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Li-Diffusion in Spinel Li[$Ni_{1/2}Mn_{3/2}$]O_4 Powder and Film Studied with μ^+SR

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A dynamic behavior in spinel Li[$Ni_{1/2}Mn_{3/2}$]O_4 has been studied with μ^+SR measurements in film and powder samples in the temperature range between 5 and 500 K. Both samples exhibited a broad ferromagnetic transition below 120 K, indicating the random distribution of Ni and Mn ions at the octahedral 16*d* site. Above 150 K, the ZF-μ^+SR spectrum showed a dynamic behavior well explained by a dynamic Kubo-Toyabe function. Assuming a jump diffusion of Li^+ at the tetrahedral 8*a* site to the vacant octahedral 16*c* site, a diffusion coefficient of Li^+ is estimated as $\sim 5\times10^{-11}$ cm^2/s at 300 K and $\sim 8\times10^{-11}$ cm^2/s at 350 K and $\sim 14\times10^{-11}$ cm^2/s at 400 K, with thermal activation energy $E_a \sim 0.1$ eV.

KEYWORDS: spinel, thin film, Li-diffusion

1. Introduction

When we use spinel $Li_4Ti_5O_{12}$ as an anode material for an all solid-state battery, cathode materials with working voltage vs. Li metal ($E_{\rm cathode}$) ranging above 4.5 V are highly required to obtain meaningful energy density for such battery. This is because, since $E_{\rm anode}$ of $Li_4Ti_5O_{12}$ ranges at about 1.5 V [1], the voltage of the all solid-state battery (E) is given by $E = E_{\rm cathode} - E_{\rm anode} = E_{\rm cathode} - 1.5$. Therefore, a spinel Li[$Ni_{1/2}Mn_{3/2}$]O_4 is expected to be a promising candidate for the cathode material in an all solid-state battery, because E of Li[$Ni_{1/2}Mn_{3/2}$]O_4 is about 4.7 V and almost independent of the Li content. i.e. the state of charge and discharge [2]. Following upon the μ^+SR work on $Li_4Ti_5O_{12}$ [3], we have measured μ^+SR spectra both for film and powder samples of Li[$Ni_{1/2}Mn_{3/2}$]O_4 in order to estimate a diffusion coefficient of Li^+ ($D_{\rm Li}$). Note that it is very difficult to estimate $D_{\rm Li}$ with Li-NMR due to the presence of magnetic ions, i.e. Ni^{2+} and Mn^{4+} [4].

2. Experimental

The powder sample was prepared by a solid-state reaction technique. The reaction mixture of $LiOH{*}H_2O$ and nickel manganese double hydroxide was pressed into a pellet of 23 mm in diameter and 5 mm thickness. The pellet was heated at 1273 K under an air flow for 12 h, then cooled down to room temperature with a cooling rate of 5 K/min.

The film was grown on a sapphire (0001) substrate with the thickness of about 200 nm using a PLD technique in AIMR of Tohoku University. According to XRD analysis, they are assigned as an epitaxially grown (111)-oriented film.

The μ^+SR spectra for the powder sample were measured using a surface muon-beam, EMU, at ISIS of RAL in U.K., and those for the films were measured using the low-energy μ^+ (LEM) beam at SμS of PSI in Switzerland. At ISIS, the powder sample was packed into a gold O-ring sealed titanium powder cell. Then, the cell was attached onto a Cu holder of the cryo-oven, which is cooled down to around 10 K with a closed cycle refrigerator and heated up to around 600 K without setup change. The details of μ^+SR are described elsewhere [6–9].

At PSI, in order to cover a 2×2 cm^2 area, four film nominally identical samples with 1×1 cm^2 each were glued onto a Ni-coated Al or stainless steel plate, which was then mounted on a cryostat or oven, respectively. The implanted beam energy ($E_\mu^{\rm im}$) was 17.5 keV, for which the μ^+ stops at an average depth of about 100 nm. The temperature range for LEM-μ^+SR measurements was between 10 and 320 K for a cryostat and 300 and 500 K for an oven. The details of LEM-μ^+SR are described elsewhere [10–13].

