# Standardless FP XRF analysis for lithium ion battery electrode materials

# Hikari Takahara\* and Hironori Kobayashi\*\*

### Abstract

Standardless FP X-ray fluorescence analysis is a quantification method using theoretical calculations including fundamental parameters. The analysis method has been widely used in the electronics and petrochemical industries, among others, since it can simply and quickly quantify sample compositions from spectral peak intensities without preparing calibration curves. In this report, the standardless FP analysis method was tested for metallic oxide compounds using cement and geological reference materials. The analysis results for Ni-based and Ni, Co, Mn-based cathode materials and SiO anode materials are shown.

# 1. X-ray Fluorescence Analysis for Lithium Ion Battery Electrode Materials

Lithium ion batteries have been widely used for mobile devices and are essential in daily life. Technological developments related to electric vehicles are an urgent requirement. In the electrode materials of electric vehicle batteries, Ni-based cathodes and silicon carbon composite anodes are used at present, and the materials are being improved by optimizing the compositions and additives to respond to the stringent requirements on energy density, homogeneity, safety and life cycles for the batteries. Since the composition and trace impurities of the electrodes directly affect battery performance, quantification analysis plays an important role.

X-ray fluorescence (XRF) analysis is an elemental quantification method. It performs qualitative and quantitative analyses by using characteristic X-ray fluorescence generated from samples. Energy dispersive XRF (EDX) covers elements from Na to U, and wavelength dispersive XRF (WDX) extends down to Be typically, and the analysis concentration ranges are from 100% down to ppm level. In contrast to ICP optical emission spectrometer (ICP-OES), an analysis method with similar sensitivity, XRF is non-distractive, thus sample preparation is simpler and non-time consuming. It is difficult to analyze Li with XRF spectrometry, but the light elements C, N, and O, and halogens F, Cl and Br are possible. Comparing XRF spectrometry to EDX integrated with SEM (SEM-EDX), SEM-EDX is an electron probe microscopy that is surface sensitive (on the order of nm in depth). XRF spectrometry uses an X-ray probe and its analyzing area is from sub mm to a few tens of mm typically to obtain average information. Because the charge-up effect commonly seen in SEM-EDX does not exist, XRF eliminates the need to pay close attention to insulating materials such as polymers

and ceramics.

XRF spectrometry is a bulk analysis method, probing from  $\mu$ m to sub mm in analysis depth. Figure 1 shows schematics of the analysis depths for C, O, Na, Mg, Si, transition metals, and heavier elements such as Nb and Zr in typical electrode materials. Analysis depth depends on the analysis line and matrices. The analysis depth can be as shallow as  $\mu$ m when the analysis element is a light element with low fluorescence X-ray energy, and can be deeper than 100 $\mu$ m when the analysis element is a heavier element with a higher XRF energy. The analysis depth is shallower for cathode materials (LiMO<sub>x</sub>; M=Ni, Co, Mn) that are composed of transition metal oxides, and deeper for anode materials mainly composed of light elements like C and Si.

# 2. Standardless FP X-ray Fluorescence Analysis Method

Quantitative analysis in XRF is normally carried out using either the calibration curve method or the standardless FP method (reference-free method, or FP method). In the calibration curve method, the X-ray intensities from unknown samples are empirically converted to concentrations using calibration curves that are created using standard samples. X-ray fluorescence intensity varies not only with concentration of the analyte but with absorption and enhancement from coexisting elements (matrix effect). The same concentration of Fe, for example, could give different intensities depending on the concentrations of coexisting elements. When using the calibration curve method, several standard samples that are composed of matrices similar to the unknown sample should be provided. The calibration curve method is suitable for routine analysis such as quality control of industrial products; therefore, accurate and precise results can be derived once the calibration curve has been created. On the other hand, the standardless FP method will be useful for research and development and failure analysis, as it can be conveniently adapted to any kind of unknown samples without creating calibration curves.

<sup>\*</sup> SBU-WDX, X-ray Instrument Division, Rigaku Corporation.

<sup>\*\*</sup> Research Institute of Electrochemical Energy, Department of Energy and Environment, Advanced Industrial Science and Technology. (AIST)



Fig. 1. Schematics of the analysis depths of C, O, Na, Mg, Si, transition metals, and heavier elements such as Nb and Zr in typical electrode materials. (a) LiMO<sub>2</sub> (M = Mn, Co, Ni), (b) Si, SiO, (c) graphite.



