Investigation into properties of highly functional oxides using quantum beam and thermodynamic measurement

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Understanding the reaction processes that can affect crystal structure and thermodynamics is important to improve the characteristics of highly functional oxides. During the charge–discharge processes of lithium-ion battery cathode materials, structural changes that accompany lithium intercalation and deintercalation are important factors that govern the characteristics. An original thermodynamic analysis of these processes was adopted and structural analysis using neutron diffraction during the charge–discharge process was successfully conducted for the first time to identify the structural changes in a coin cell-sized cathode. Structural analysis also employed quantum beams (neutron, synchrotron radiation), and the bonding characteristics were investigated with the maximum entropy method (MEM) by determination of the electron density distribution. Moreover, a pioneering application of the crystal pair distribution function (PDF) analysis for the bulk material together with X-ray absorption fine structure (XAFS) analysis enabled examination of the local structural changes that average structural analyses could not reveal. The diversified approach of this research involved a combination of these methods. Consequently, the structural and thermodynamic stability were determined to be important for improvement of the characteristics of highly functional oxides.

Key-words : Highly functional oxide, Quantum beam, Thermodynamic measurement, Crystal structure, Neutron, Synchrotron X-ray

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1. Introduction

Highly functional oxides present a broad research subject. Our research has focused on cathode materials for Li ion batteries, ferroelectric random-access memory (FeRAM), ferroelectric materials for piezoelectrics, high-temperature superconductive oxides, and electrolytic materials for solid-electrolyte fuel cells. The structural and thermodynamic stability of these materials are important in understanding factors associated with changes in their characteristics.

Among the highly functional oxides, this paper mainly describes and introduces cathode materials for lithium-ion batteries, which continue to face demands for higher capacity and longer life.

Firstly, there has not been much research regarding thermodynamic stability of these materials. The relationship between such thermodynamic data, physical properties and characteristics, and an attempt to use this information to guide material design represent the originality and significance of this research. In this work, the heats of dissolution for simple oxides of the constituent elements and the complex oxide were analyzed. From these results, the enthalpy change for the reactions to obtain the intended complex oxide from the simple oxides and the standard enthalpy of formation for the complex oxide were determined. Subsequent study on the thermodynamic stability of various highly functional oxides revealed a correlation between the chemical and thermodynamic stability, and the characteristics of many battery and superconductor materials.

Next, the characteristics of many battery and ferroelectric materials are structurally sensitive. Thus, crystal structural analysis from a micro perspective is necessary. In the context of this paper, many oxides are employed as electrode materials and electrolyte materials for lithium-ion batteries and fuel cells. Their main components are light elements such as hydrogen, lithium, and oxygen, and they frequently contain transition metals with proximate atomic numbers. The oxides are also host–guest materials that conduct the intercalation of light elements such as hydrogen and lithium; therefore, neutron beam diffraction is a powerful tool for crystal structural analysis of such materials.

For structural analysis, peaks from Bragg reflections are measured, and Rietveld analysis is used to determine the average crystal structure. However, the average structure of electrode materials alone cannot always explain the battery characteristics, so that local structure analysis becomes necessary. The pair distribution function (PDF) method is available, in which the relationship between the reduced pair distribution function \(G(r)\), and interatomic distance \(r\), is determined. This method enables detailed structural study, such as that of ordered and unordered structures. The time-of-flight (TOF) method enables analysis of the total scattering intensity \(I(Q)\) from various banks over a wide range; the structure factor \(S(Q)\) is then determined, and \(G(r)\) can be derived by Fourier transform. Pioneering application of crystal PDF analysis has enabled local structural analysis for lithium-ion battery cathode materials, and the use of neutron beam and synchrotron X-ray radiation has been employed to elucidate local structural changes (distortion, ordered-unordered, chemical and thermodynamic stability, and the characteristics of many battery and superconductor materials.

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substitution sites) that average structural analysis has not revealed.\(^ {13}\) The crystal structure factor determined from crystal structural analysis data can be used to derive the nuclear density or electron density of materials. The maximum entropy method (MEM) can be used to study the substitution effect of atomic sites, diffusion paths of lithium ions and oxygen, and bonding between respective elements. Neutron beam and synchrotron X-ray radiation are employed to complement such pioneering research of the relationship between these parameters and the material characteristics.

