Applicability of X-ray Fluorescence Analysis for Lithium-ion Battery Recycling Materials

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Abstract

The recycling of rare metals (Li, Ni, Co) from used lithium-ion batteries (LIBs) is important and the demand for compositional analysis of LIB recycling materials is increasing. Currently, ICP atomic emission spectrometry (ICP-AES) is widely used for the analysis of LIB recycling materials, but since it requires the use of acid and advanced processing techniques, a simpler analytical method is needed. In this report, the composition of black powder (BP) and black mass (BM), which are LIB recycling materials, was analyzed by X-ray fluorescence analysis (XRF) and the agreement with ICP-AES analysis values was confirmed. BP samples showed good agreement with ICP-AES analysis results using the balance estimation model with the scattering fundamental parameter (FP) method. For heterogeneous BM samples, oxidation treatment and fusion bead sample preparation were carried out to improve the analysis results.

Introduction

In recent years, the demand for lithium-ion batteries (LIBs) has increased significantly due to the accelerated development of electric vehicles as one of the efforts to achieve the goal of carbon neutrality. Due to this trend, regulations on the recycling of rare metals such as lithium, nickel and cobalt (Li, Ni, Co) used in LIBs have been tightened, and efforts to recycle these metals have been intensified in many countries. Figure 1 shows the LIBs recycling flow. LIBs collected by disposal companies are processed through intermediates that undergo crushing, sorting and roasting. Rare metals are refined, converted into resources, and reused in the battery manufacturing process. The intermediates include black powder (BP), which is obtained by crushing and sorting waste materials from the cathode manufacture process. The intermediates also include black mass (BM), which is the concentrate of cathode active material obtained from used LIBs. In the refining process of rare metals from BP and BM, elemental analysis is important because the composition of raw materials is strictly controlled. ICP atomic emission spectrometry (ICP-AES) is currently usually used for this purpose. However, since BP and BM contain various components such as carbon and transition elements derived from LIB constituents, there are many issues when acid decomposition is performed. The use of strong acids, processing conditions examination, waste liquid treatment issues remained when using ICP-AES.

We have been researching the use of X-ray fluorescence analysis (XRF) as a safer and simpler alternative for elemental analysis. In this paper, we evaluated the applicability of XRF for the composition analysis of BP and BM samples, and examined quantitative analysis method and sample preparation method to obtain more accurate analysis results.

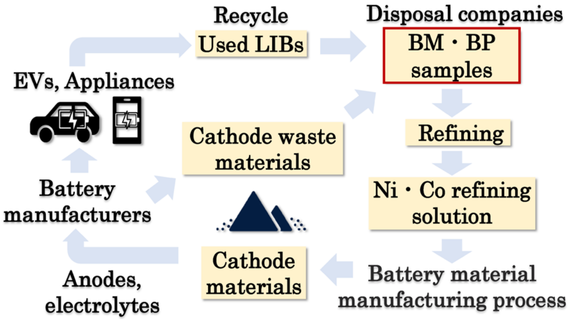

Fig. 1. Recycling flow of lithium-ion batteries.

1. Challenges of X-ray Fluorescence Analysis in LIB Recycling Materials Composition Analysis

Our group has analyzed the composition of LIB cathode and anode materials using the standardless fundamental parameter (FP) analysis method and reported the usefulness and validity of the analysis results. In standardless FP analysis, qualitative scan analysis is run first and then composition is calculated by the FP method using X-ray intensities of detected elements and FP sensitivity libraries registered in the software in advance(1). Since setting up calibration curves is not required, this method is suitable for the analysis of samples for which the preparation of standard samples is difficult. In the standardless FP analysis method, the effect of absorption and excitation of coexisting elements on the X-ray fluorescence intensity of each element generated from the sample is calculated theoretically using physical constants (fundamental parameters). In order to perform accurate theoretical calculations, it is important to know about all the elements contained in the sample, and the sample

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type information, such as metal or oxide. In the case of polymers and oils, specifying the non-measured components (calculation model) is also necessary.

