SiO_4 are formed; and after cycling, a-Si and Li_4SiO_4 remain.



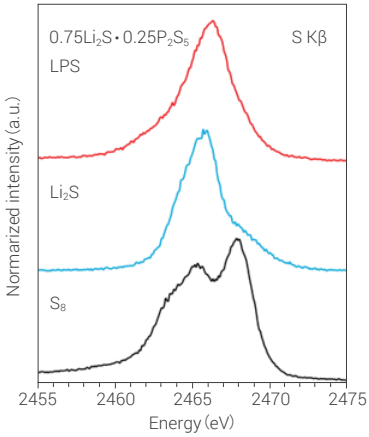
Si Kβ XES spectra of SiO/C composite anodes during first charge and discharge cycle, and the LCF results using standard reference materials

With XES Chimica, vacuum capability enables high-sensitivity analysis of light elements.

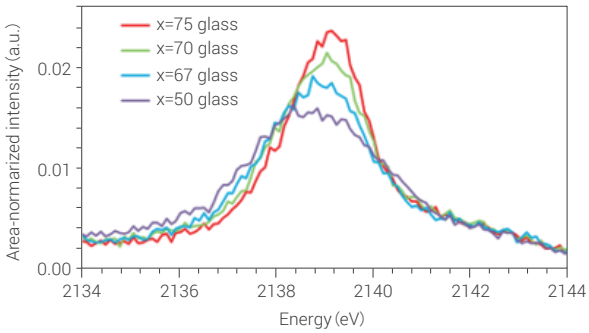
Sulfide-based Solid Electrolytes for Next-generation Batteries

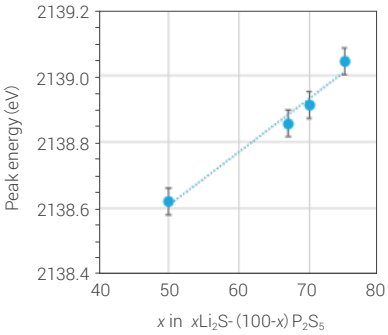
S P

As a key next-generation battery for electric vehicle (EV) adoption, the development of all-solid-state batteries, which do not use liquid electrolytes, has become a pressing priority. Sulfide-based materials used as solid electrolytes have structures that strongly influence battery performance. Since the XES spectra of sulfur (S) and phosphorus (P) vary with chemical state, they can be used to analyze composition and structure.



S Kβ XES spectra of sulfur and sulfides





The peak energy of the P spectra decreases and the peak width increases depending on the composition.

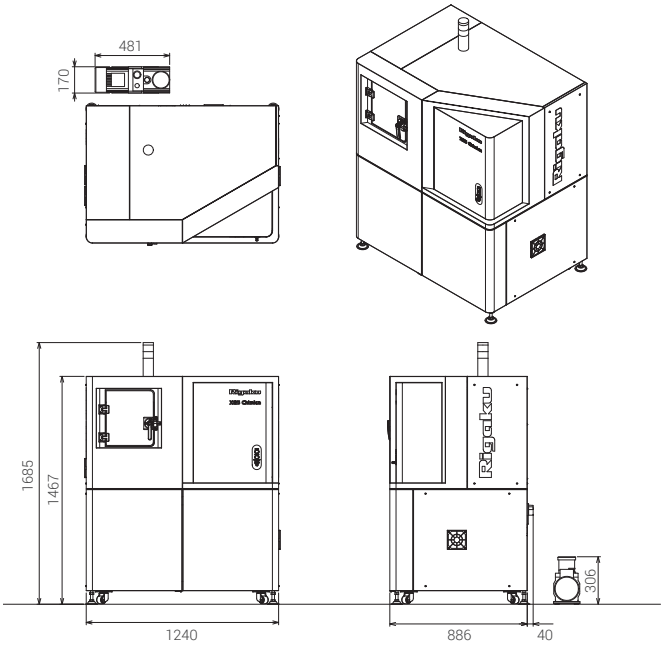
With XES Chimica, local structural information can be obtained from changes in peak energy and peak width, regardless of whether the material is crystalline or amorphous.

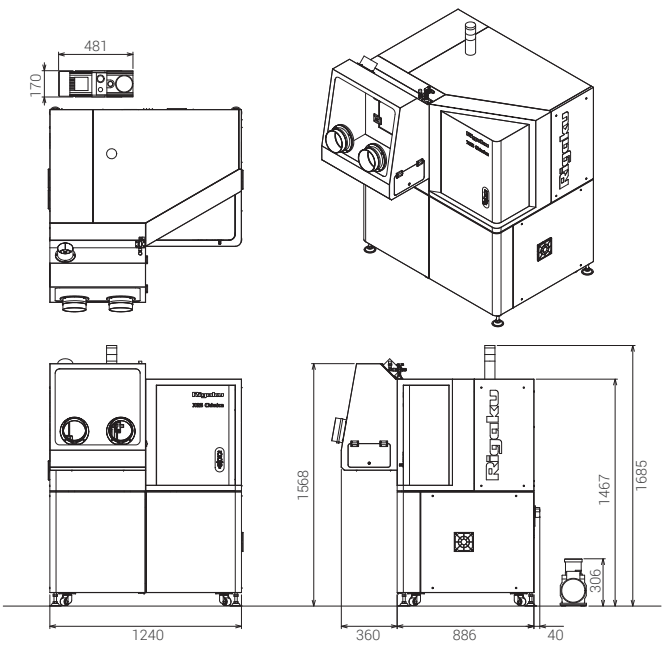
Specification

X-ray generator	X-ray tube	End window type, Rh target 4 kW
Spectrometer	System	Double-crystal spectrometer
	Angular range (2θ)	40–148°
	Step size	0.0001–0.05°/step
	Crystal exchanger	3-crystal automatic exchange mechanism
	Analyzing crystal	Si (220), Ge (220), Ge (111), InSb (111), ADP (101), (TAP (001): Soft X-ray analysis option)
	Analysis area diaphragm	20, 10 mm diameter
	Measurement Environment	Vacuum
Counting system	Detector	F-PC (Gas flow type proportional counter)
Sample size	Single-sample holder, 6-sample turret	□50 mm x 5 mm H / □35 mm x 5 mm H

Power	3 phase 200 V 40 A, Single phase 100 V 15 A (PC)
Cooling water	Temperature: Lower than 30℃, Pressure: 0.29–0.49 MPa, Flow: More than 5 L/min, Quality: Equivalent to drinking water
Gas for F-PC	P-10 gas: Ar 90%, Methane 10%, mixture gas: Gas pressure : 0.15 MPa, Gas flow : 7 ml/min
Room temperature	25–27℃ (with daily variation within ±1 ℃)

Dimensions (Unit: mm)





Controlled-atmosphere Chamber (Optional) **Weight**: 750 kg

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