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Synchrotron radiation-based ^{61}Ni Mössbauer spectroscopic study of Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ cathode materials of lithium ion rechargeable battery

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Abstract Layered rocksalt type oxides, such as Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$, are widely used as the cathode active materials of lithium-ion rechargeable batteries. Because the nickel ions are associated with the role of the charge compensation at discharge and charge, the ^{61}Ni Mössbauer measurements at 6 K using synchrotron radiation were performed to reveal the role of Ni. The Ni ions of the active materials play two roles for the redox process between the charge and discharge states of lithium-ion batteries. Half of the total Ni ions change to the low-spin Ni^{3+} with Jahn-Teller distortion from the Ni^{2+} ions of the discharge state. The remainder exhibit low-spin state divalent Ni ions.

1 Introduction

Lithium nickel manganese cobalt oxides, such as Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ (NMC) [1], have a lamellar structure similar to that of $\alpha-$NaFeO$_2$ (space group R$\bar{3}$m, No. 166) and are widely used as cathode materials such as the lithium-ion (Li-ion) battery for electric vehicles. In the NMC rhombohedral unit cell, Li and O occupy the Wyckoff positions $3a$ and

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6c, respectively, with the *3b* sites occupied by transition metals (i.e., Ni, Co or Mn). In the discharge state of NMC, the transition metals exist as high-spin Ni^{2+}, high-spin Mn^{4+} and low-spin Co^{3+} ions. Based on the results of X-ray absorption spectrometry, a previous study has concluded that the charge compensation during delithiation is provided by the transformation of Ni^{2+} to Ni^{3+} and then to Ni^{4+} over the entire range of the state of charge (SOC) and formation of oxygen vacancies neighbouring the cobalt [2]. However, another recent X-ray absorption investigation found that Ni^{3+} is present even in NMC of 100 % SOC [3].

Mössbauer spectroscopy is able to reveal chemical information in not only the qualitative analysis but also in the quantitative evaluation of condensed matter through the hyperfine interactions and is therefore well suited for the investigations of the change in the Ni state during delithiation. However, the ^{61}Co (1.65 h) or ^{61}Cu (3.333 h) short half-life radioactive nuclides must be prepared for the ^{61}Ni Mössbauer measurement. This is inconvenient because of the many restrictions involved in handling radioactive materials.

Recently, a method to detect recoilless nuclear resonant absorption that does not require radioisotopes has been developed [4, 5]. The use of synchrotron radiation sources instead of radioisotopes eliminates the restrictions and makes it much easier to perform Mössbauer spectroscopic studies. Therefore, by using synchrotron radiation, ^{61}Ni Mössbauer measurements were carried out.

2 Experimental

Synchrotron radiation at the SPring-8 was used for the ^{61}Ni Mössbauer measurements with the storage ring operating at several bunches mode (203 bunches) to accommodate the 5.3 ns half-life of the ^{61}Ni nuclear transition from the excited state (nuclear spin I_e = 5/2) to the ground state (nuclear spin $I_g = 3/2$). A Si(333) double-crystal premonochromator and a Si(111) monochromator were used to obtain 67 keV X-rays. A scatterer consisted of a 4-μm-thick ^{61}Ni-enriched (86 %) $Ni_{86}V_{14}$ foil was moved with a velocity transducer. The scatterer and transmitter were cooled in a cryostat to 30 and 6 K, respectively. The experimental setup is almost the same as that used in ref. 5. The delayed signals after prompt synchrotron radiation pulses with a time window of 4.3–17.3 ns were measured with a multi-element Si avalanche photodiode detector. The velocity of the transducer was calibrated using a laser interferometer and the measurement was performed in the range of ± 12 mms^{-1}. The hyperfine field and electric gradient field tensors were evaluated using a full Hamiltonian for the ^{61}Ni nucleus [6] and MossWinn 4.0 program package [7].

The Li-ion battery cathode consisted of 86 wt.% commercially supplied NMC with 8 wt.% acetylene black and 6 wt.% polyvinylidene fluoride. Graphite was used as the anode, and 1 M $LiPF_6$ dissolved in an ethylene carbonate: diethyl carbonate solution at a volume ratio of 1:1 was used as the electrolyte. The Li-ion cells with 0 and 50 % SOC were disassembled in glove box. The chemical compositions of all the samples were determined using the inductively coupled plasma spectrometry and powder X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The sample XRD patterns were attributed to the layered rocksalt type structure of the space group $R\bar{3}m$. The measured samples and their chemical components are summarized in Table 1.

Table 1 Sample name and chemical components in at.%

Sample name	Li	Ni	Mn	Co
0 % SOC	0.917	0.334	0.339	0.327
50 % SOC	0.677	0.336	0.333	0.331

3 Results and discussion

The synchrotron radiation-based ^{61}Ni Mössbauer spectra of NMC (0 and 50 % SOC) at 6 K are depicted in Fig. 1. The spectrum of 0 % SOC exhibited a symmetric lineshape, whereas an asymmetric lineshape, implying the presence of Jahn-Teller distortion, was observed in the case of 50 % SOC (Fig. 1). Because Ni^{3+} ions that are octahedrally coordinated by six oxygen atoms in the charged state of NMC exhibit Jahn-Teller distortion [3], the nonzero electric field gradient will lead to the appearance of an asymmetric lineshape in the experimental spectrum of NMC. In both spectra, singlet contributions, which have no magnetic and quadrupole interactions, are observed at around zero velocity. Therefore, we analysed each spectrum with two components (singlet (A) and other states (B)) and extracted the Mössbauer spectroscopic parameters. In each least-square fitting, the value of the full width at the half maximum of 0.8 mms^{-1} was used. The asymmetric parameters $\eta = 0$ and isomer shift $\delta = 0$ mms^{-1} were assumed. Moreover, the direction of the internal magnetic field was assumed to be parallel to the electric field gradient V_{zz}. The internal magnetic field $B_{int.}$, electric field gradient V_{zz}, area ratio I and value of reduced χ^2 obtained from the least-square fitting are listed in Table 2.