**Fig. 2.** Schematics of theoretical calculation of X-ray intensity in FP method. (a) The primary excitation: X-ray fluorescence of element i ( $I_i(1)$ ) is generated by irradiation of the primary X-ray ( $I0(\lambda)$  and reduced by the absorption of the sample matrix. (b) The secondary excitation: X-ray fluorescence of element i ( $I_i(2)$ ) is generated by fluorescence X-ray of element j in sample matrix. The  $\phi$  and  $\psi$  are the incident angle of the take-off angle of X-rays, respectively.

In the standardless FP method, theoretical calculation of X-ray intensities with fundamental parameters is applied to quantitative analysis. The X-ray fluorescence intensity of the analyte is affected by coexisting elements, and this effect can be calculated using fundamental parameters such as the mass attenuation coefficient, fluorescence yield, and so on (Fig. 2). Geometric factors such as the incident and take-off angles of the X-rays are also applied to this theoretical calculation. In the quantification calculation, all elemental components are determined iteratively until the theoretical intensities of the sample model converge with the measured intensities scaled to theoretical intensity. The standardless FP analysis method provides quantification results quickly and simply, although care must be taken to guard against possible analytical errors. Theoretical X-ray intensities are calculated based on sample models, which become more accurate by inputting sample information into the model such as: bulk or thin film, non-measured components of organic components, binder and polymer film used for sample preparation. Correction of the sensitivities using a few known standard samples will be effective in improving the accuracy of the results. Validation with reference materials is important in evaluating the sample model, sample preparation, and sensitivity of the analysis method.

#### 3. Experimental

Table 1 lists the ten cathode materials and two anode materials of commercially available lithium battery electrode powders that were used in this study. To validate the analysis method, certified reference materials of cement (NIST Portland cement,

Table 1. Lithium ion battery electrode material samples.

	Abbreviation	Composition
А	NCA (0.85/0.10/0.05)	LiNi <sub>0.85</sub> Co <sub>0.10</sub> Al <sub>0.05</sub> O <sub>2</sub>
В	NCM (0.85/0.10/0.05)	LiNi <sub>0.85</sub> Co <sub>0.10</sub> Mn <sub>0.05</sub> O <sub>2</sub>
С	NCM (0.82/0.15/0.03)	LiNi <sub>0.82</sub> Co <sub>0.15</sub> Mn <sub>0.03</sub> O <sub>2</sub>
D/E/F	NCM (0.5/0.2/0.3)	LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub>
G/H/I	NCM (0.33/0.33/0.33)	LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>
J	NCM (0.36/0.34/0.3)	LiNi <sub>0.36</sub> Co <sub>0.34</sub> Mn <sub>0.3</sub> O <sub>2</sub>

(b) Anode material powders					
	Abbreviation	Condition			
K	SiO	(Non C-coated)			
L	c-SiO	C-coated			

1881a–1889a) and geological materials (GSJ, JA-1, JA-2, JA-3, JB-2, JB-2a, JB-3, JB-3a) were used. Chemical reagents Si and amorphous  $SiO_2$  (a- $SiO_2$ ) were employed as reference samples. The cathode material powders, cement, and geological reference materials were pressed into pellets using 32 mm diameter aluminum rings at a pressure of 8–10 MPa. Binder (Chemplex SpectroBlend) was added to the sample powders at a rate of 10 mass%. For SiO anode material powders, Si and a-SiO<sub>2</sub> reagents were pressed using a 14 mm diameter cylinder type die at 6 MPa.

XRF measurements were performed using the ZSX Primus IV wavelength dispersive XRF spectrometer (Rigaku). Measurements were done with a Rh target X-ray tube in a vacuum atmosphere. The default measurement condition settings of the spectrometer



Fig. 3. The relationship between standardless FP analysis values and certified values for cement and geological certified reference materials.

software were used for the standardless FP analysis (SQX analysis). A wide elemental range is scanned with the goniometer in the default condition. To improve the precision of trace elements, appropriate integration times can be added at the fixed angles for the specified elements (fixed angle measurement mode). The elemental range from  $_{9}F$  to  $_{92}U$  and a 30 mm diameter analysis area were preset for the cathode material powders, cement and geological reference materials. The elemental range from  $_{6}C$  to  $_{92}U$  and a 10 mm diameter analysis area were set for SiO anode material powders, Si and a-SiO<sub>2</sub> reagents. For elements with standard values less than 0.1 mass% in the reference materials, a fixed angle measurement of 20 s on the peaks and 10 s for the backgrounds were preset.

