8Li β-NMR study of epitaxial Li$_x$CoO$_2$ films

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Abstract. In order to investigate the diffusive motion of Li$^+$ in a thin film electrode material for Li-ion batteries, we have measured β-NMR spectra of 8Li$^+$ ions implanted into epitaxial films of Li$_{0.7}$CoO$_2$ and LiCoO$_2$ in the temperature range between 10 and 310 K. Below 100 K, the spin-lattice relaxation rate (1/T$_1$) in the Li$_{0.7}$CoO$_2$ film increased with decreasing temperature, indicating the appearance and evolution of localized magnetic moments, as observed with μ$^+$SR. As temperature is increased from 100 K, 1/T$_1$ starts to increase above ∼200 K, where both Li-NMR and μ$^+$SR also sensed an increase in 1/T$_1$ due to Li-diffusion. Interestingly, such diffusive behavior was found to depend on the implantation energy, possibly because the surface of the film is decomposed due to chemical instability of the Li$_{0.7}$CoO$_2$ phase in air. Such diffusive behavior was not observed for the LiCoO$_2$ film up to 310 K.

1. Introduction

In order to improve the safety and increase the volumetric energy density of Li-ion batteries, the present solid-liquid battery will be replaced by an all-solid-state battery in the near future (Fig. 1). For such solid-state batteries, the overall performance, particularly the charge/discharge rate, is mainly governed by Li diffusion in the electrodes and the interface between electrode and electrolyte. There is, thus, a pressing need to measure the Li diffusive behavior along the direction from cathode to anode, through the electrolyte of a solid-state layered Li-ion battery (vertical direction in Fig. 1). Therefore, we have initiated a program utilizing the “β-NMR” technique as a probe of the diffusion coefficient of Li$^+$ ions (D$_{Li}$) [1, 2] in battery materials and hopefully as a tool to obtain the depth profile of D$_{Li}$ in solid-state battery materials, and hence to elucidate the role of the interface. Since mobile Li ions always pass through such an interface, the change in D$_{Li}$ at the interface is crucial for developing solid-state batteries. It is worth noting that such information is detectable by β-NMR and/or low-energy...
The present solid-liquid battery design and (b) the near-future solid-state battery.

In the present battery, a typical cathode material is LiCoO$_2$, electrolyte an ethylene carbonate-diethyl carbonate solution of LiPF$_6$, and anode material graphite.

\mu^+SR, but is very difficult, if not impossible, to obtain by electrochemical, NMR or neutron scattering measurements.

For NMR and other spin relaxation techniques, one principle mechanism for spin-lattice relaxation (the only one for pure magnetic species, like the spin 1/2 muon) is the existence of a magnetic field transverse to the spin polarization that fluctuates at the Larmor frequency of the spin in the static magnetic field. The pioneering work of Bloembergen, Purcell, and Pound [3] showed how diffusive motion that varies the local magnetic environment of a nucleus can produce such fluctuations and cause spin relaxation, and hence how spin relaxation (in the absence of other relaxation pathways) could be used to measure diffusion rates [4]. In contrast to conventional Li-NMR [5], the effect of localized moments\textsuperscript{1} in the paramagnetic (PM) state on the $\beta$-NMR signal is very limited at high $T$, because the PM fluctuations are usually too fast to cause a measurable spin relaxation, as in the case for $\mu^+\text{SR}$.

In fact, making comparison with the NMR results, $\mu^+\text{SR}$ provides relatively reliable $D_{\text{Li}}$ for Li$_x$CoO$_2$ [6]. However, due to the mass difference between $\mu^+$ and Li$^+$, the $D_{\text{Li}}$ estimated from $\mu^+\text{SR}$ might be affected by muon diffusion.

Here we use $^8\text{Li}^+$ that is, unlike the $\mu^+$, unambiguously an isotope of Li. Therefore, we could, in principle, estimate $D_{\text{Li}}$ directly from the dynamic behavior of $^8\text{Li}^+$ detected by $\beta$-NMR. In addition, since the $\beta$-NMR timescale is much longer than $\mu^+\text{SR}$, as the radioactive lifetime $\tau$ is 1.21 s, rather than the $2.2 \times 10^{-6}$ s for $\mu^+$, it is expected to provide unique information on a different timescale. This is our primary motivation to perform these $\beta$-NMR experiments.

