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Development of Simultaneous Measurement System for X-ray Absorption Spectra at Two Absorption Edges

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Abstract

Dispersive X-ray absorption fine structure (DXAFS) spectroscopy is a versatile measurement technique for analyzing chemical reactions in real time. We have developed a novel time-resolved DXAFS instrument based on two polychromators and a wide-range position-sensitive detector that permits direct observation of the synergistic effects of two elements. This system enables simultaneous acquisition of the X-ray absorption spectra for two different elements without any mechanical movement of the X-ray optics. The developed system was successfully applied to monitor both the synthesis of a Ni–Cu bimetallic catalyst, which revealed that the reduction of Ni occurred at a higher temperature than that of Cu, and the charge–discharge processes of a Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$-based lithium-ion battery, which demonstrated that the redox reactions of Ni and Mn occurred sequentially at specific electrode potentials.

**Keywords:** Dispersive XAFS, time-resolved, transition metal, heterogeneous catalyst, secondary battery.
Introduction

Synergistic effects involving multiple elements have recently attracted great interest in the field of materials science. Combinations of multiple metal elements are extensively utilized as heterogeneous catalysts, and numerous bimetallic catalysts are used in energy and environmental applications.\(^1\)\(^-\)\(^3\) The addition of another metal element to a supported metal catalyst can improve its activity, selectivity, and lifetime in addition to reducing the cost of the source material. For example, a SiO\(_2\)-supported Au–Ni catalyst was reported to exhibit superior activity for the NO–CO reaction compared with individual Au and Ni catalysts.\(^2\)\(^,\)\(^4\) The synergistic effect of the Au–Ni catalyst was ascribed to the stabilities of adsorbed species such as oxygen and nitrogen atoms on the metallic surfaces. The preparation method can affect the performance of multi-element catalysts. For example, the activity and selectivity of a ZrO\(_2\)-supported Ni–Cu catalyst for the methanol steam reforming reaction were reported to depend on the order of addition of the metal precursor solutions during successive impregnation.\(^5\)\(^,\)\(^6\) Nanoparticle surface composition was also reported to influence the H\(_2\) yield and CO selectivity.\(^6\)\(^,\)\(^7\) Synergistic effects can also occur between the active metal particles and support material. The role of the Ce species in a Pt–CeO\(_x\) electrocatalyst was analyzed via \textit{in situ} X-ray absorption fine structure (XAFS) measurements,\(^8\) which revealed that the cerium oxide contributes to preventing the oxidation of the Pt species. Thus, the cerium oxide can control the effect of oxygen in addition to its function as the support material for the Pt nanoparticles. The catalytic properties of numerous pairs of metals have been extensively investigated to evaluate their possible roles in heterogeneous catalysis. The chemical and physical states of these metal species under the reaction conditions are clearly of fundamental importance for understanding the performance of such functional materials. The pretreatment process is also important because it determines the initial state of the catalyst. For example, it has been reported that both redox reactions during the pretreatment process and the support material can affect the state of bimetallic catalysts.\(^9\)
Electrochemistry is another field in which synergistic effects of metal species are expected to assist the realization of novel functions. Transition-metal ions are key elements in the electrode materials of lithium-ion batteries (LIBs). The most promising materials for the positive electrodes of LIBs contain more than one transition-metal element, such as spinel LiNi_{0.5}Mn_{1.5}O_4\textsuperscript{10–12} and layered LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2\textsuperscript{13–15}. Moreover, mixtures of these active compounds and their derivatives have also been investigated\textsuperscript{10,16}. The additional transition-metal ion(s) improves the battery performance compared with materials based on a single transition-metal element, such as LiCoO_2, LiMn_2O_4, and LiFePO_4. For example, LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2, which possesses a layered rock-salt structure, displays a higher available capacity than LiCoO_2 owing to redox reactions of the Ni ion and the structural stability provided by the Mn ion. However, the electrochemical reactions of such materials containing multiple metal elements are inherently complicated, and it is thus difficult to precisely determine the redox couples with respect to the electrode potential in Ni–Co–Mn systems\textsuperscript{17}. The reaction at spinel LiNi_{0.5}Mn_{1.5}O_4 cathodes occurs at a higher voltage than that at spinel LiMn_2O_4 cathodes. The substitution of metal species contributes to increasing the operating voltage owing to the compact crystal fields imposed by the spinel framework of oxygen linked by tetravalent Mn ions\textsuperscript{18}. Although it is apparent that the addition of the transition-metal ion improves the battery performance, the understanding of how such metal species contribute to the electrode reactions during the actual charge–discharge process remains insufficient. Information regarding the chemical states of the metal species during the reactions occurring in the battery cell is essential for understanding their degradation during long-term use and determining guidelines for developing next-generation battery materials.