#### 4. Results and Discussion

Figure 3 shows the standardless FP analysis results for cement and geological reference materials. The analysis values showed good agreement with certified values for the range greater than 0.1 mass%. The relative errors were less than 10% for K, Ca, and most of the heavy elements. For Na and Al, the relative errors increased to approximately 20–30%, presumably because lighter elements with lower fluorescence X-ray energies are more influenced by heterogeneity effects such as the grain size, mineral structure, and segregation of powders. In addition, only Mg in the geological reference materials was part of the lower trend in analysis values. This could perhaps be caused by the mineralogical effect, stated in a previous report<sup>(1)</sup>. As for the trace elements with concentrations from 100 ppm (0.01 mass%) to 0.1 mass%, the relative errors were 20–30% regardless of the element. For the trace level of 10 ppm (0.001 mass%), the analysis errors increase, and Cl in cement reference materials showed a constant overestimation.

For the cathode materials of lithium ion batteries, the main components are transition metal oxides, which are different from CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> in the cement and geological materials. However, cathode materials and the reference materials are both composed of metallic oxide compounds. Therefore, when referring to the results in the reference materials, we considered accepting that the errors would be about 10% for the main components and 30% for minor components larger than 100 ppm. The analysis values for trace elements around the 10ppm level showed larger discrepancies and thus they were treated just for reference purposes only. Table 2 shows standardless FP analysis results for the main components in Ni-based or Ni, Co, Mn-based (NCM) cathode materials. The results are shown in molar ratio as x values in  $LiM_xO_2$ . The analysis values were consistent with ICP analysis values within 5% in relative error, although the relative errors were 20% for Al and Mn in sample A, B and C, which were the minor additives of 0.03 to 0.05 in x. In regard to the impurities of the samples, 10 ppm to 0.1 mass% of Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Sr, Zr, and W were detected (Table 3). The higher concentration impurities around 0.1-0.2 mass% of Al, Zr, and W were contained in sample F. Figure 4 shows the spectra of Na, Mg, Cl, Fe, and Sr in sample A, B, and D, for example. In general, Fe impurities in NCM cathode samples are

**Table 2.** Standardless FP analysis results for cathode material samples: the main components. The results are shownin molar ratios as x values in  $LiM_xO_2$ . The ICP analysis values and the relative errors are also shown.

Sample A				Sample F			
1	Al	Со	Ni	1	Mn	Со	Ni
XRF	0.042	0.156	0.803	XRF	0.304	0.197	0.49
ICP	0.05	0.15	0.80	ICP	0.30	0.20	0.50
Error (%)	-16.8	3.88	0.32	Error (%)	1.30	-1.34	-0.25
Sample B				Sample G			
	Mn	Со	Ni		Mn	Со	Ni
XRF	0.056	0.098	0.846	XRF	0.342	0.326	0.332
ICP	0.05	0.10	0.85	ICP	0.33	0.33	0.33
Error (%)	12.7	-2.09	-0.50	Error (%)	3.65	-1.24	0.61
Sample C				Sample H			
	Mn	Со	Ni		Mn	Со	Ni
XRF	0.036	0.152	0.812	XRF	0.341	0.327	0.331
ICP	0.03	0.15	0.82	ICP	0.33	0.33	0.33
Error (%)	19.0	1.30	-0.93	Error (%)	3.40	-0.78	0.41
Sample D				Sample I			
	Mn	Со	Ni		Mn	Со	Ni
XRF	0.309	0.201	0.490	XRF	0.343	0.326	0.331
ICP	0.30	0.20	0.50	ICP	0.33	0.33	0.33
Error (%)	3.03	0.43	-1.99	Error (%)	3.88	-1.15	0.29
Sample E				Sample J			
	Mn	Со	Ni		Mn	Со	Ni
XRF	0.303	0.204	0.493	XRF	0.295	0.33 <sub>6</sub>	0.370
ICP	0.30	0.20	0.50	ICP	0.30	0.34	0.36
Error (%)	1.00	2.11	-1.44	Error (%)	-1.83	-1.30	2.75

 Table 3.
 Standardless FP analysis results for cathode material samples: the trace impurities. The values inside the parentheses are for reference.