2. Experimental

The LiCoO$_2$ (110) epitaxial film of $\alpha$-NaFeO$_2$ structure with space group $R\bar{3}m$ was grown on an Au(110) single crystal substrate using a pulsed laser deposition technique (Fig 2) [7]. The thickness of the film was about 200 nm. The Li-deficient Li$_{0.7}$CoO$_2$ film was prepared by an electrochemical reaction between the LiCoO$_2$ film and Li metal sheet using a Li$|$LiPF$_6$-ethylene carbonate-diethyl carbonate$|$LiCoO$_2$ cell.

The $\beta$-NMR spectra were measured using the $^8\text{Li}$ beam produced at the Isotope Separator and Accelerator (ISAC) at TRIUMF in Canada. The nuclear spin is polarized using a collinear optical pumping method, producing a spin polarized $^8\text{Li}^+$ beam with about 70% polarization.

\textsuperscript{1} In this compound the valence (and magnetic moment) of Co ions changes with the degree of Lithiation, $x$.
The LiCoO<sub>2</sub> epitaxial film on an Au substrate; that is, a dark blue film on a gold plate. For scale, the Au is affixed to an 8 mm × 10 mm sapphire plate that is clamped (by the visible screws) to the Al sample holder that mounts into the cold finger of an ultrahigh vacuum cryostat.

Finally, the beam is implanted into the Li<sub>x</sub>CoO<sub>2</sub> sample. The implanted beam energy \(E_{\text{im}}^{\text{Li}}\) was 28 keV, for which the \(^8\)Li stops at an average depth of about 120 nm.

In the \(\beta\)-decay of \(^8\)Li, an electron is emitted preferentially opposite to the direction of the nuclear polarization and is detected by scintillation counters, as in \(\mu^+\)SR. Therefore, we can measure the change in asymmetry as a function of time for a pulsed beam or as a function of frequency of an applied RF magnetic field. The details of setup and experimental procedure of \(\beta\)-NMR are described elsewhere [8, 9, 10].

### 3. Results and discussion

#### 3.1. Spin-lattice relaxation

Figure 3 shows the \(\beta\)-NMR time spectrum for the Li<sub>0.7</sub>CoO<sub>2</sub> film obtained at 310 and 200 K in an applied field of 6.55 Tesla. At this field, the \(^8\)Li is effectively decoupled from the stable \(^6\)Li spins that have nearly the same gyromagnetic ratio [11]. The \(^8\)Li pulse starts at \(t = 0\) and continues for \(\delta = 4\) s, resulting in the pronounced kink in the time spectrum at \(t = \delta\). The \(\beta\)-decay asymmetry is measured both during and after the beam pulse [10]. As can be seen in Fig. 3, the relaxation at 310 K is clearly faster than at 200 K, indicating an increase in the
spin-lattice relaxation rate ($1/T_1$) with temperature. The time spectrum was best fit by a power exponential relaxation function for the fraction of $^{8}$Li implanted in the sample at $t_p$ [10];

$$A_0 P_z(t) = A_0 \int_0^t \exp\left[-\frac{t - t_p}{\tau}\right] \exp\left[-\left(\frac{t - t_p}{T_1}\right)^\beta\right] dt_p \quad t \leq \delta,$$

$$A_0 P_z(t) = A_0 \int_0^\delta \exp\left[-\frac{\delta - t_p}{\tau}\right] \exp\left[-\left(\frac{\delta - t_p}{T_1}\right)^\beta\right] dt_p \quad t > \delta,$$

(1)

where $A_0$ is the initial asymmetry, $P_z(t)$ is the $^{8}$Li spin polarization function, $\beta$ is the power (fixed at 0.5), and $A$ is the asymmetry for the power exponential relaxation signal. Since we assumed a single component decay, $A_0 = A$.