Finally, quantum chemical calculations are also indispensable for the additional scope of material design. Research that incorporates quantum chemical calculations is starting to be conducted in the fields of batteries and ferroelectrics, by our group amongst others.\(^ {21}\) For example, we investigate the effects of Li content and cation mixing on electronic structure in Li\(_{1}\)Ni\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) by Rietveld analysis and first principle calculation. From the result of structure relaxation by calculation, it was found that the structure was stabilized by cation mixing and thus cation mixing is possible to happen theoretically. This result is caused by increase of covalent bond near the cation mixing atom. In the sample of Li\(_{1}\)Ni\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) which shows good cycle performance, electron density between the transition metal and oxygen showed maximum among the investigated samples by MEM (experiment) and calculation. The result suggests that host structure stability plays an important role for the cycle performance.\(^ {22}\) Such an arrangement enables a comparative assessment between empirical and theoretically calculated results, which concern both structural analysis involving thermodynamic data and X-ray diffraction, and electron density distribution derived from the MEM. The assessment validates the reliability of the work and is an important feature of this research.

To obtain guidance to improve the characteristics of highly functional oxides, an understanding of the reaction processes associated with the characteristics is important. For the charge–discharge processes of lithium-ion battery cathode materials presented here, the structural changes during lithium intercalation and deintercalation are important factors that govern the characteristics. Structural analysis of the charge–discharge process using neutron diffraction was successfully achieved for the first time to identify the structural changes in a coin cell-sized cathode.

Through a combination of these methods, this research intends to clarify the factors that govern battery characteristics and to obtain guidance for the development of electrode materials.

This paper describes the correlations between thermodynamic stability, average and local crystal structure, electronic structure, and the battery characteristics including the charge and discharge processes. For the reader, reference to several papers is made on research conducted from a similar perspective on ferroelectrics,\(^ {45-48}\) high-temperature superconducting oxides,\(^ {9-11}\) and solid-electrolyte fuel cell electrolyte materials.\(^ {12}\)

### 2. Relationship between thermodynamic stability, average crystal structure, and battery characteristics for the lithium-ion battery cathode material Li\(_{1}\)Mn\(_{1-3}\)Co\(_{1}\)Ni\(_{1}\)O\(_2\) synthesized using different methods

LiCoO\(_2\) is the dominant cathode material used in lithium-ion batteries in the market today. Cobalt is expensive and toxic; therefore, research into alternative materials is active.\(^ {13}\) The layered structure, large capacity, and superior thermal stability of the Li\(_{1}\)Mn\(_{1-3}\)Co\(_{1}\)Ni\(_{1}\)O\(_2\) system has stimulated interest for its use as an alternative to LiCoO\(_2\). To date, the authors have examined this material and its substitution products, and studied the relationship between the physical properties, crystal structure, thermodynamic stability, and the battery characteristics.\(^ {14}\) The authors have also reported on an observed correlation between the crystal structure and thermodynamic stability, and the cycling characteristics for spinel-structured LiMn\(_{1-3}\)M\(_{0.4}\) and orthorhombic Li(Mn,M)O\(_2\).\(^ {15,16}\)

The relationship between the physical properties, thermodynamic stability, average crystal structure, and the battery characteristics of lithium secondary-battery cathode material Li\(_{1}\)Mn\(_{1-3}\)Co\(_{1}\)Ni\(_{1}\)O\(_2\) synthesized using different methods are described here.\(^ {17}\) Three different methods were employed to synthesize LiMn\(_{1-3}\)Ni\(_{1}\)Co\(_{1}\)O\(_2\). For the solid-phase method, the respective simple oxides were mixed at the prescribed ratio, presintered, fully calcined, and either rapidly cooled or gradually cooled (1°C/min) to room temperature to produce the target samples. For the solution method, respective metal acetate solutions were mixed at the prescribed ratio, dried, pre-calcined, fully calcined, and rapidly cooled to room temperature to produce the target samples. Crystal structure analysis employed TOF powder neutron diffraction analysis (Facility; GPPD, IPNS, USA: NPDF, LANSCE, USA). Average structures were investigated by Rietveld analysis (GSAS)\(^ {18}\) for the space group R\(_3\)m to determine the Li and Ni cation mixing quantities. Thermodynamic data (\(\Delta H_\text{f}\) and \(\Delta H^\text{f}\)) was calculated for the obtained samples by analyzing heats of dissolution with a twin-type heat conductive calorimeter.\(^ {19,20}\) A similar study was conducted for samples with Li compositions that were chemically modified by immersion for various times in 0.5 N (NH\(_4\))\(_2\)S\(_2\)O\(_8\).\(^ {21}\) The HS cell (Hosen, Co, Ltd.) was used for electrochemical measurement. Neutron diffraction analysis (HERMES, IRR-3) and XRD analysis were conducted on samples with modified Li composition. Structural analysis was conducted using the Rietveld method (Rietan\(^ {22}\)), and nuclear density and electron density distributions were determined by the MEM (Primsa\(^ {25}\)).

