MLF Experimental Report	提出日 Date of Report June 09, 2009
課題番号 Project No. 2008A0010 実験課題名 Title of experiment Lithium diffusion in lithium-transition-metal-oxides 実験責任者名 Name of principal investigator Jun Sugiyama 所属 Affiliation Toyota Central Research and Development Laboratories, Inc.	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/（BL No.） D1 実施日 Date of Experiment February 20, 2008 – February 26, 2008

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Lithium nickel dioxides, $Li_{1-x}Ni_{1+x}O_2$ with x~0 and x~0.07.
A powder sample was pressed in a disc with 30 mm diameter and 2 mm thickness, and then the disc was packed in an Au-sealed cell.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In order to confirm the unique power of mSR for detecting the diffusion coefficient of Li+ ions (D_{Li}) in solids, we have measured ZF-, wLF-, and wTF-mSR spectra for lithium nickel dioxides, which were heavily investigated as a cathode material for the next-generation Li-ion batteries, in the temperature range between 60 and 450 K. In the rhombohedral $LiNiO_2$ lattice with space group R3-m, the NiO_2 plane and the Li layers form alternating stacks along the c_H-axis in the hexagonal setting (see Fig. 1). In the NiO_2 planes, Ni ions form a two-dimensional triangular lattice (2DTL) by a network of edge-sharing NiO_6 octahedra. In contrast to $LiCoO_2$, a stoichiometric $LiNiO_2$ has been never prepared so far. That is, the excess Ni is usually present in the Li layer of the $LiNiO_2$ samples due to the similarity in ionic radii between Li^+ and Ni^{3+}. The ionic distribution of the Ni-excess $LiNiO_2$ is thus given by $(Li^+{}_{1-x}Ni^{2+}{}_x)_{3b}[Ni^{2+}{}_xNi^{3+}{}_{1-x}]_{3a}O_2$, where 3$b$ and 3a are the Li and Ni site in the regular $LiNiO_2$ lattice. Besides of an interesting change in low-T magnetism of $Li_{1-x}Ni_{1+x}O_2$ with x, the $(Ni^{2+})_{3b}$ ions are naturally expected to affect D_{Li} at high T, because of planer hindrance of $(Ni^{2+})_{3b}$ in the Li layer, in which Li^+ ions move relatively easily. Nevertheless, there is, to authors' knowledge, less systematic work on the relationship between D_{Li} and x, mainly due to lack of a proper tool for detecting D_{Li}. The μSR experiment on $Li_{1-x}Ni_{1+x}O_2$ with x~0.03 and ~0.15, therefore, provides crucial information on the effect on D_{Li}, resulting in clear insight how to improve cathode materials.

In fact, both ZF- and LF-spectra for the x~0.03 sample were well fitted by a dynamic Kubo-Toyabe function, which is expected for a random nuclear magnetic field due to mainly ^{7}Li. By using a global fit technique for ZF-, LF-, and wTF-spectra, the field distribution width (Δ) and field fluctuation rate (ν) were estimated at each temperature (Fig. 2). As temperature increases from 70 K, ν looks almost T-independent (~0.2 x 10^6 s^{-1}) up to 250 K, and then increases rapidly with increasing T until ~370 K, and finally decreases with T. That is, the ν(T) curve exhibits a peak around 370 K. On the contrary, Δ decreases linearly with T below 200 K, and then Δ seems to level off to ~0.28 x 10^6 s^{-1} up to ~300 K, and finally decreases with T until 450 K.

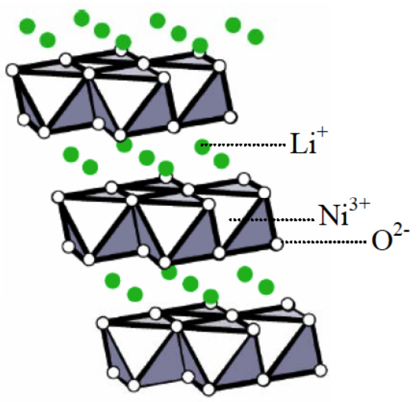

Fig.1 The crystal structure of $LiNiO_2$

Assuming that ν–ν(T<250 K) corresponds to the jump rate of the Li ions between the neighboring sites, D_{Li} is estimated as ~8 x 10^{-12} cm^2/s at 370 K. This value is quite large compared with D_{Li} obtained by the ^{7}Li-NMR experiment (6 x 10^{-15} cm^2/s at 500 K). This is probably due to the effect of the Ni spins on the ^{7}Li nuclear spin-lattice relaxation rate of NMR, particularly of the Ni^{2+} ions in the Li plane.

In order to confirm that ν really corresponds to the jump rate of the Li ions, we also planed to measure the sample with x~0.15. This is because the Ni^{2+} ions in the Li plane naturally reduce D_{Li}. However, because of the unexpected low power of the proton/muon beam in J-PARC, the counting rate was almost 1/10 to that of ISIS, where it takes 2 hours per one T point. Therefore, although we used 13 shifts in total, we measured only three T points for the x~0.15 sample. The preliminary result looks to be consistent with our expectation, but we need more data to know the T dependences of both ν and Δ for the x~0.15 sample in detail. Such experiment will be performed in the summer of 2009.

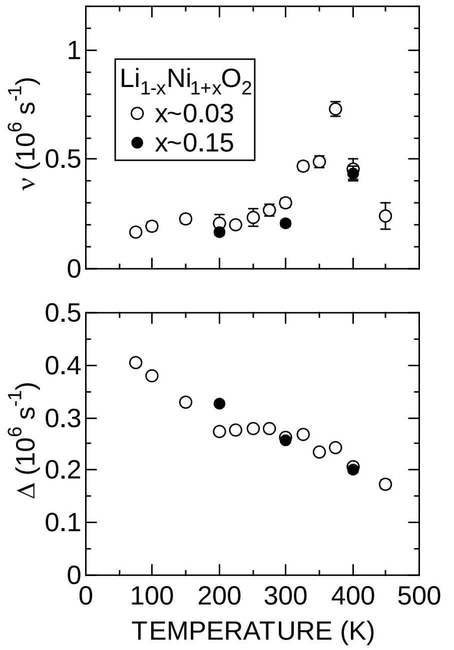

Fig. 2 Temperature dependences of (top) field fluctuation rate n and (bottom) field distribution width for $Li_{1-x}Ni_{1+x}O_2$ with x~0.03 and ~0.15. The data were obtained by global-fitting the ZF-, LF-, and wTF-spectra.

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