Lithium diffusion in lithium-transition-metal oxides detected by \( \mu^+\text{SR} \)

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Abstract

Diffusion of Li\textsuperscript{+} ions in solids is a basic principle behind the operation of Li-ion batteries. Such diffusive behavior is represented by the diffusion equation (Fick’s law), \( J = -D \times \phi \times \text{d}/\text{d}x \), where \( J \) is the diffusion flux, \( D \) is the self diffusion coefficient, \( \phi \) is the concentration, and \( x \) is the position. Although \( D \) of Li\textsuperscript{+} ions (\( D_{\text{Li}} \)) in solids is usually evaluated by \( ^7\text{Li-NMR} \), difficulties arise for materials that contain magnetic ions. This is because the magnetic ions contribute additional spin-lattice relaxation processes that is considerably larger than the \( 1/T_1 \) expected from only Li diffusion [1, 2, 3]. This implies that \( ^7\text{Li-NMR} \) provides a rough estimate of \( D_{\text{Li}} \) for the positive electrode materials of Li-ion batteries, which include transition metal ions in order to compensate charge neutrality during a Li\textsuperscript{+} intercalation/deintercalation reaction. This is an unsatisfactory situation since \( D_{\text{Li}} \) is one of the primary parameters that govern the charge/discharge rate of a Li-ion battery.

We have, therefore, attempted to measure \( D_{\text{Li}} \) for lithium-transition-metal-oxides with muon-spin relaxation (\( \mu^+\text{SR} \)) since 2005 [4, 5, 6]. Muons do not feel fluctuating magnetic moments at high \( T \), but instead sense the change in nuclear dipole field due to Li diffusion. Even if magnetic moments still affect the muon-spin depolarization rate, such an effect is, in principle, distinguishable from that of nuclear dipole fields. In particular, a weak longitudinal field can be applied that decouples the magnetic and nuclear dipole interactions [7, 8]. Here, we wish to summarize our \( \mu^+\text{SR} \) study on the lithium-transition-metal-oxides, Li\textsubscript{x}CoO\textsubscript{2}, LiNiO\textsubscript{2}, and LiCrO\textsubscript{2}.

Keywords: Self-diffusion and ionic conduction in nonmetals, Lithium-ion batteries, Muon-spin relaxation

1. Introduction

In Li\textsubscript{1.5}CoO\textsubscript{2}, as \( T \) increases from 50 K, the field fluctuation rate (\( \nu \)) is initially constant (eventually 0), but starts to increase above 160 K [6], around which the \( ^7\text{Li-NMR} \) line width suddenly decreases due to a motional narrowing [9].

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Furthermore, the $T$ dependence of $\nu$ was well explained by a thermal activation process in the $T$ range between 160 and 250 K. Assuming a random-walk jump of the Li$^+$ ions between the neighboring sites, $D_{Li}(300 \text{ K})$ for Li$_{0.7}$CoO$_2$ is estimated as about $6.2 \times 10^{-10} \text{ cm}^2/\text{s}$ [6], which is comparable to the prediction from first principles calculations [10]. In order to further confirm the unique power of $\mu^+\text{SR}$ for detecting $D_{Li}$ in solids, it is definitely necessary to measure $D_{Li}$ for other materials by means of $\mu^+\text{SR}$.

Then, we are moving to LiNiO$_2$ and related materials, because they have been heavily investigated as a positive electrode material for the next-generation Li-ion batteries [11]. In the rhombohedral LiNiO$_2$ lattice with space group $R\bar{3}m$, the NiO$_2$ plane and the Li layers form alternating stacks along the $c_{\text{H}}$-axis in the hexagonal setting [12]. In the NiO$_2$ planes, Ni ions form a two-dimensional triangular lattice (2DTL) by a network of edge-sharing NiO$_6$ octahedra. Since the Ni$^{3+}$ ions are in a low-spin state with $S = 1/2$, LiNiO$_2$ was proposed to be an ideal half-filled 2DTL [13]. In contrast to LiCoO$_2$, stoichiometric LiNiO$_2$ has never been prepared so far [14, 15]. 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$^{3+}$ [16, 17, 18]. The ionic distribution of the Ni-excess LiNiO$_2$ is, thus, given by $\text{Li}^{1-}\text{Ni}^{2+}_{1-x}\text{Ni}^{3+}_x\text{O}_2$ [17], where $3b$ and $3a$ are the Li and Ni site in the regular LiNiO$_2$ lattice.

Such (Ni$^{2+}$)$_{3b}$ ions are naturally expected to reduce $D_{Li}$ at high $T$ [11, 19], because of the hindrance of diffusion by (Ni$^{2+}$)$_{3b}$ in the Li$^+$ diffusion plane, in which Li$^+$ ions move relatively easily. Nevertheless, there is, to the authors’ knowledge, less systematic work on the relationship between $D_{Li}$ and $x$, while the charge/discharge performance was studied as a function of $x$ [11, 19]. The $\mu^+\text{SR}$ experiment on Li$_{1-x}\text{Ni}_{1+x}\text{O}_2$ with $x \geq 0$, therefore, provides crucial information on the effect of $x$ on $D_{Li}$.