Phase identification by XRD analysis for LiMn\(_{1-3}\)Co\(_{1}\)Ni\(_{1}\)O\(_2\) synthesized using the solid-phase and solution methods indicated that the products of both methods could be assigned to hexagonal crystals (space group R\(_3\)m) and were single phases. The battery characteristics were examined and the initial discharge capacity for the solution method samples was somewhat higher (140 mA\(\text{h/g}\)) than that for the solid-phase method samples. Excellent cycling characteristics with discharge capacity retention up to 50 cycles were obtained for the products from both synthesis methods.

The thermodynamic stability of the samples was investigated first to consider factors associated with the cycling characteristics.

The thermodynamic stability of an oxide is typically evaluated according to the Gibbs free energy, \(\Delta G\), which consists of an enthalpy term, \(\Delta H\), and an entropy term, \(\Delta S\). The value of \(\Delta S\) is negligible for a solid phase at room temperature, as confirmed by measurement of the electromotive forces (EMF) of several oxides to determine their \(\Delta S\) values. Therefore, instead of using \(\Delta G\) of the reaction to form Li\(_x\)(Mn\(_{1-3}\)Co\(_{1}\)Ni\(_{1}\))O\(_2\) from simple oxides, \(\Delta H\) can be used. The number of atoms in the formula unit of any particular oxide is different from that of another; therefore, it is necessary to take into account the difference in the number of atoms when discussing stability from a thermodynamic perspective. Values of \(\Delta H\) and \(\Delta H^\text{f}\) can be predicted from the heats of dissolution of the oxides and application of Hess’s law. The values of \(\Delta H\) and \(\Delta H^\text{f}\) are thus normalized in such a manner that all the oxides contain the same number of moles of atoms per mole.
of material. Accordingly, the thermodynamic stability is evaluated by determining the enthalpy change per mole of atoms for the formation reaction from simple oxides, \( \Delta H_R \). Details of this computation are provided in the literature. The thermodynamic stability was examined with respect to \( \Delta H_R \) for these samples. Figure 1 shows \( \Delta H_R \) values for \( \text{Li}_{x}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2 \) prepared by the solid-phase and solution methods. Samples from both respective syntheses exhibited increases in \( \Delta H_R \) and greater thermodynamic instability as the Li composition decreased. \( \Delta H_R \) varied linearly with the change of Li composition for both samples of the respective syntheses; therefore, no structural change is considered to occur in the range of \( 0.4 < x < 1.0 \). The thermodynamic data indicate that the solution-processed \( \text{Li}_{x}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2 \) was more thermodynamically stable than that obtained by the solid state method and independent of the Li content. Regardless of the synthesis method used to produce a sample, \( \Delta H_R \) for \( \text{Li}_{x}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2 \) was less than that for \( \text{LiMn}_2\text{O}_4 \) and thus \( \text{Li}_{x}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2 \) is thermodynamically more stable. Combining these results and those of discharge capacity retention, better cycling performance was observed for the more thermodynamically stable samples.

Powder neutron diffraction analysis was conducted for samples produced by both synthesis methods and with Li compositions that had been decreased. The analysis pattern for a solution-phase sample with \( x = 0.556 \) is shown as a representative sample in Fig. 3. A single phase of hexagonal crystals (R-3m) is retained despite Li elimination, and a good match to the experimental results was observed. These results also correspond to the results in Fig. 1. No significant change was observed for cation mixing, despite the decrease in the Li composition. The Li nuclear density (see Fig. 4) decreased, the Li–O bond length increased, and the M–O (M: 3b site) bond length decreased as the Li composition decreased. The bond valence sum at the 3b site corresponded to Li elimination and showed a tendency to increase. These results indicate a correlation between thermodynamic stability and cycling performance, as well as the structural stability.

3. Local structure, electronic structure, and battery characteristics for lithium-ion battery layered-cathode active material \( \text{Li}_{x}\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2 \) according to crystal PDF and XAFS

The crystal structural analysis described in Section 2 comprises analysis of the average structure based on the Rietveld method, so that cation mixing and the transition metal distribution, which are considered important for the system at hand, could not be fully studied, and the influence of crystal structure on the battery
characteristics remained unclear in many respects. Therefore, this section describes the local structural analysis according to neutron total scattering analysis, complementary crystal PDF analysis and X-ray absorption fine structure (XAFS) analysis using X-ray synchrotron radiation. In this case as well, LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ was prepared through different syntheses: the solid-phase (rapid and gradual cooling) and solution methods. The analyses led to a detailed study regarding the distribution and ordered-unordered structure of transition metals that could not be previously expressed under the average structure and thus made discussion difficult.