When the composition of NCM cathode active material ($LiMO_2$; M = Ni, Co, Mn) was analyzed by standardless FP analysis, the component type was set as oxide. The content of Li, which cannot be measured by XRF, was set as a fixed value. By setting up such a calculation model, the concentrations and molar ratios of Ni, Co and Mn could be accurately analyzed(2). However, the same method was unable to obtain stable and accurate analysis results when applied to LIB recycling materials that have unclear compositions and heterogeneous samples. Based on the differences in the composition of cathode active materials and LIB recycling materials, we considered the following two issues and conducted various studies. Issue (1): Unlike cathode active materials, it is difficult to obtain information about lithium content in BP and BM, and the samples contain a high amount of carbon derived from binders and anode active materials. Issue (2): BM samples are heterogeneous with a mixture of metal components such as Al, Cu and Fe derived from the current collector foil and battery exterior, which is difficult to improve by pulverization(3),(4). As an example, an X-ray CT photograph of a BM powder sample used in this analysis is shown in Fig. 2. It was found that there were many fragments that seem to be metal components mixed in the sample, indicating that the BM powder sample was highly heterogeneous.

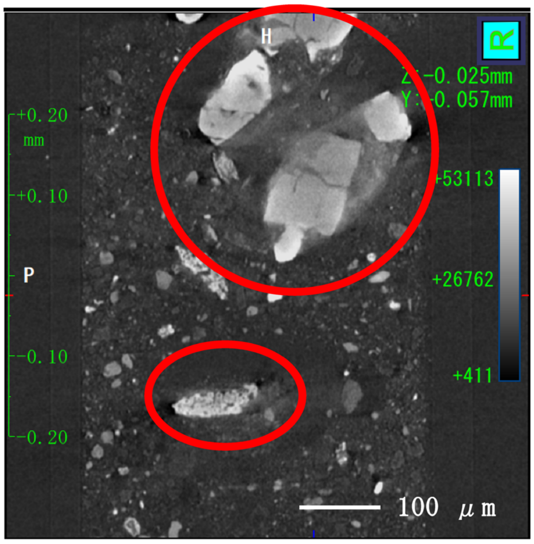

Fig. 2. X-ray CT photograph of BM powder sample (sample 1).
The area circled in red is presumed to be metal fragments from the contrast.
Captured by high-resolution X-ray microscope nano3DX (Rigaku product).

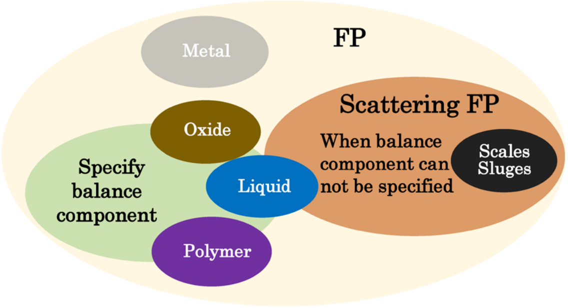

Fig. 3. Calculation models of the standardless FP method and examples of applicable samples.

For issue (1), we examined the calculation model and balance setting of the standardless FP method for BP and BM samples. Figure 3 shows the calculation models of the standardless FP method and examples of applicable samples. The composition of metal samples can be determined from only the measured X-ray intensity of the analytical line. In samples such as polymers, a model that sets the light elements component of the sample as the balance (balance setting model) is often used. This is because light elements such as carbon have an extremely shallow analyzing depth and are easily affected by the surface condition and heterogeneity of the sample. For these reasons the balance setting model provides better analysis results than using the measured X-ray intensity of carbon. For example, when analyzing trace impurities in graphite anode materials, carbon is set as the balance component(2). Moreover, the scattering FP method is effective for analyzing samples for which the balance component is difficult to specify. The scattering FP method uses the intensity of the scattering line to estimate the effect of ultralight elements below oxygen(5). It is therefore suitable for samples that contain immeasurable components such as sludge and scale. Since BP and BM samples contain a high amount of carbon, we first examined a calculation model in which carbon was set as the balance (C balance model). Since not only carbon but also a certain amount of lithium is contained, a model to estimate the balance using the scattering FP method (Balance estimation model) was also examined, and XRF results were compared with the ICP-AES analysis values.

For issue (2), we examined fusion bead sample preparation for LIB recycling materials. Fusion method is a sample preparation method in which a powder sample is melted with alkali flux to form a fusion bead. The fusion method results in a homogeneous sample by reducing grain size and mineralogical effects that cannot be removed by pulverization(6),(7). However, samples that contain a substantial amount of carbon and metal fragments such as BM do not vitrify homogeneously during melting and may cause an alloying reaction with the platinum crucible. Therefore, we investigated a method of oxidation treatment of BM samples before fusion bead processing.