2. Experimental

A powder sample of Li$_{0.98}\text{Ni}_{1.02}\text{O}_2$ was prepared by a solid-state reaction technique using reagent grade LiNO$_3$ and Ni(NO$_3$)$_2$ powders as starting materials. A mixture of the two powders with the molar ratio of Li/Ni=1 was well mixed with a mortar and pestle, then pressed into a pellet of 23 mm diameter and 5 mm thickness. The pellet was heated at 650°C for 12 h in an air flow, and then ground and pressed into a pellet again. Then, the pellet was annealed for 12 h in an oxygen flow at 750°C. In order to prepare Li$_{0.88}\text{Ni}_{1.15}\text{O}_2$, the pellet heated at 650°C was annealed for 12 h in an oxygen flow at 950°C. On the other hand, a powder sample of LiCrO$_2$ was prepared by a solid-state reaction technique using reagent grade LiOH·H$_2$O and Cr$_2$O$_3$ powders as starting materials. A stoichiometric mixture of the two powders was heated at 1000°C for 12 h in an air flow.

The $\mu^+\text{SR}$ spectra were measured at the surface muon beam lines using the ARGUS spectrometer of ISIS/Riken-RAL in U.K. and the D-OMEGA1 spectrometer of MUSE/MLF/J-PARC in Japan, after the low-$T$ measurements in TRIUMF to clarify their magnetism. In Riken-RAL and J-PARC, a ~2 g powder sample was pressed into a disc with 27 mm diameter and 1 mm thickness, and packed into an Au O-ring sealed titanium cell. The window of the cell was made of a Kapton film with 50 $\mu$m thickness. The cell was mounted onto the Cu plate of a liquid-He flow-type cryostat in the $T$ range between 10 and 500 K.

3. Results and Discussions

In the paramagnetic state, the ZF-$\mu^+\text{SR}$ spectrum exhibits a Kubo-Toyabe relaxation due to a nuclear magnetic field ($H^N_{\text{int}}$) mainly caused by $^6\text{Li}$ and $^7\text{Li}$. Figure 1 shows the ZF- and longitudinal field (LF-) $\mu^+\text{SR}$ spectrum for the $x = 0.02$ sample obtained at 300 K, 350 K, and 450 K, together with that for LiCrO$_2$ at 450 K. Here, LiCrO$_2$ poses the same $R\bar{3}m$ crystal structure as LiNiO$_2$, but is electrochemically inactive [20, 21], i.e. Li$^+$ ions are not deintercalated from the lattice by a usual electrochemical reaction.

Although the applied LF clearly decouples $H^N_{\text{int}}$ at 300 K, such a “decoupling” effect is weak at 350 K, indicating the increase in a field fluctuation rate ($\nu$). Interestingly, the same LF apparently decouples again at 450 K. This means that $H^N_{\text{int}}$ shows a static nature at 300 K, but slightly dynamic at 350 K, and then becomes static again at 450 K. On the other hand, the ZF- and LF-spectra for LiCrO$_2$ demonstrate the static nature even at 450 K.

In order to estimate the KT parameters, the ZF- and LF-spectra were fitted simultaneously by a combination of a dynamic Gaussian KT function [$G^{DGKT}(\Delta, \nu, t, H_{\text{LF}})$] [7] and an offset background (BG) signal from the fraction of
muons stopped mainly in the sample cell, which is made of high-purity titanium;

\[ A_0 P_{LF}(t) = A_{KT} G^{DGKT}(\Delta, \nu, t, H_{LF}) + A_{BG} \]

where \( A_0 \) is the initial \((t = 0)\) asymmetry, \( A_{KT} \) and \( A_{BG} \) are the asymmetries associated with the two signals. \( \Delta \) is the static width of the local field distribution at the disordered sites, and \( \nu \) is the field fluctuation rate. We fitted all the ZF- and LF-spectra using common \( A_{KT} \) and \( A_{BG} \) in the whole \( T \) range and common, i.e. \( H_{LF} \)-independent, \( \Delta \) and \( \nu \) at each \( T \) in Eq. (1).

Figure 1: ZF- and LF-\( \mu^+ \)SR spectra for Li\(_{0.98}\)Ni\(_{1.02}\)O\(_2\) obtained at (a) 300 K, (b) 350 K, and (c) 450 K. In (d), the spectra for LiCrO\(_2\) at 450 K are shown for comparison. Solid lines represent the fit result using Eq. (1).

Figure 2: \( T \) dependences of (a) \( \Delta \) and (b) \( \nu \) and (c) the relationship between \( \nu \) and \( 1/T \) for Li\(_{0.98}\)Ni\(_{1.02}\)O\(_2\), Li\(_{0.85}\)Ni\(_{1.15}\)O\(_2\), and LiCrO\(_2\), together with Li\(_{0.73}\)CoO\(_2\) [6]. The data were obtained by global-fitting the ZF- and LF-spectra using Eq. (1). The straight lines in (c) show the thermally activated behavior discussed in the text. According to dipole field calculations, \( \Delta \) at 0 K is predicted as \( 0.52 \times 10^{6} \text{s}^{-1} \) for LiNiO\(_2\), \( 0.53 \times 10^{6} \text{s}^{-1} \) for LiCrO\(_2\), and \( 0.60 \times 10^{6} \text{s}^{-1} \) for LiCoO\(_2\).

