Lithium-ion diffusion in novel battery materials

J. Sugiyama,1, H. Nozaki,1 M. Harada,1 Y. Higuchi,1 I. Umegaki,1 K. Mukai,1 M. Månsson,2 and I. Watanabe3

Diffusion coefficient of Li+ ions ($D_{Li}$) in solids is usually evaluated by $^7$Li-NMR.1 However, for materials containing magnetic ions, Li-NMR provides very limited information on $D_{Li}$, because of the effect of electron spins on the spin-lattice relaxation rate (1/$T_1$).2,3 Note that positive electrode materials of Li-ion batteries all include transition metal ions to compensate charge neutrality during the Li+ intercalation and deintercalation reaction. On the contrary, $\mu$+ see an internal magnetic field caused by both electrons and nuclei in a zero field (ZF). Thus, $\mu$+SR extracts the nuclear field of Li, because of the effect of ionic radii between Li+ and Ni3+(see Fig. 2). Thus, the correct formula of LiNiO$_2$ with $x = 0.67$, 0.85, 0.90, 0.95, and 1.

A solid solution system between LiCoO$_2$ and LiNiO$_2$, i.e. Li(Co$_{1-x}$Ni$_x$)O$_2$ in the rhombohedral symmetry with space group $R_3m$ is widely used in commercial Li-ion batteries. According to the previous experiment on Li(Co$_{1-x}$Ni$_x$)O$_2$ with $x = 0$, 0.33, 0.67, and 1, $\nu$ above ambient $T$ drastically increased with increasing $x$. Since the $\nu(T)$ curve for the $x = 0.67$ sample is clearly different from that for LiNiO$_2$, we have measured ZF- and LF- spectra for the samples with $x = 0.85$, 0.90, and 0.95.

Figure 1 shows the $T$ dependences of the field distribution width ($\Delta$) and $\nu$ for the $x = 0.67$ – 1 samples. For all the samples, as $T$ increases from 50 K, $\Delta$ decreases linearly up to $\sim$ 250 K, then looks to be $T$-independent until $\sim$ 400 K, and finally decreases with further increasing $T$. Here, $\Delta$ is mainly determined by the nuclear field of Li, because $\mu$+ locates at the vicinity of the O$^2-$ ion with $d_{\mu-O} = 1$ Å, but not in the Co$_{1-x}$Ni$_x$O$_6$ octahedron. As a result, $\Delta$ is not sensitive to $x$. On the other hand, for the present three samples, $\nu$ increases with $T$ until 225 K, then decreases with $T$ until 450 K, and then increases again with $T$.

Note that a stoichiometric LiNiO$_2$ has never been obtained by a solid state reaction technique. A small amount of Ni ions are always located in the Li plane2,3 due to the similarity in ionic radii between Li+ and Ni$^{3+}$. (see Fig. 2). Thus, the correct formula of LiNiO$_2$ is (Li$_{1-y}$Ni$_y^{3+}$)(Ni$_{1-y}^{3+}$Ni$_y^{3+}$)O$_2$ with $y \leq 0.02$. The Ni ions in the Li plane suppress Li-diffusion.6 But, Co substitution for Ni is known to reduce $y$.8 Thus, it is expected that Li-diffusion increases with the Co content, against to the present result. In order to further understand the diffusion nature, it is highly required to investigate the Li-deficient samples, which is prepared by the Li$^+$ deintercalation reaction, with $\mu$+SR, because the direct jump of Li$^+$ from the regular site to the nearest deficient site is predominant for Li-diffusion.

References
5) R. S. Hayano et al., PRB 20, 850 (1979).