2. Experimental

2.1. Sample Preparation

Five BP and three BM samples were ground for 2 minutes using a mixer mill. These BP and BM samples were then pelletized using a flat die and a PVC ring at a pressure of 100 kN.

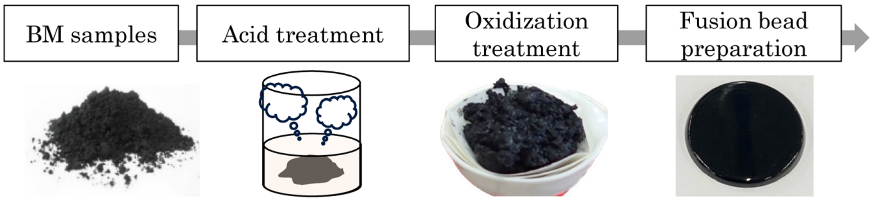

Fig. 4. Flow of oxidization treatment and fusion bead sample preparation for BM samples.

The BM samples were oxidized and prepared as fusion bead according to the flow shown in Fig. 4. Hydrochloric acid and nitric acid were added to the BM samples to dissolve the metal components contained in the samples while heating. Cellulose powder was then added to the BM dissolving solution and collected as a solid sample. The BM samples were then placed in an electric furnace at 850°C and heated to oxidize all the components to oxides. The oxidized BM samples were mixed with lithium tetraborate flux (FUJIFILM Wako Pure Chemical Corporation®) at a ratio of 1 : 20 and melted at 1150°C for 7 minutes using a benchtop high frequency bead sampler to prepare fusion bead samples.

2.2. XRF Measurement

The prepared BP and BM samples were measured with a Rigaku wavelength dispersive X-ray fluorescence spectrometer ZSX PrimusIV in vacuum with a measurement diameter of 20 mm. For each sample, qualitative analysis from F to Cm was performed, and the results obtained were used for standardless FP analysis.

Regarding the calculation model for standardless FP analysis, for the (1) C balance model, the component type of the detected elements was set as oxide, and the balance was set as carbon. XRF results were recalculated as elements by using the element/oxide conversion function in the software. For the (2) balance estimation model, the detected elements were set as elements instead of oxides and the balance was estimated using the scattering FP method.

3. Results

3.1. Quantitative Analysis for BP Powder Samples: Examination Results of the FP Calculation Method

Qualitative analysis of F to Cm was performed on five BP samples that were ground and pelletized, and standardless FP analysis was performed. In addition to the main components Ni and Co, components such as Al and F were detected (details of the analysis results are shown in 3.3). In this study, we focused on rare metals Ni and Co, and conducted two FP calculation models. (1) C balance model in which all the residues are assumed to be carbon, and (2) balance estimation model using the scattering FP method. Table 1 compares the XRF analysis results for Ni and Co with the ICP-AES analysis values. In the (1) C balance model, XRF analysis values were roughly correlated with the

Table 1. XRF analysis results of Ni and Co components in BP samples.

Unit : mass%

#		Ni	Co
1	ICP-AES	16.9	5.6
	C balance	12.6	4.3
	Balance estimation	17.2	5.9
2	ICP-AES	43.5	5.6
	C balance	39.5	5.3
	Balance estimation	43.9	5.9
3	ICP-AES	52.2	2.4
	C balance	34.7	1.7
	Balance estimation	55.0	2.7
4	ICP-AES	21.7	7.5
	C balance	16.4	5.7
	Balance estimation	22.7	7.8
5	ICP-AES	50.1	3.5
	C balance	35.6	2.6
	Balance estimation	52.4	3.8

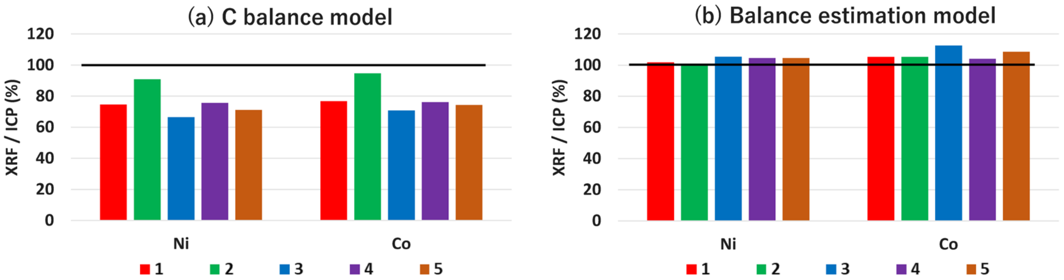

Fig. 5. XRF and ICP-AES analysis values of BP samples by different FP calculation models: (a) C balance model, (b) balance estimation model.