Figure 4 shows the temperature dependence of $1/T_1$ for the Li$_{0.7}$CoO$_2$ and LiCoO$_2$ films. For Li$_{0.7}$CoO$_2$, as temperature increases from 10 K, $1/T_1$ shows a local maximum around 30 K due to localized Co moments [12], then, levels off to a constant value ($\sim 1.7$ s$^{-1}$) up to 200 K, and then, increases monotonically with further increasing temperature. Since Li-NMR [13] and $\mu^{+}$SR [6] measurements on bulk Li$_{0.7}$CoO$_2$ also sensed an increase in $1/T_1$ above $\sim 200$ K, we attribute this increase to Li-diffusion. On the other hand, for LiCoO$_2$, $1/T_1$ is almost temperature independent up to 310 K, besides the anomaly below 75 K due to antiferromagnetic order in LiCoO$_2$ with $T_N = 30$ K [14, 12]. Considering the absence of Li vacancies in stoichiometric LiCoO$_2$, Li-diffusion in LiCoO$_2$ is predicted to be strongly suppressed compared to Li$_{0.7}$CoO$_2$ [15]. The present $\beta$-NMR result is very consistent with this.

Interestingly, when $E_{im}^{Li}$ is decreased from 28 keV to 20 and 10 keV for the Li$_{0.7}$CoO$_2$ film, such diffusive behavior was not observed up to the maximum available temperature, 310 K. This is probably due to a partial decomposition of the surface of the Li$_{0.7}$CoO$_2$ film, because the Li$_{0.7}$CoO$_2$ phase is very hygroscopic, easily reacting with water in the air. Currently, mounting the sample into the spectrometer requires exposure to ambient air for a period up to several minutes.

![Figure 5](image1.png)

**Figure 5.** The nuclear resonance spectra of $^{8}$Li for the Li$_{0.7}$CoO$_2$ film measured at 310 and 200 K. The data at 310 K is offset by -0.005 for clarity. Solid lines represent the fit using a Lorentz function.

![Figure 6](image2.png)

**Figure 6.** The temperature dependence of the full width at half maximum (FWHM) of the resonance for the Li$_{0.7}$CoO$_2$ film. The data were obtained by fitting the $\beta$-NMR resonance spectrum using a Lorentz function.
3.2. Resonance line

In a noncubic material like Li$_x$CoO$_2$, the $I = 2$ nuclear spin of $^8$Li couples through its nuclear quadrupole moment $Q$ to the electric field gradient (EFG) tensor created by its charge environment. This usually yields a quadrupole split resonance [16, 17, 18]. However, we observed only a single broad line, even at 200 K, see Fig. 5. We note that the $^7$Li-NMR exhibits a quadrupole splitting on the order of 30-40 kHz in bulk LiCoO$_2$ [19]. If the implanted $^8$Li$^+$ stops at the same site, we would expect a quadrupole splitting scaled down by the ratio of the quadrupole moments, $|Q(^8\text{Li})/Q(^7\text{Li})|$, i.e. about 0.75, which is larger than the observed linewidth by about a factor of 2. Static crystalline disorder resulting in a random distribution of EFGs, may account for the lack of a resolved quadrupole splitting. Alternatively, diffusive motion of Li may dynamically average the quadrupole splitting, yielding a narrowed line. But, this would imply that $^8$Li moves rapidly even at 200 K, which seems unreasonable. We note that a single broad line is sometimes observed for the materials without Li-diffusion[16], likely due to the effects of disorder. At 310 K, the linewidth is found to decrease, suggesting motional narrowing (dynamical averaging). In fact, the temperature dependence of the full width at half maximum (FWHM) of the resonance line (Fig. 6) shows a clear decrease with temperature above 200 K. However, more measurements over a wider range of temperature are required to confirm the relation between the resonance width and the diffusion of Li in this system.

4. Summary

We have measured $\beta$-NMR spectra for Li$_{0.7}$CoO$_2$ and LiCoO$_2$ film samples below 310 K. This is, to our knowledge, the first attempt to use $\beta$-NMR to measure Li-diffusion in a film sample containing paramagnetic ions. For Li$_{0.7}$CoO$_2$, possible motional narrowing behavior due to Li-diffusion was observed above 200 K both in the spin-lattice relaxation and resonance line measurements. For LiCoO$_2$, such behavior was not observed up to 300 K due to the absence of Li vacancies.

Acknowledgments

We thank the staff of TRIUMF for help with the $\beta$-NMR experiments. This work was supported by MEXT KAKENHI Grant No. 23108003 and JSPS KAKENHI Grant No. 26286084.

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