XAFS spectroscopy is a versatile technique for the \textit{in situ} observation of the metal species in rechargeable batteries and heterogeneous catalysts. XAFS measurements are typically performed by scanning a monochromator in an energy range that includes the absorption edge of the target element. Wide-angle scanning of the monochromator is generally necessary to obtain
spectra for multiple elements.\textsuperscript{19} Dispersive XAFS (DXAFS) is an XAFS measurement technique commonly used to analyze fast chemical reactions in real time. In DXAFS experiments, a curved crystal referred to as a polychromator is used to obtain the X-ray absorption spectrum.\textsuperscript{20} The incident X-ray beam is monochromatized to the energy corresponding to the incident angle at each position on the curved crystal surface. By observing the transmitted X-ray intensities from the sample using a position-sensitive detector, the XAFS spectrum over a fixed energy range can be obtained without any mechanical movement of the X-ray optics. The angle of the polychromator is fixed for the absorption edge of the target element. To measure the spectra for multiple elements, it is therefore necessary to repeat the separate DXAFS measurement for each element. The separate measurements diminish the advantage of real-time observation using the DXAFS technique. To overcome this limitation, we have designed a novel DXAFS instrument, which we refer to as double-edge DXAFS (DE-DXAFS), that permits the direct observation of two elements. In this study, the newly developed measurement system was applied to the \textit{in situ} analysis of a representative heterogeneous catalyst and secondary battery samples to evaluate its applicability to these research fields. We analyzed the preparation process of a Ni–Cu bimetallic catalyst and the charge–discharge process of a Li$_{x}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ electrode. The obtained results demonstrate the remarkable potential of the simultaneous observation of multiple elements, such as Ni/Cu and Mn/Ni, using the DE-DXAFS system.

\section*{Experimental}

\subsection*{Sample preparation}

The Ni–Cu bimetallic catalyst precursor was prepared via the conventional impregnation method. The SiO$_{2}$ powder support material was added to an equimolar aqueous solution of Cu(NO$_{3}$)$_{2}$ and Ni(NO$_{3}$)$_{2}$ (Cu:Ni molar ratio: 1:1), such that the final Ni–Cu/SiO$_{2}$ catalyst contained 5 wt\% Cu. After drying at 343 K in air, a powder sample of the precursor was obtained.
In a typical preparation process, the precursor is reduced to obtain the active metallic phase. In this study, the chemical states of Ni and Cu were simultaneously monitored during the reduction process using the newly developed DE-DXAFS instrument. The precursor powder was heated in a stainless steel in situ XAFS cell under a flow of 10 vol% H₂ diluted with He. The sample temperature was increased from 300 to 873 K at a rate of 10 K/min.

A pouch-type cell of an LIB was prepared as reported previously.²¹ Commercial LiNi₀.₅Mn₁.₅O₄ powder (Toshima, Japan) was used as the positive electrode material. The LiNi₀.₅Mn₁.₅O₄ powder, acetylene black, and polyvinylidene difluoride binder were mixed in a weight ratio of 14:3:3 in N-methyl-2-pyrrolidone (NMP). The resulting slurry was applied onto a piece of aluminum foil with a thickness of 100 µm. The electrode sheet was dried at 353 K in air for 1 h and then in a vacuum oven for 24 h to remove the residual NMP. The LiNi₀.₅Mn₁.₅O₄ electrode was assembled to the LIB cell with a lithium metal of the negative electrode in a glove box filled with Ar. Polypropylene sheets were placed between the electrodes as a separator. A 1 mol dm⁻³ solution of LiPF₆ in a mixed solvent of ethylene carbonate and diethyl carbonate (3:7, v/v) was used as the electrolyte. The prepared LIB cell was fully charged to a constant voltage of 4.9 V at a rate of 0.2 C after an initial charge–discharge cycle between 4.9 and 3.5 V. The voltage profile for the pretreatment process is presented in Fig. S1 (Supporting information). The discharge process until 2.0 V from the state of Li₀.₁Ni₀.₅Mn₁.₅O₄ and the subsequent charge process until 4.9 V were monitored using the DE-DXAFS instrument. These discharge and charge processes included a constant voltage step after the constant current step of 1 C.