ICP-AES analysis values, but there were some samples with large errors. On the other hand, XRF analysis values obtained by the (2) balance estimation model showed good agreement with ICP-AES analysis values over a wide concentration range.

Figure 5 compares the XRF and ICP-AES analysis values of the BP samples for each FP calculation model. The percentages of the XRF analysis value obtained for each sample relative to the ICP-AES analysis value were calculated. The difference from 100% indicates the magnitude of the relative error. The relative errors between XRF and ICP-AES for Ni and Co components in the (1) C balance model were about 20–30%, while in the (2) balance estimation model, the relative errors for both components were within about 10%. Since lithium is also present in the BP samples, a sample model that only assumes carbon as the residue is insufficient. The balance estimation model based on the scattering FP method estimates the average atomic number and total content of the components with atomic numbers smaller than oxygen using the scattering X-ray intensity, and thus is considered to be more accurate in analyzing the content of Ni and Co components.

Table 2. XRF analysis results of Ni, Co, Al and Cu components in BM samples.

Unit : mass%

#		Ni	Co	Al	Cu
1	ICP-AES	6.36	31.3	15.2	8.68
	Powder (Balance estimation)	5.17	32.8	32.2	5.55
	Fusion bead	6.45	31.0	12.1	7.34
2	ICP-AES	17.2	17.7	8.5	4.41
	Powder (Balance estimation)	17.4	16.7	15.7	2.66
	Fusion bead	19.7	20.3	7.7	4.83
3	ICP-AES	26.9	18.8	14.5	2.54
	Powder (Balance estimation)	29.1	10.2	14.2	0.54
	Fusion bead	26.0	20.8	12.7	2.50

3.2. Quantitative Analysis for BM Samples: Examination Results of Powder Samples and Fusion Bead Samples

In addition to the rare metals Ni and Co, we also focused on Al and Cu, which are important control elements in the recycling process, and evaluated the agreement between XRF and ICP-AES analysis values. Comparisons with ICP-AES values were made for both BM powder samples and BM fusion bead samples. Table 2 shows the results of each sample.

Figure 6(a) shows a graph comparing XRF and ICP-AES analysis values using the balance estimation model for BM powder samples. The relative errors were different for each sample and element, and the relative errors for Al and Cu were large. The Al analysis values tended to be over analyzed and the Cu analysis values tended to be under analyzed. BM samples contained not only the cathode active materials but also the battery constituent materials. The FP method performs quantitative calculation on the assumption that the sample is in a homogeneous state, so heterogeneity is a factor that may cause analysis error.

Figure 6(b) shows a graph comparing XRF and ICP-AES analysis values of BM fusion bead samples. Compared to BM powder samples, the XRF analysis values of each component in the fusion bead samples generally agreed with the ICP-AES analysis values, and the relative errors with the ICP-AES analysis values were within 20%. In particular, the analysis values of Al and Cu were greatly improved. This is thought to be due to the fact that Al and Cu, which existed in the BM powder samples as metal fragments and alloys, were dissolved, oxidized, and homogenized by sample preparation.

3.3. Qualitative Analysis Results Including Trace Components of BP and BM Samples

In order to accurately conduct the refining process to extract rare metals from BP and BM samples, it is important to know the concentrations of not only Li, Ni and Co, but also elements such as Al, Fe, Cu, F and P. In particular, fluorine derived from lithium hexafluorophosphate ($LiPF_6$) electrolyte and polyvinylidene fluoride (PVDF) binder must be known because of the risk of generating toxic hydrofluoric acid (HF) gas upon heating. Before performing these procedures, proper measures must be taken by

