Lithium-ion diffusion in novel battery materials

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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, μ^+ *sees* an internal magnetic field caused by both electrons and nuclei in a zero field (ZF). Thus, μ^+SR extracts the nuclear field even in such positive electrode materials[4] by combining with weak longitudinal field (LF) measurements.[5] For the positive electrode materials, since Li ions are known to be more mobile than μ^+ due to a strong μ^+-O bond, the hopping rate (ν) estimated by μ^+SR reflects the dynamics of the Li ions.[4,6]

A solid solution system between $\mathrm{LiCoO_2}$ and $\mathrm{LiNiO_2}$, i.e. $\mathrm{Li(Co_{1-x}Ni_x)O_2}$ in the rhombohedral symmetry with space group $R\bar{3}m$ is widely used in commercial Li-ion batteries. According to the previous experiment on $\mathrm{Li(Co_{1-x}Ni_x)O_2}$ with $x = 0$, 0.33, 0.67, and 1, ν 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 $\mathrm{LiNiO_2}$, 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 (Δ) and ν for the $x = 0.67 - 1$ samples. For all the samples, as T increases from 50 K, Δ 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, Δ is mainly determined by the nuclear field of Li, because μ^+ locates at the vicinity of the $\mathrm{O^{2-}}$ ion with $d_{\mu-\mathrm{O}} = 1$ Å, but not in the $\mathrm{Co_{1-x}Ni_xO_6}$ octahedron. As a result, Δ is not sensitive to x. On the other hand, for the present three samples, ν increases with T until 225 K, then decreases with T until 450 K, and then increases again with T.

Note that a stoichiometric $\mathrm{LiNiO_2}$ has never been obtained by a solid state reaction technique. A small amount of Ni ions are always located in the Li plane[7] due to the similarity in ionic radii between Li^+ and Ni^{3+} (see Fig. 2). Thus, the correct formula of $\mathrm{LiNiO_2}$ is $(\mathrm{Li}^+_{1-y}\mathrm{Ni}^{2+}_y)(\mathrm{Ni}^{3+}_{1-y}\mathrm{Ni}^{2+}_y)\mathrm{O_2}$ 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 μ^+SR, because the direct jump of Li^+ from the regular site to the nearest deficient site is predominant for Li-diffusion.

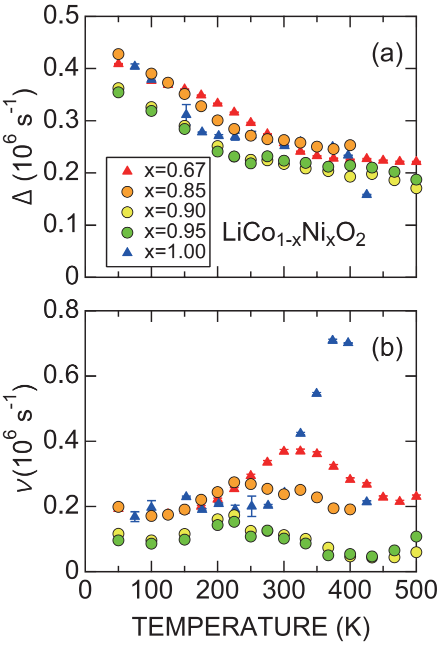

Fig. 1. Temperature dependences of Δ and ν for $\mathrm{LiCo_{1-x}Ni_xO_2}$ with $x = 0.67$, 0.85, 0.90, 0.95, and 1.

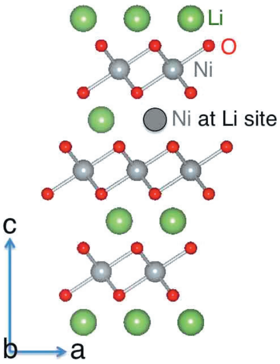

Fig. 2. Crystal structure of $\mathrm{LiNiO_2}$.

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