**Double-edge DXAFS instrument**

The DE-DXAFS instrument was developed at BL-5 of the Synchrotron Radiation (SR) Center of Ritsumeikan University. BL-5 is a beamline for DXAFS experiments using a white X-ray beam from the bending-magnet light source of AURORA. In a typical DXAFS experiment,
the white X-ray beam is dispersed using a cylindrically bent crystal (polychromator). In contrast, DE-DXAFS uses two polychromators to acquire the XAFS spectra of two different elements. Figure 1(A) presents the configuration of the DE-DXAFS instrument and the arrangement of the polychromators. In this system, the two polychromators are installed in an acrylic resin chamber. The white X-ray beam passes through a molybdenum mask with two rectangular holes with a width of 5 mm and a spacing of 5 mm, and the resulting two white X-ray beams irradiate the two sets of polychromators. The polychromator chamber is equipped with a manual Z stage and was designed to be portable to allow experiments to be performed at other synchrotron facilities. In this study, some of the DE-DXAFS measurements were conducted using beamline NW2A at the Photon Factory Advanced Ring (The High Energy Accelerator Research Organization, KEK). The chamber is fitted with a Be window for the incident white X-ray beam and a wide polyimide film window, which covers 2θ angles from −5° to 60° for the diffracted X-ray beam from the polychromator. Rotation and linear X–Y stages are located inside the chamber to control the polychromator position and incident angle. Each polychromator consists of a Si(111) crystal with dimensions of 40 mm × 25 mm and a thickness of 0.5 mm, which is cylindrically bent to a fixed curvature in the crystal holder, through which cooling water is circulated. The diffracted and polychromatic X-rays are focused at a point outside the polychromator chamber with slight aberration. With the DE-DXAFS instrument, it is necessary to achieve the same focal point, at which the sample is placed, for two polychromatic X-ray beams with different X-ray energies. The diverged X-ray beams transmitted through the sample reach a position-sensitive detector. A wide-type photodiode array (PDA) detector with a 2048-channel sensing element (Hamamatsu Photonics, Japan) was fabricated for this study. A Tl-doped CsI scintillator with a fiber plate was optically coupled with the PDA to convert the X-rays to visible light. To eliminate undesirable X-ray scattering, the polychromator chamber and light paths were filled with He.

The curvature of the polychromator crystal determines the position of the focal point, as
described by Eq. (1),

\[ q = \frac{Rp \sin \theta}{2p - R \sin \theta}, \tag{1} \]

where \( q \) is the distance between the center of the polychromator and the focal point, \( \theta \) is the incident angle of the center of the X-ray beam on the polychromator crystal, \( p \) is the distance between the polychromator and the light source, and \( R \) is the curvature radius of the polychromator. \( \theta \) is equivalent to the Bragg angle \( \theta_B \) of the polychromator, which is first selected after considering the crystal surface and target element. The focal points of the two X-ray beams reflected by the required Bragg angle \( \theta_B \) must overlap at the same position (i.e., the sample position), as depicted in Fig. 1(B). Therefore, the geometric conditions described in Eqs. (2) and (3) should be satisfied:

\[ q_L \sin 2\theta_L = q_H \sin 2\theta_H + \Delta x \tag{2} \]

where the subscripts \( L \) and \( H \) denote the polychromators located at the upstream and downstream positions, respectively, and \( \Delta x \) is the horizontal offset of the incident X-rays (see Fig. 1(B)). The distance between the two polychromators, \( \Delta p \), is an adjustable parameter in the geometric setting, as given by Eq. (3):

\[ \Delta p = q_L \cos 2\theta_L - q_H \cos 2\theta_H \tag{3} \]