Local structure was studied by deriving the reduced pair distribution function $G(r)$, from the total scattering intensity and according to PDF analysis (PDFgetN,26 PDFFIT27). The structural model used for PDF analysis employed structure parameters obtained by Rietveld analysis as default values. The ordering pattern of transition metals at the 3b sites was investigated. Cation mixing was studied on the basis of quantitatively determined values from the Rietveld analysis. The measured value $G_{\text{obs}}(r)$, average structure $G_{\text{ave}}(r)$, and local structure $G_{\text{local}}(r)$ were compared, along with local structure according to XAFS.

The results of charge-discharge testing showed that samples prepared using the -performed to elucidate the differences in electrode properties according to the synthesis method. Average structure analysis based on the Rietveld method resulted in satisfactory fitting for all samples to the hexagonal crystal ($R3m$). The occupancy of the respective metal sites indicated cation mixing of the respective samples at 2.0 to 5.3%, with no large differences between the samples. Based on the results related to the average crystal structure, a detailed study was made for the cation mixing sites and transition metal ordering with local structural analysis according to the PDF method. As evident from the reduced pair distribution function in Fig. 5, good fitting of the observed reduced pair distribution function was accomplished by considering the local structures, and peaks unable to be assigned under the average structure were reproduced. Therefore, of the models shown in Fig. 6, the optimum model for samples prepared by the solid-phase method is I, and that for samples prepared by the solution method is II. The optimum model for samples prepared by the solid-phase method under varied cooling conditions is III. The differences between these models suggest that the local structures are different. These
results are reasonable with respect to the atomic coordinates of the cation mixing. As a common tendency, the respective samples tend to order pairs of three types of atoms at the most proximate distance of any atom, which suggests the presence of short-distance-ordered transition metal layer. Among the samples prepared by the different methods, differences in crystal structure were observed that could not be expressed under the average structure, and moreover, the optimum models for the best fitting differed. Thus, the samples were found to possess local structures. This tendency is observed using extended EXAFS with X-ray synchrotron radiation.\textsuperscript{11} Neutron diffraction followed by Rietveld analysis, PDF analysis of neutron total scattering, and XAFS analysis were conducted for Al-substituted LiMn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} and Co\textsubscript{2}Al\textsubscript{1/3}O\textsubscript{2}, and the average and local crystal structures were examined. A similar trend was observed for the Al-substituted product.\textsuperscript{28}

As another example, Li\textsubscript{1/3}MnO\textsubscript{2}LiMO\textsubscript{2} (M = Mn, Ni, Co) with a layered rock-salt structure has reportedly exhibited high capacities of 200 mAh/g or more by charging to 4.6 V or higher, and has attracted attention as an electrode material with high energy density. The battery characteristics were evaluated. Rietveld, PDF and XAFS analyses were conducted to study the average, local, and electronic structures for 0.5Li\textsubscript{3}MnO\textsubscript{2}–0.5LiMn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} (x = 1/3, 5/12) samples and for reductive heat-treated samples of these compositions under vacuum. With respect to valence, the presence of Ni\textsuperscript{2+}, Mn\textsuperscript{4+}, and Co\textsuperscript{3+} for x = 1/3 and partial presence of Ni\textsuperscript{3+} ions for x = 5/12 were suggested. Reductive heat treatment of these samples under vacuum resulted in the elimination of Li and O and lower valences than Ni\textsuperscript{2+}, Mn\textsuperscript{4+}, and Co\textsuperscript{3+} were identified (see Fig. 7). The battery characteristics indicated high capacities through reductive heat treatment. Increased Mn redox involvement for x = 1/3 and increased Ni redox involvement for x = 5/12 were suggested as factors. The results of Rietveld analysis by employing a neutron diffraction and the PDF analyses for the 0.5Li\textsubscript{1/3}MnO\textsubscript{2}–0.5LiMn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} (x = 1/3, 5/12) samples showed that Li and Mn preferentially occupied 2b and 4g sites, respectively, and Ni and Co occupied either the 2b or 4g sites of the Li\textsubscript{1/3}MnO\textsubscript{2} -type structure (space group C2/m). This suggests an ordered arrangement within the transition metal layer. Increasing order was also observed for the reductive heat-treated samples.\textsuperscript{29}