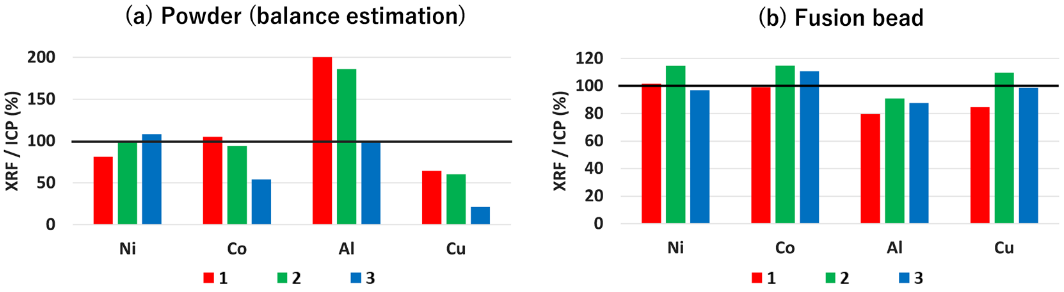

Fig. 6. XRF and ICP-AES analysis values of BM samples: (a) powder, (b) fusion bead.

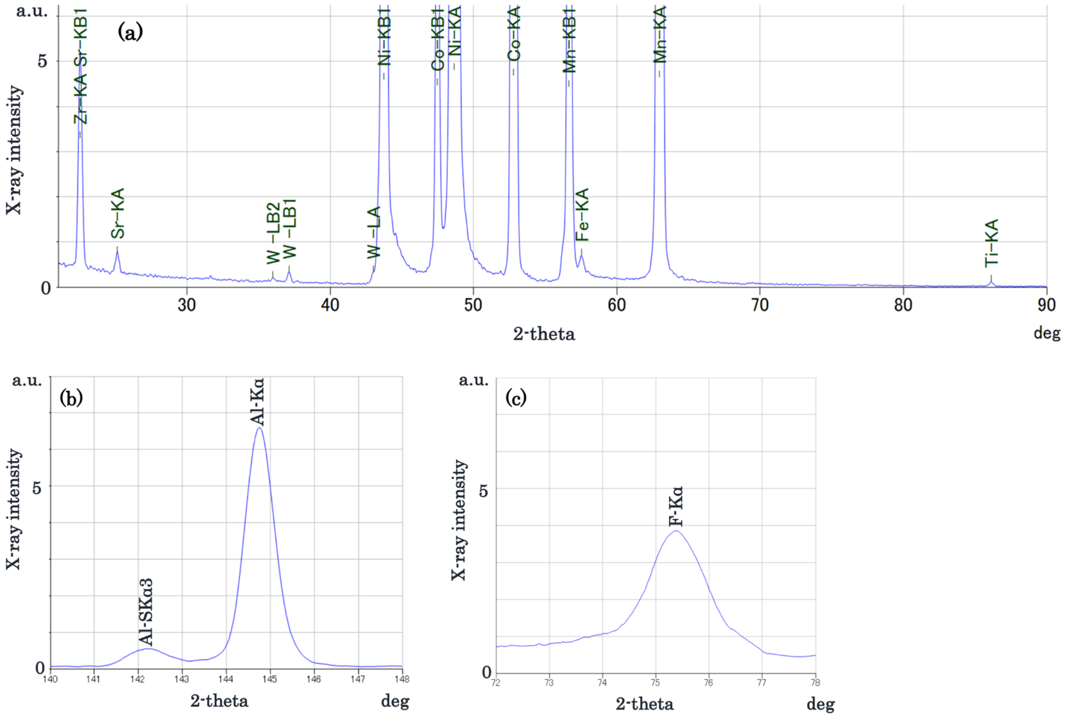

Fig. 7. Qualitative spectra of BP powder sample 1: (a) heavy elements region, (b) Al, (c) F.