We have prepared Si(111) polychromators with curvature radii of 3.0, 2.4, and 1.8 m to cover various combinations of 3d transition-metal elements. For the combination of Mn and Ni K edges, the typical alignment parameters are as follows: \( q = 0.29 \) m for the Mn K edge (\( \theta_{B,Mn} = \)}
17.6°) for the polychromator with \( R = 1.8 \) m and \( q = 0.38 \) m for the Ni K edge (\( \theta_{B,Ni} = 13.7° \)) for the polychromator with \( R = 3.0 \) m. For the combination of Ni and Cu K edges, the typical parameters are as follows: \( q = 0.30 \) m for the Ni K edge for the polychromator with \( R = 2.4 \) m and \( q = 0.35 \) m for the Cu K edge (\( \theta_{B,Cu} = 12.7° \)) for the polychromator with \( R = 3.0 \) m. The alignment parameters for some additional pairs of 3d transition metals are listed in Table 1. By adjusting the positions of the polychromators (\( \Delta p \)), the focal points can be made to overlap. The parameter \( \Delta q \) in Table 1 is the error originating from the use of the polychromator with the stated value of \( R \), which is not ideal for the element. The actual focal points and light paths of the polychromatic X-rays were monitored by scanning the horizontal slit to precisely align the two polychromators.

**Results and Discussion**

**DE-DXAFS alignment and performance**

Figure 2 depicts the measured X-ray paths for the two pairs of absorption edges, Ni/Cu and Mn/Ni. A slit was placed in front of the polychromator, and the X-ray paths were detected by varying the position of the PDA detector from upstream to downstream of the focal points. Figure 2 clearly shows that each polychromatic X-ray made a focal point and their positions were in agreement. At the crossing point of two focal beams, the half width of the focal beams was 0.25 mm for the Ni/Cu pair and 0.35 mm for the Mn/Ni pair. These beam sizes were adequate for DXAFS measurements of uniform samples.

The X-ray energy was calibrated using the absorption edges of reference metal foil samples. Figure 3 presents XANES spectra measured at the Ni and Cu K edges. The XANES spectra of Ni foil and Cu foil were simultaneously acquired using the DE-DXAFS instrument, as shown in Fig. 3(C) and (D). Comparison of these spectra with those measured at the conventional XAFS station with a standard double-crystal monochromator revealed that the DE-DXAFS instrument covered...
energy ranges of 260 and 280 eV at the Ni and Cu K edges, respectively. The accessible energy range, $\Delta E$, can be calculated using Eq. (4),\textsuperscript{22,23}

$$
\Delta E = \frac{EL}{\tan \theta_B} \left( \frac{1}{R} \sin \theta \right),
$$

(4)

where $E$ is the X-ray energy at the Bragg angle of $\theta_B$ and $L$ is the horizontal length of the X-ray beam footprint on the crystal surface. The calculated values of $\Delta E$ were 270 eV for both Ni and Cu, which is in reasonable agreement with the experimental values of $\Delta E$. The covered energy ranges are narrow compared with general DXAFS experiment, e.g. $\Delta E = 800$ eV at Cu K edge with a polychromator of the curvature radius of 3 m and the incident beam width of 15 mm. This is due to the limited incident beam width (5 mm for each polychromator) in the DE-DXAFS arrangement.

Several factors are important for determining the energy resolution of DXAFS optics, including the horizontal width of the X-ray source ($\Delta S$), the spatial resolution of the detector ($\Delta r$), the intrinsic angular width of diffraction at the polychromator crystal ($\omega$), and the penetration depth of X-rays into the crystal ($l$). The overall energy resolution, $\delta E$, can be calculated using Eqs. (5)–(10).\textsuperscript{22,24–26}

$$
\delta E = \sqrt{\delta E_1^2 + \delta E_2^2 + \delta E_3^2 + \delta E_4^2}
$$

(5)

$$
\delta E_1 = \frac{E}{\tan \theta_B} \frac{\Delta S}{\frac{R \sin \theta - k}{R(p-k) \sin \theta}}
$$

(6)

$$
k = \left( \frac{2}{R \sin \theta} - \frac{1}{q+d} \right)^{-1}
$$

(7)

$$
\delta E_2 = \frac{E}{\tan \theta_B} \frac{\Delta r}{d \frac{p-R \sin \theta}{2p-R \sin \theta}}
$$

(8)

$$
\delta E_3 = \frac{E}{\tan \theta_B} \frac{\omega}{d}
$$

(9)

$$
\delta E_4 = \frac{E}{\tan \theta_B} \frac{l \cos \theta \sin \theta}{d} \frac{p+q+d-2R \sin \theta}{2p-R \sin \theta}
$$