For the reader, reference is made to recent research conducted from a similar perspective on the Li\textsubscript{1/3}MnO\textsubscript{2}–LiMO\textsubscript{2} (M = Mn, Ni, Co) system.\textsuperscript{30}

4. Ex situ crystal structure analysis of cathode materials Li(Ni,Cu,M)O\textsubscript{2} (M = Cu) by neutron diffraction during charge–discharge process of a coin cell-sized lithium-ion battery

As an alternative material to the lithium-ion battery cathode material LiCoO\textsubscript{2}, the Li(Ni,Co)O\textsubscript{2} system with the layered structure is a substitution product of LiNiO\textsubscript{2} with Co. The system has the advantages of a small cobalt content and relatively high capacity; however, a problematic capacity decline can occur from cation mixing of Li\textsuperscript{+} and Ni\textsuperscript{2+}, due to their close ionic radii.\textsuperscript{31} To determine the quantity of cation mixing for Li and Ni, neutron diffraction analysis followed by Rietveld refinement has been employed for average structural analysis.\textsuperscript{11,17} However, reports thus far have mainly analyzed powders before charge and discharge. Identifying the structural changes during the charge–discharge process is also important for investigation of the battery characteristics. However, the electrodes employed in coin cells have an extremely small amount of active material, as little as 10 mg. Thus, until now, structural analysis using neutron diffraction could not be performed for samples after charge–discharge cycling.

In this section, ex situ analysis of crystal structural changes during charge–discharge cycling is described for a new study of a coin-sized cell (1 cm diameter). Neutron diffraction analysis by the TOF method was conducted before and after charging for the cathode with LiNi\textsubscript{0.8}Co\textsubscript{0.19}Cu\textsubscript{0.01}O\textsubscript{2} as the cathode active material (8.5 mg) synthesized by the solid-phase method and mixed with a conducting material and binder. For the first time, neutron diffraction has been successfully employed to identify detailed changes in the crystal structure of a lithium-ion battery cathode material during the charge–discharge process of a coin cell-sized lithium-ion battery.

The LiMO\textsubscript{2} (M = transition metal) system lithium-ion battery cathode material is noted for its layered rock-salt structure (see Fig. 8). The crystal structure of the active material in the cathode (8.5 mg) was analyzed after discharge using the Rietveld method (see Fig. 9). Powder neutron diffraction, followed by Rietveld refinement, was performed for LiNi\textsubscript{0.8}Co\textsubscript{0.19}Cu\textsubscript{0.01}O\textsubscript{2} powder synthesized by the solid-phase method and for the same material from a coin cell cathode before and after charge–discharge. The structural parameters of the pristine powder and the ex situ active material in the cathode (including conducting material and
binder) before charging were in good agreement. For the first time, structural analysis by neutron diffraction was demonstrated to be possible for 8.5 mg of active material in the cathode. These results also verify that the Li composition, Li and Ni cation mixing quantity, M-O6 octahedral distortion, and the presence of a minor second phase could be quantitatively analyzed (see Table 1). Furthermore, it was revealed that, in this system, mixed Li was not eliminated during the charge and discharge processes, and charging caused a second-phase of Li2CO3 to disappear. Structural analysis by neutron diffraction for only 8.5 mg of active material sample constitutes a success that will create a pathway to in situ analysis and elucidation of electrode properties and causes of degradation during the charge–discharge process that have to date remained undetermined and has hindered the development of longer life Li-ion batteries.32)

5. Conclusion

The characteristics of lithium-ion batteries, and those of highly functional oxides, are related to the crystal and electronic structures. The structural analyses described here have employed important tools that have revealed these relationships. The pioneering application of crystal PDF analysis for bulk material has enabled local structural analysis. The use of neutron diffraction has clarified local structural changes that the average structure could not be used to elucidate. The structural and thermodynamic stability of the material itself is also important. Thus, the crystal structure and thermodynamic studies described in this paper can be accomplished, in addition to the elucidation of the characteristics during the charge and discharge processes, such that correlations with the electrode properties have become evident. Several of the described methods can be combined together with thermodynamic data and other physical property data for comprehensive comparison and investigation to obtain guidance for the design and development of high performance electrode materials. As shown here, complementary utilization of neutron beam and X-ray synchrotron radiation is important and highly effective. Moreover, quantum chemical calculations are being employed to produce structural models that consider these studies. Theoretical calculations and experimental results can thus be compared to evaluate their consistency. In addition to simulations for crystal and electronic structures and thermodynamic quantities, research will continue with an aim toward the development of structural control and design to obtain high performance materials.

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