Investigations on average and local structures of Li(Li$_{1/6}$Mn$_{1/2}$Ni$_{1/6}$Co$_{1/6}$)O$_2$ by the pair distribution function and the density functional theory

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HIGHLIGHTS

- Atomic configuration by neutron total scatterings, and the density functional theory.
- A local atomic ordering denoted as LiMn$_6$ in the transition-metal layer by DFT.
- The $G(r)$ suggests a local distortion along the c axis perpendicular to the layer.

ARTICLE INFO

ABSTRACT

We synthesize Li(Li$_{1/6}$Mn$_{1/2}$Ni$_{1/6}$Co$_{1/6}$)O$_2$ with a coprecipitation method, and study the electrochemical properties and the atomic configuration by means of galvanostatic charge−discharge test, neutron total scatterings, and the density functional theory calculation. From the average-structure analysis using the Bragg profile, that is, the Rietveld analysis, it is found that the sample has the Li$_2$MnO$_3$-type layered structure (space group; $C2/m$) and Ni and Co exist at both the two sites ($4g$ and $2b$ sites) in the transition-metal layer. The DFT calculation indicates that there is a local atomic ordering denoted as LiMn$_6$ in the transition-metal layer in the same way as Li$_2$MnO$_3$. Moreover, such a local structure can explain a reduced pair distribution function, $G(r)$, derived from neutron total scatterings. Detailed investigation on the $G(r)$ also suggests a local distortion along the c axis perpendicular to the layer.

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1. Introduction

The lithium-ion battery has been used widely as an energy source for many portable electronic devices, such as a mobile phone and a laptop computer. Nowadays, however, applications of the battery to a vehicle and a storage device are expected highly, and thus many researches have devoted their efforts to discover a novel cathode active material with higher discharge capacity and superior energy density than LiCoO$_2$-based materials with the layered rock-salt structure. Li$_2$MnO$_3$-Li(Mn, Ni, Co)O$_2$ solid solution,

which is also denoted as Li(Li, Mn,Ni,Co)O$_2$, can be regarded as one of the promising candidates because it has a potential of higher discharge capacity than 250 mAh g^{-1} [1−9]. According to these previous works, Li at transition-metal sites seems to form a local atomic ordering like LiMn$_6$ and LiM$_{6-x}$M$_x$ (M=Ni and Co), and it is believed that this ordering play an important role for the excellent electrochemical property. However, it is quite difficult to determine the local structure accurately only by the typical experimental method like NMR and X-ray absorption fine structure analysis, and thus it is necessary to establish new approaches to investigate the local ordering.

In recent years, we have prepared Li$_2$MnO$_3$-LiMn$_x$Ni$_x$Co$_{(1-2x)}$O$_2$ (x = 1/3, 5/12) solid solutions, and investigated their atomic configurations systematically [10−12]. From the results of the Rietveld analysis using neutron and synchrotron Bragg reflections, it was

found that crystallographic sites of the metals were influenced by the solid-solution ratio and charge/discharge processes. As is well known, however, this approach cannot determine the local metal orderings in the materials. Therefore, we have also focused on the pair distribution function (PDF) which can be derived from neutron total scattering. By assuming various metal orderings in the transition metal layer, we performed PDF simulation and then compared them with the experimentally-obtained reduced pair distribution function, $G(r)$, in our previous work [10]. In order to get deeper understanding on the local structures, however, the atomic configurations must be refined by a fitting of $G(r)$.

From such background, we performed the PDF fitting as well as the Rietveld analysis in this work for $Li(Li_{1/6}Mn_{1/2}Ni_{1/6}Co_{1/6})O_2$ among the materials mentioned above. For the purpose of efficient analysis, this PDF refinement was carried out under a support of the density functional theory (DFT) [13]. Based on the result, we discussed not only the average structure but also the local metal ordering of this material.

2. Experimental and calculation methods

2.1. Sample preparation and characterization

$Li(Li_{1/6}Mn_{1/2}Ni_{1/6}Co_{1/6})O_2$ was synthesized by means of a coprecipitation method [1,3,7,8,11,12]. $Co(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.), $Mn(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.), $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries Ltd.) was dissolved into distilled water in an appropriate proportion, and then the solution was dropped into an aqueous solution of $LiOH \cdot H_2O$ (Wako Pure Chemical Industries Ltd.). An obtained precursor was dried at 70 °C for 8 h in air and the metal composition was evaluated by the inductive coupled plasma emission spectroscopy (ICP: ICPE-9000, Shimadzu). An appropriate amount of $LiOH \cdot H_2O$ was added to the precursor, and then calcined at 600 °C for 15 h in air. A final heat-treatment was carried out at 900 °C for 15 h in air.