(10)
Here, $d$ is the distance from the focal point to the detector. For the measurements at the Ni and Cu K edges using the Si(111) polychromator at BL-5 of the SR Center, the following values were used to estimate the energy resolution: $\Delta S = 3.0$ mm, $p = 6$ m, $l = 100$ μm for Cu and 75 μm for Ni, $d = 0.6$ m, and $\omega = 2.7 \times 10^{-5}$ rad. The contributions of each factor are $\delta E_1 = 4.9$ eV, $\delta E_2 = 0.7$ eV, $\delta E_3 = 0.9$ eV, and $\delta E_4 = 0.5$ eV for Ni, and $\delta E_1 = 5.1$ eV, $\delta E_2 = 0.8$ eV, $\delta E_3 = 1.1$ eV, and $\delta E_4 = 0.7$ eV for Cu. The total energy resolution was calculated to be 5.1 eV for Ni and 5.3 eV for Cu. The size of light source dominates these values, and therefore the energy resolution improves at low emittance light sources. The XANES spectra of the metal foils obtained using the DE-DXAFS instrument shown in Fig. 3(C) and (D) suggest an energy resolution comparable to the calculated values, which was sufficient for XANES analysis.

**Preparation process of a Ni–Cu bimetallic catalyst**

Figure 3(E) presents the XANES spectra of the SiO$_2$-supported Ni–Cu bimetallic catalyst with an exposure time of 30 s before and after reduction. The absorption edges of the XANES spectra before reduction were consistent with those of Ni(II) and Cu(II) reference samples, and their intense white lines were characteristic for the corresponding oxide species, NiO and CuO.

The XANES spectra and absorbance changes at the respective white lines of the precursor samples were represented in Fig. 4(A) and (B) during temperature-programmed reduction under H$_2$ atmosphere. Upon reduction the absorption edges shifted to lower energy and the white line peaks disappeared, suggesting that both the Ni(II) and Cu(II) oxides were reduced to form the Ni–Cu metallic alloy species. Figure 4(B) shows that the Cu(II) species underwent reduction between 610 and 650 K, which is in accordance with that reported for CuO.$^{27}$ The DE-DXAFS measurements clearly indicated that the reduction of NiO started to occur at almost the same temperature as the reduction of CuO (ca. 620 K). The reduction of CuO was complete at approximately 650 K, whereas the higher temperature of ca. 750 K was necessary to completely
reduce the NiO species. It should be noted that a portion of the NiO underwent reduction at approximately 620–650 K. The reduction temperature of SiO$_2$-supported NiO depends on the particle size.\textsuperscript{28} The NiO particle does not undergo higher temperature, and therefore it will be smaller than that after the calcination process. The observed reduction temperature is lower than expected temperature based on the previous report for SiO$_2$-supported NiO.\textsuperscript{28} This observation clearly indicates that the reduced Cu species facilitated the reduction of NiO, suggesting the dissociative adsorption of hydrogen on the metallic Cu particles.

**Charge–discharge processes of a Li$_{x}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ electrode**

DE-DXAFS measurements were also conducted to examine the charge and discharge processes occurring at the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode of an LIB. The XANES spectra at the Mn and Ni K edges were measured simultaneously during operation of the LIB. Figure 5 shows the observed changes in the XANES spectra. For both edges, the top of the white line peak shifted to lower energy during discharge and returned to the original energy after charging.

Figure 6 presents plots of the edge energy ($E_0$), which was defined as the maximum energy of the first-derivative function of the XANES spectrum, against the value of $x$ in Li$_{x}$Ni$_{0.5}$Mn$_{1.5}$O$_4$, which was estimated from the measured battery capacity, alongside the variation of the observed cell voltage. The initial state prior to discharge was estimated as Li$_{0.1}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ from the current measured during the pretreatment process as shown in Fig. S1. Constant-current (1 C) discharge to 2.0 V generated the lithiated state with $x \approx 0.8$, and subsequent discharge at a constant voltage of 2.0 V afforded the over-lithiated state ($x \approx 1.3$). The discharge capacity was calculated to be 180 mA h g$^{-1}$, which corresponded to 123% of the theoretical capacity (146 mA h g$^{-1}$) of LiNi$_{0.5}$Mn$_{1.5}$O$_4$. Charging to 4.9 V recovered the initial state (Li$_{0.1}$Ni$_{0.5}$Mn$_{1.5}$O$_4$) prior to discharge, and the charge capacity was 179 mA h g$^{-1}$, which was in accordance with the discharge capacity.