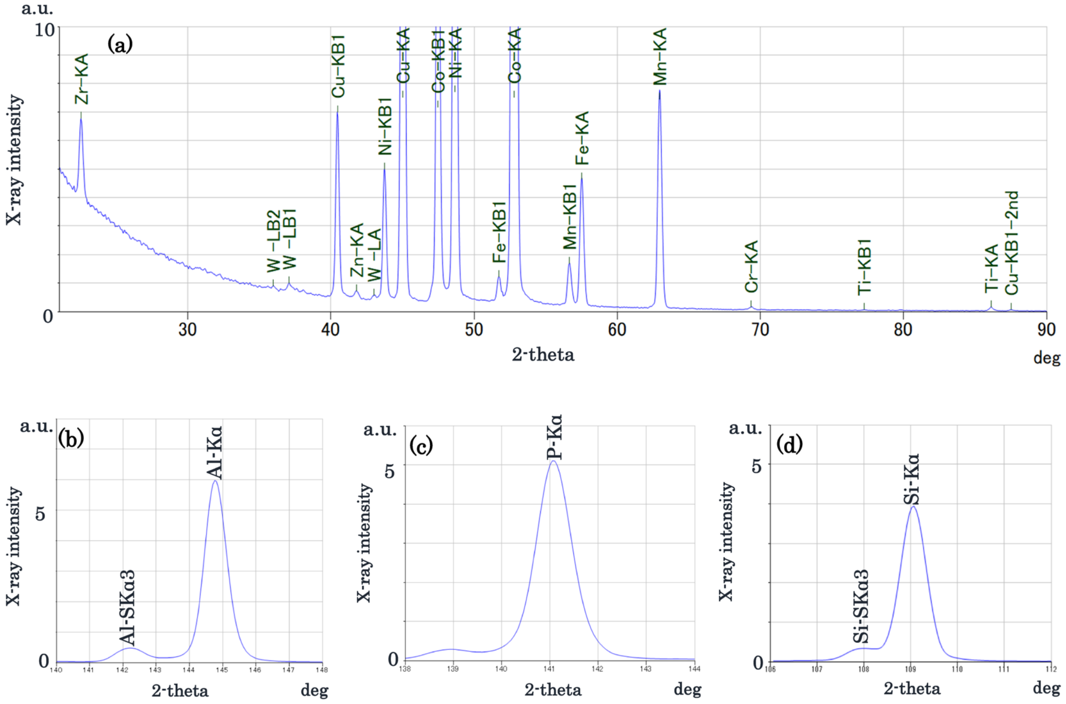

Fig. 8. Qualitative spectra of BM fusion bead sample 1: (a) heavy elements region, (b) Al, (c) P, (d) Si.

in a responsible laboratory to ensure safety of the operation. The results of the quantitative analysis for the major components of BP and BM samples have been discussed, and the results of the qualitative analysis of F to Cm, including trace elements, are described here. BP powder samples were analyzed by the balance estimation model, and BM fusion bead samples were analyzed by standardless FP method.

Figure 7 shows the qualitative spectra of BP powder sample 1. Large peaks of Ni, Co, Mn and Al were detected. Since BP samples are mainly obtained from the waste materials of cathode manufacture process, Ni, Co and Mn are believed to be derived from the cathode active material and Al from the cathode current collector foil. Small peaks of Ti, Fe, Sr, Zr and W were detected in the chart. These elements may be derived from additives and coatings added to cathode materials to improve battery performance and cycle characteristic.

One issue when trying to detect trace amount of Fe is the fact that, the 2θ angle of the Mn-Kβ peak, which is derived from the main component, is close to the 2θ angle of the Fe-Kα peak. By using a wavelength dispersive X-ray fluorescence spectrometer with high spectral resolution, Mn-Kβ and Fe-Kα peaks can be clearly resolved allowing the detection of trace amount of Fe impurity. The detection of the F-Kα peak implies the presence of a fluorine-based material such as the PVDF binder.

Figure 8 shows the qualitative spectra of BM fusion bead sample 1. Unlike the BP sample, in addition to Ni, Co and Mn, large peaks of Fe and Cu were observed in the chart of the heavy element region (Figure 8(a)). Ni, Co and Mn are believed to be derived from the cathode active material, while Fe and Cu come from the battery exterior and anode current collector foil. In addition, peaks attributed to Ti, Cr, Zn, Zr and W were detected. BM samples were obtained by dismantling and roasting used LIBs, and were found to contain more components than BP samples, which mainly consist of only the cathode material. Furthermore, peaks attributed to Al and P were also observed. It can be inferred that Al was derived from the battery exterior and current collector foil, and P was from the LiPF$_6$ electrolyte. An Si component, which is thought to have been mixed in during the recycling process, was also detected. Elements such as Si that are difficult to analyze with ICP-AES can be easily analyzed with XRF.

Table 3 shows the results of standardless FP analysis (balance estimation model) for five BP powder samples. Even within the same BP sample classification, the

Table 3. Standardless FP analysis results of BP powder samples (balance estimation model).