													(ppm)
	Na	Mg	Al	Si	Р	S	Cl	K	Ca	Fe	Sr	Zr	W
А	201	152	14915	291	(20)	832	(23)	ND	ND	(66)	ND	ND	ND
В	(61)	ND	(40)	339	(19)	619	(92)	ND	ND	(80)	ND	ND	ND
С	(61)	(17)	(31)	115	(15)	1117	ND	ND	ND	(87)	ND	(16)	ND
D	160	(44)	(50)	258	(28)	1050	ND	(56)	(54)	145	(30)	ND	ND
Е	227	(79)	164	381	(36)	1073	ND	(59)	(44)	(21)	103	ND	ND
F	655	(30)	1119	256	(24)	1521	(41)	ND	(11)	104	ND	1269	2149
G	152	(72)	(57)	361	(29)	661	ND	ND	(86)	112	ND	ND	ND
Η	300	(68)	(43)	246	(27)	682	(19)	ND	118	118	ND	ND	ND
Ι	330	(75)	(51)	428	(21)	1450	(16)	ND	(43)	(24)	ND	ND	ND
J	256	(63)	(36)	454	(37)	798	ND	ND	(97)	(97)	ND	(43)	ND

difficult to detect with energy dispersive XRF (EDXRF) since the Mn K $\beta$  line interferes with the Fe K $\alpha$  line. Trace Fe impurities were detected in the present report, using wavelength dispersive XRF (WDXRF), which

deconvolutes Fe K $\alpha$  peaks from the Mn K $\beta$  peak.

Tables 4 and 5 show standardless FP analysis results for SiO anode materials. In order to examine the molar ratio of Si and O (x value in  $SiO_x$ ) and quantification of



Fig. 4. X-ray fluorescence spectra of cathode material powders of samples A (blue), B (red), and D (green): (a) Na, (b) Mg, (c) Cl, (d) Fe, and (e) Sr.

Table 4.	Standardless FP analysis results for anode material
	samples: the molar ratio of Si and O (x value in
	$SiO_x$ ).

Si/O molar ratio (x value in SiO <sub>x</sub> )				
	x			
SiO	1.05			
c-coated SiO	1.04			
Si	0.03			
a-SiO <sub>2</sub>	2.04			

the amount of carbon coating, C and O were included in the analyzing elemental range. Regarding the molar ratio of Si/O, x values were 1.0. The reference sample results showed x=0.0 for Si reagent and 2.0 for  $a-SiO_2$ reagent. The expected values were obtained, suggesting the amount of oxygen could be analyzed by this method. Fig. 5(a) shows C K $\alpha$  spectra for SiO samples with/ without carbon coating. The C K $\alpha$  spectrum often shows pseudo peaks for samples that do not contain carbon due to high background. Since a slight C K $\alpha$  peak was shown for the SiO sample without carbon coating, this spectrum was used as a blank spectrum to correct the background effect of the carbon-coated SiO sample. The amount of carbon coating was estimated to be 2.1 mass% in the standardless FP analysis result, which was close to 1.6 mass% obtained by the BET surface area analysis method. As for trace impurities, a few tens ppm level of Al and Fe were detected. Zr from 100 to

Table 5.Standardless FP analysis results for SiO anode<br/>material samples: the amount of carbon coating and<br/>trace impurities. (a) non C-coated sample and (b)<br/>C-coated sample. The values inside the parentheses<br/>are for reference. The ICP analysis or BET analysis<br/>values and the relative errors are also shown.

(a) Non C-coated S	iO		(ppm)
	Al	Fe	Zr
XRF	(39)	(80)	174
ICP	11	14	129
(b) C-coated SiO			
	(mass%)		
	С		
XRF	2.1		
BET	1.6		
			(ppm)
	Al	Fe	Zr
XRF	(40)	134	146
ICP	16	23	175

200 ppm was also detected (Fig. 5(b)), which showed good agreement with ICP analysis values.

#### Conclusion

The standardless FP analysis results of the Ni/Co/



Fig. 5. X-ray fluorescence spectra of SiO anode material powders of non C-coated (blue) and C-coated (red): (a) C and (b) Zr.

Al or Ni/Co/Mn compositions showed good agreement with ICP analysis values for the commercially available Ni-based and NCM cathode material powders. In addition, trace impurities of Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Sr, Zr, and W from 10 ppm to 0.1 mass% were quantified. For the analysis of SiO anode materials, C and O were included in the elemental range and the molar ratio of Si/O and the amount of carbon coating were examined. Validation of the standardless FP analysis for cement and geological reference materials resulted in approximately 10% in the relative error for the range greater than 0.1 mass% for K, Ca, and most of the heavy elements. The relative errors were 20 to 30% for Na and Al and for the trace elements from 100 ppm to 0.1 mass% regardless of the element. The analysis values for trace elements around the 10 ppm level showed larger discrepancies and thus should be treated just for reference purposes only. The standardless FP analysis method enables simple and quick quantification of the elements from main components to trace impurities. We expect the method will be used widely in the lithium ion battery field, referring to the validation result in this report.

# Reference

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