At the beginning of the discharge process, the $E_0$ values of Mn and Ni were 6551 and 8342.
eV, respectively. The subsequent changes in the $E_0$ values during discharge clearly demonstrate that the reduction of Ni preceded the valence change of Mn, as shown in Fig. 5(C) and (E). The discharge capacity at a cell voltage over 4 V originated from reduction of the Ni sites, while the Mn sites retained the same valence state. The valence change of the Ni sites was complete once the cell voltage reached 3.5 V. Subsequently, the change in the valence state of the Mn sites occurred during the constant-voltage discharge process at 2.0 V, during which the Ni sites remained unchanged. Conversely, charging was initiated by oxidation of the Mn sites at cell voltages of approximately 3.5–4.2 V. The Mn oxidation was followed by oxidation of the Ni sites after the cell voltage had reached 4.5 V. These results clearly indicate the different phases of the valence changes of 3d transition-metal elements during the charge–discharge processes of LIBs.

**Conclusion**

In this study, a DE-DXAFS system based on two polychromators and a wide-range position-sensitive detector was developed. This system permits the simultaneous acquisition of XAFS spectra for two different 3d transition-metal elements with sufficient energy range and resolution to analyze valence changes. The DE-DXAFS technique was applied to simultaneously measure changes in the chemical states of Ni and Cu during the preparation of a Ni–Cu bimetallic catalyst and those of Mn and Ni during the charge–discharge processes of a Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ electrode for the first time. The obtained results demonstrate that DE-DXAFS is a valuable tool for directly observing the synergistic effects of two elements.

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**Supporting Information**

The voltage profile for the pretreatment process of the examined lithium ion battery. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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Table 1. DE-DXAFS alignment parameters for several pairs of 3d transition-metal elements using Si(111) polychromators.

| Pair  | Element | $\theta_B$ / ° | $R$ / m | $q$ / m | $\Delta q$ / m |
|-------|---------|----------------|--------|--------|----------------|
| Mn-Ni | Mn      | 17.60          | 1.80   | 0.285  |                |
|       | Ni      | 13.73          | 3.00   | 0.379  |                |
| Fe-Ni | Fe      | 16.14          | 1.80   | 0.261  |                |
|       | Ni      | 13.73          | 2.59\textsuperscript{a} | 0.324  |                |
|       |         |                | 2.40\textsuperscript{b} | 0.299  | −0.027         |
| Co-Ni | Co      | 14.86          | 1.80   | 0.240  |                |
|       | Ni      | 13.73          | 2.25\textsuperscript{a} | 0.279  |                |
|       |         |                | 2.40\textsuperscript{b} | 0.299  | −0.013         |
| Ni-Cu | Ni      | 13.73          | 2.40   | 0.299  |                |
|       | Cu      | 12.72          | 2.96\textsuperscript{a} | 0.344  |                |
|       |         |                | 3.00\textsuperscript{b} | 0.350  | +0.006         |

\textsuperscript{a} Ideal curvature for the element. \textsuperscript{b} Curvature used in this study.
Figure Captions

Fig. 1. Configuration of the DE-DXAFS instrument (A) and its geometric parameters for the alignment (B). In (A), the double-holed mask (a), Be window (b), acrylic resin chamber (c), polychromators (d and e), polyimide film window (f), focal point (g), photodiode array detector (h), and 2θ stage (i) are depicted.

Fig. 2. Experimentally obtained X-ray paths and beam sizes at the focal points for the pairs of Ni/Cu (A) and Mn/Ni (B). The X-ray paths were determined by detecting the X-ray position by the PDA detector from upstream to downstream of the focal points.

Fig. 3. XANES spectra of Cu foil (A and C), Ni foil (B and D), and the SiO$_2$-supported Ni–Cu catalyst (E) measured using a conventional XAFS beamline with a Si(220) double-crystal monochromator (A and B) or the DE-DXAFS instrument (C, D, and E).

Fig. 4. Changes in the XANES spectra at the Ni and Cu K edges (A) and absorbance at the peak top energy of the initial precursor state (B) during temperature-programmed reduction of the SiO$_2$-supported Ni–Cu bimetallic catalyst.

Fig. 5. Changes in the XANES spectra during the discharge and charge processes of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode simultaneously measured at the Mn K edge (A) and Ni K edge (B).

Fig. 6. Discharge and charge profiles (A and B) and absorption edge energies of Mn (C and D) and Ni (E and F) in the Li$_3$Ni$_{0.5}$Mn$_{1.5}$O$_4$ LIB during the discharge (A, C, and E) and charge (B, D, and F) processes.
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Graphical Index

Double-Edge DXAFS