The prepared sample was identified by an X-ray diffraction measurement with a Cu $K\alpha$ radiation (X'Pert-Pro, PANalytical), and the lattice constants were estimated by a least square technique using the diffractions. The metal composition was studied by the ICP in the same way as the precursor. The particle morphology was observed by the scanning electron microscopy (SEM: S-2600N, Hitachi High-Technologies). In cathode-property measurements, a mixture of the sample, acetylene black (AB), KS-6 and poly-vinylidene difluoride (PVdF) with a weight ratio of 80:5:5:10 was used as a cathode. A paste of the mixture was prepared by using N-methyl-2-pyrrolidone (NMP), and then was coated on an Al foil. The cathode was cut into a disk with a diameter of 1 cm followed by a uniaxial pressing at 40 MPa, and was dried at 110 °C for 24 h under vacuum. A loaded amount of the active material could be estimated as 8.7 mg cm^{-2}. A Li metal, 1 mol l^{-1} LiPF$_6$-dissolved ethylene carbonate (EC)/diethyl carbonate (DMC) solution with a volume ratio of 1:2 (Kishida Chemical Co., Ltd.), and a polypropylene film were used as an anode, an electrolyte, and a separator, respectively. By using these components, an HS cell was assembled in an Ar-filled grove box. The cell was aged overnight before a charge/discharge cycle test to ensure full absorption of the electrolyte into the cathode. Charge and discharge properties were studied galvanostatically with a current density of 20 mA g^{-1} corresponding to ca. 0.1 C rate (HJR-110m SM8, Hokuto Denko). The cycle test was carried out at room temperature with cut-off voltages of 2.5–4.8 V vs. Li/Li$^+$ for 1st–3rd cycles (an activation process of Mn) and 2.5–4.6 V vs. Li/Li$^+$ for 3rd–50th cycles with an open-circuit interval of 2 min between each charge/discharge process.

2.2. Atomic-configuration analysis

For an average-structure analysis, a neutron diffraction measurement was performed with HERMES installed at JRR-3, Japan. The obtained pattern was analyzed based on the Rietveld method (Rietan-FP [14]). A neutron total-scattering spectrum was recorded by HIPPO installed at LANSCE, and then the local structure was investigated. In this analysis, a normalized structure factor, $S(Q)$, was converted to a reduced pair distribution function, $G(r)$, by a PDFgetN program [15], and then a fitting of the G(r) was conducted by a PDFFIT interface [16].

An atomic configuration of the $Li(Li_{1/6}Mn_{1/2}Ni_{1/6}Co_{1/6})O_2$ was also investigated by the density functional theory. In order to estimate structure stabilities, configurations constructed on the basis of the Rietveld refinement were relaxed by using a VASP code [17]. As the exchange and correlation function, the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) was utilized [18], and the electron–ion interaction was represented by the projector augmented wave (PAW) method [19], in which plane waves up to an energy of 500 eV were considered. Internal atomic positions in the cell were optimized under the condition of residual force below 0.02 eV Å^{-1}, setting a k point mesh of the Brillouin zone sampling to $1 \times 2 \times 3$. For an electronic-structure analysis, we optimized wave functions with the WIEN2k [20], in which GGA-PBE was adopted as the exchange and correlation function, using a value of 7 as $R_{MT}K_{max} = 7.0$.

3. Results and discussion

3.1. Characterization

Fig. 1(a) shows an X-ray diffraction pattern of a synthesized $Li(Li_{1/6}Mn_{1/2}Ni_{1/6}Co_{1/6})O_2$. All peaks can be attributed to the Li_2MnO_3-type layered structure with a space group of $C2/m$, and thus the obtained sample can be regarded as a single phase. It can be considered that broadening of the peaks at 20–23° is due to stacking faults along the c axis [3,21–23]. Its metal composition is evaluated by the ICP measurement as $Li_{1.135(4)}Mn_{0.524(1)}Ni_{0.1693(3)}Co_{0.1699(3)}O_2$, which is almost equal to the nominal one, i. e., $Li_{1.167}Mn_{0.5}Ni_{0.167}Co_{0.167}O_2$. From the SEM observation [Fig. 1(b)], the average particle size was estimated as ca. 0.5 μm. Charge and discharge curves, and a cycle performance of this sample are shown Fig. 2. As reported previously [1,2,4–9], this sample exhibited a plateau around 4.5 V vs. Li/Li$^+$ in a first charge process due to oxygen loss. Therefore, the result suggests that there is a Li_2MnO_3 domain in the sample. By this activation process at the first charging, a discharge capacity became larger than 200 mAh g^{-1}, and was kept around 200 mAh g^{-1} even after 50 cycles although the discharge voltage got lower.

3.2. Average-structure analysis

In order to clarify an average structure of the $Li(Li_{1/6}Mn_{1/2}Ni_{1/6}Co_{1/6})O_2$, we measured a neutron diffraction pattern and then performed the Rietved analysis in which a space group was assumed to be $C2/m$ according to literature. In the analysis, the site occupancies of the metals were refined under a hypothesis that Ni can occupy Li sites, and the refined metal composition was fixed to be the same as the analytical composition mentioned above. Fig. 3 shows the Rietveld refinement pattern and Table 1 lists the structure parameters. From the site occupancies, Li and Mn tends to localize the 2b and 4g sites, respectively, in the transition-metal layer even though Ni and Co occupy the both sites. Such a localization of Li and Mn indicates a local arrangement like a Li_2MnO_3