Figure 2 shows the \( T \) dependences of both \( \Delta \) and \( \nu \) for Li\(_{1-x}\)Ni\(_{1+x}\)O\(_2\) and LiCrO\(_2\) together with those for Li\(_{0.73}\)CoO\(_2\), which was prepared from LiCoO\(_2\) by an electrochemical reaction [6]. For Li\(_{0.98}\)Ni\(_{1.02}\)O\(_2\), as \( T \) increases from 150 K, \( \Delta \) is almost \( T \)-independent until 300 K, and then decreases monotonically with \( T \) up to 450 K. On the contrary, \( \nu \) starts to increase around 300 K with \( T \) and reaches a maximum around 375 K, and finally decreases with further increasing \( T \), as expected from the ZF- and LF-spectra [see Figs. 1(a)-1(c)]. Since the muons are stable in the vicinity of the \( \text{O}^2- \) ions until 450 K, the maximum in the \( \nu(T) \) curve and the decrease in the \( \Delta(T) \) curve are assigned to be caused by Li diffusion; that is, as \( \nu \) becomes rather large compared with \( \Delta \), such diffusion is too fast to be visible by \( \mu^+ \)SR. Thus, \( \nu \) decreases with \( T \) above 375 K, and finally, \( \nu (\Delta) \) would correspond to those for the rest NiO\(_2\). Indeed, the rapid increase in \( \nu \) with \( T \) is well explained by a thermal activation process, \( \nu \propto \exp(E_a/k_B T) \), for all the samples [see Fig. 2(c)], as expected for the Li\(^+\) diffusion. Here, \( E_a \) is the activation energy. Furthermore, according to dipole field
calculations, $\Delta (0 K) = 0.52 \times 10^6$ s$^{-1}$ for LiNiO$_2$ and 0.016 $\times 10^6$ s$^{-1}$ for NiO$_2$ at the muon site in the vicinity of the O$^{2-}$ ion. A very similar behavior is also observed for Li$_{0.77}$CoO$_2$ [6] and LiFePO$_4$ [22].

For Li$_{0.85}$Ni$_{1.15}$O$_2$, $v$ is clearly smaller than $v$ for Li$_{0.98}$Ni$_{1.02}$O$_2$ in the $T$ range between 300 and 400 K, indicating the reduction effect of the (Ni$^{2+}$)$_{02}$ ions on Li diffusion. In addition, $E_a(=115$ meV) for Li$_{0.85}$Ni$_{1.15}$O$_2$ is 1.5 times larger than $E_a(70$ meV) for Li$_{0.98}$Ni$_{1.02}$O$_2$. Assuming a random-walk jump of the Li$^+$ ions between the neighboring sites [23] and an offset value of $v$ ($v_{\text{off}} \sim 1.0 \times 10^{-5}$ s$^{-1}$) due to a dynamic Jahn-Teller distortion of the Ni$^{3+}$ ions [24], $D_{Li}(300$ K) is estimated as $\sim (0.72) \times 10^{-11}$ cm$^2$/s for Li$_{0.98}$Ni$_{1.02}$O$_2$ but almost 0, i.e. below the measurement limit, for Li$_{0.85}$Ni$_{1.15}$O$_2$ [25]. This is because the rapid increase in $v$, which is well explained by $v \propto \exp(E_a/k_B T)$ with $E_a = 115$ meV, is observed only above $\sim 330$ K for Li$_{0.85}$Ni$_{1.15}$O$_2$ [see Fig. 2(c)]. Therefore, it is clarified that $\mu^+SR$ provides information on the change in $D_{Li}$ with $x$ in Li$_{1-x}$Ni$_{1+x}$O$_2$. For LiCrO$_2$, on the other hand, $v$ is found to be almost $T$-independent from 275 K to the highest $T$ measured (475 K). This demonstrates that both $\mu^+$ and Li$^+$ ions are static in the LiCrO$_2$ lattice at least until 475 K. This is very consistent with the electrochemical behavior of LiCrO$_2$ [20, 21]. Moreover, since $E_a$ for LiCrO$_2$ (19 meV) is very small compared with those for the other compounds (70 meV-115 meV), the small increase in $v$ with $T$ for LiCrO$_2$ is likely caused by another mechanism, such as, an electron contribution.

Finally, we wish to emphasize the unique power of $\mu^+SR$ for the research of Li-ion batteries through $D_{Li}$ measurements. Particularly for future solid-state batteries, the overall performance is mainly governed by Li diffusion in the positive electrode and the interface between electrode and electrolyte. Therefore, $\mu^+SR$ would be a crucial tool for the research of Li-ion batteries.

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