#	Ni (mass%)	Co (mass%)	Mn (mass%)	Al (mass%)	Cu (mass%)	Fe (ppm)	F (mass%)	P (ppm)	Si (ppm)
1	17.2	5.9	7.0	4.4	N.D.	458	2.6	14	225
2	43.9	5.9	9.4	0.4	N.D.	216	1.6	N.D.	97
3	55.0	2.7	0.1	1.8	N.D.	428	N.D.	22	151
4	22.7	7.8	9.2	0.1	N.D.	431	(0.5)	23	147
5	52.4	3.8	2.0	0.6	1.4	1027	N.D.	6451	375

#	Na (ppm)	Mg (ppm)	S (ppm)	Ti (ppm)	Cr (ppm)	Sr (ppm)	Zr (ppm)	Ba (ppm)	W (ppm)
1	701	N.D.	1628	427	N.D.	113	798	N.D.	1053
2	(217)	N.D.	562	N.D.	N.D.	200	1391	N.D.	1027
3	N.D.	347	143	N.D.	N.D.	N.D.	174	N.D.	1662
4	563	N.D.	886	N.D.	N.D.	N.D.	2292	N.D.	N.D.
5	(414)	286	568	1151	(75)	N.D.	1833	904	N.D.

※ N.D.：less than LLD (detection limit value)
LLD: 3 times statistical error in background intensity (3σ)
※ Values in ()：less than LOQ (limit of quantitation)
LOQ: 9 times statistical error in background intensity (9σ)

Table 4. Standardless FP analysis results of BM fusion bead samples.

#	Ni (mass%)	Co (mass%)	Mn (mass%)	Al (mass%)	Cu (mass%)	Fe (mass%)	P (mass%)	Si (mass%)	Na (ppm)	Mg (ppm)
1	6.5	31.0	4.6	12.1	7.3	1.8	0.5	0.4	(851)	1263
2	19.7	20.3	10.2	7.7	4.8	4.9	0.5	0.7	(942)	1542
3	26.0	20.8	0.6	12.7	2.5	0.9	0.1	0.6	(1996)	1272

#	S (ppm)	Ti (ppm)	Cr (ppm)	Zn (ppm)	Zr (ppm)	Mo (ppm)	Sn (ppm)	W (ppm)	La (ppm)	
1	896	3100	833	454	1115	N.D.	N.D.	(825)	N.D.	
2	533	N.D.	1101	915	317	N.D.	202	N.D.	N.D.	
3	910	996	(351)	611	(122)	376	2897	N.D.	6909	

※ N.D.：less than LLD (detection limit value)
LLD: 3 times statistical error in background intensity (3σ)
※ Values in ()：less than LOQ (limit of quantitation)
LOQ: 9 times statistical error in background intensity (9σ)

rare metal Ni contents varied from 10 to 60%, and Co contents varied from 2 to 6%, respectively. In addition to Al, Cu, Fe, F, P and Si, which are believed to be constituents of electrodes, small amounts (at the level of ~2000 ppm) of cathode additives and components that are believed to have been mixed in during the recycling process, were also detected.

Table 4 shows the results of standardless FP analysis of three BM fusion bead samples. BM samples contained higher percentages of Al, Cu and Fe than BP samples, which is believed to be due to the high content of current collector foil and battery exterior in the recycling materials. Concentrations of other trace components also increased compared to BP samples, especially heavy elements such as Cr, Zn, Mo, Sn and La, which were detected in higher amounts, ranging from 200 to 7000 ppm.

4. Conclusions

In this paper, the compositions of BP and BM samples, which are LIB recycling materials, were analyzed by X-ray fluorescence analysis, and the agreement with ICP-AES analysis values was examined for rare metals (Ni, Co) and impurity components (Al, Cu). The quantitative calculation models of standardless FP analysis and sample preparation method were studied to evaluate the applicability of XRF analysis for LIB recycling materials.

It was shown that the balance estimation model based on the scattering FP method is effective for the analysis of BP samples. On the other hand, XRF analysis of BM samples in powder form did not agree with the ICP-AES analysis results even in the balance estimation model. Oxidation treatment and fusion bead sample preparation were necessary to reduce the analysis error. Although the sample preparation method is time-consuming, it may be applicable in cases when ICP-AES analysis is not available. BM samples used in this paper contained many metal fragments and were highly heterogeneous, requiring additional sample preparation. However, many BM samples are homogeneous depending on how the materials are processed, and the balance estimation model may be applicable to these BM powder samples as in the case of BP samples.

Going forward, we plan to further investigate various perspectives on this topic, including creating calibration curves, simplifying the sample preparation method, and exploring the use of machine learning. Herewith, we have established that X-ray fluorescence analysis can be used as an effective composition analysis method for the rapidly growing LIB recycling industry.

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