The experimental spectrum of 0 % SOC was deconvoluted using the singlet and magnetic states with the internal magnetic field of 4 T. This approach is consistent with the results of previous studies that divalent octahedrally coordinated Ni ions show magnetic ordered states with internal magnetic field distributions between 2–9 T at a liquid helium temperature [8, 9]. The area ratios of the I_A and I_B were evaluated as approximately 25:75.

As mentioned above, the appearance of an asymmetric spectrum of 50 % SOC is thought to be related to the nonzero electric field gradient resulting from the Jahn-Teller effect. Because Ni ions are coordinated octahedrally, the Jahn-Teller-distorted Ni^{3+} exists as a low-spin state. The internal magnetic field was estimated to be 1 T by least-square fitting for the sub-spectrum B of 50 % SOC in Table 2. However, considering the natural line width of 0.8 mms^{-1} for ^{61}Ni, the existence of the small internal magnetic field is not conclusive and Ni ions of sub-spectrum B may be the non-magnetic properties. The value of V_{zz} of sub-spectrum B was -21×10^{21} Vm^{-2}; this is larger than the absolute value of V_{zz} of $+12.8 \times 10^{21}$ Vm^{-2} found in the d^8 charge configuration in tetrahedrally coordinated Ni in the $NiCr_2O_4$ material [10]. Furthermore, the ratio of the integrated intensities for A (I_A) and B (I_B) for 50 % SOC was approximately 50:50. The singlet state may be due to the low-spin Ni^{2+} (d^8, S = 0), as shown in the previous work of $LiNiO_2$ [11]. This implies that the delithiation of the cathode leads to the transformation of half the total number of NMC Ni ions to the low-spin Ni^{3+} (d^7, S = 1/2) state at 50 % SOC from the high-spin Ni^{2+} state at 0% SOC with the remaining Ni ions at 50% SOC corresponding to the low-spin Ni^{2+} (d^8, S = 0).

Because X-ray absorption fine structure gives the averaged chemical information and local structures, the mixed valence oxide nature of delithiated NMC complicates extended
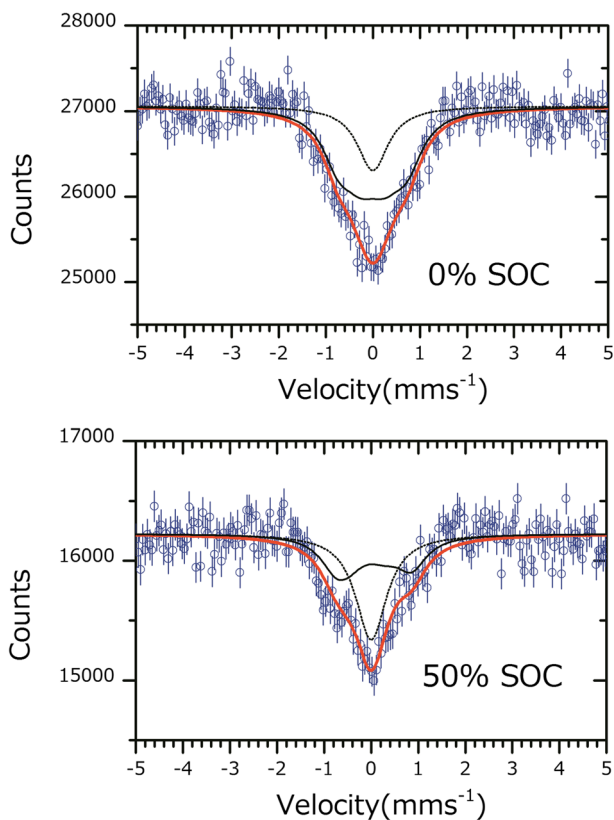
Fig. 1 Synchrotron radiation-based ^{61}Ni Mössbauer spectra of $Li_x(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ at 6 K

Table 2 Obtained Mössbauer spectroscopic parameters

Sample name	Index	$B_{int.}$ (T)	V_{zz} (10^{21} Vm^{-2})	I (%)	Reduced χ^2
0 % SOC	A	–	–	25	1.299
	B	4	–	75	
50 % SOC	A	–	–	53	1.201
	B	1	−21	47	

X-ray absorption fine structure analysis of the local structure of its Ni–O contributions. Therefore it is possible that individual evaluations of the redox process in NMC were concluded in the previous works [2, 3].

4 Conclusion

To investigate the charge compensation of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$, synchrotron radiation-based ^{61}Ni Mössbauer measurements were carried out at 6 K. The divalent Ni ions of the

discharge state consist of a high-spin and low-spin ratio of 75:25. From the spectrum of the charge state, the Ni ions of the active material play two roles in the redox process. Half of the total Ni ions changes to low-spin Ni^{3+} with the Jahn-Teller distortion from the Ni^{2+} ions of the discharge state. The remainder show low-spin state divalent Ni ions.

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