3. Results and Discussion

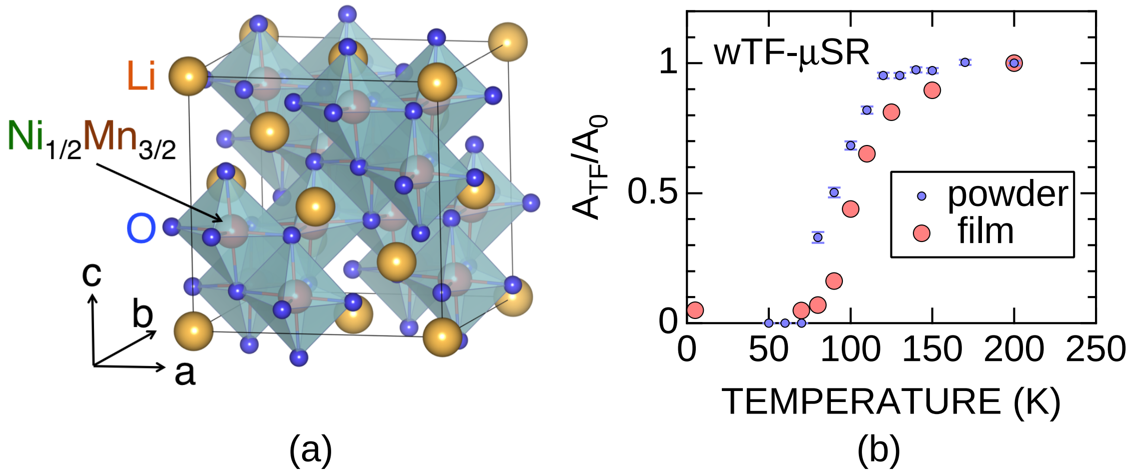

Fig. 1. (a) The crystal structure of cubic spinel $Li[Ni_{1/2}Mn_{3/2}]O_4$ with space group $Fd\bar{3}m$ and (b) the temperature dependence of the normalized weak transverse field asymmetry ($A_{\rm TF}/A_0$) for powder and film samples. In (a), Li^+ ions occupy at the tetrahedral 8*a* site, while Ni and Mn ions occupy at the octahedral 16*d* site. The data in (b) were obtained by fitting the weak transverse spectrum with an exponentially relaxing cosine signal, $A_0(t) = A_{\rm TF}\exp(-\lambda_{\rm TF}t)\cos(2\pi f_{\rm TF}t + \phi_{\rm TF})$.

Figure 1 shows the crystal structure of spinel $Li[Ni_{1/2}Mn_{3/2}]O_4$ and the the temperature dependence of the normalized weak transverse field asymmetry ($A_{\rm TF}/A_0$) for powder and film samples. Both samples exhibit a broad ferromagnetic transition below around 120 K. Such broad transition is a signature of the random distribution of Ni and Mn ions at the octahedral sites, i.e. a cubic spinel with space group $Fd\bar{3}m$ [14, 15].

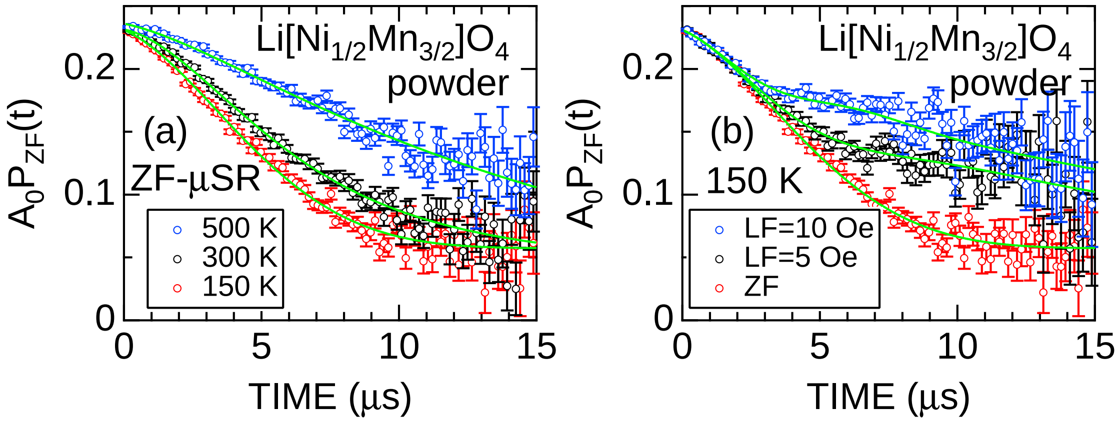

Fig. 2. (a) The ZF-μ^+SR spectrum recorded at 150, 300, and 500 K and (b) ZF- and LF-μ^+SR spectrum recorded at 150 K for the powder sample of Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$.

Figure 2 shows the temperature variation of the zero field (ZF) μ^+SR spectrum for Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ measured at 150, 300, and 500 K. The ZF-spectrum exhibits a static behavior at 150 K, while it becomes dynamic with increasing temperature. The ZF- and longitudinal field (LF) μ^+SR spectrum were fitted by a combination of a dynamic Kubo-Toyabe signal from the sample and a background signal caused by muons stopped at a sample cell for the powder sample and a sample plate for the film sample;

$$A_0\,P(t) \quad = \quad A_{\rm KT}G^{\rm DGKT}(\Delta, \nu, t, H_{\rm LF}) + A_{\rm BG}, \tag{1}$$

where A_0 is the initial ($t = 0$) asymmetry, $A_{\rm KT}$ and $A_{\rm BG}$ are the asymmetries associated with the two signals. Δ is the static width of the local field distribution at the disordered sites, and ν is the field fluctuation rate, i.e. the hopping rate. When $\nu = 0$ and $H_{\rm LF} = 0$, $G^{\rm DGKT}(t, \Delta, \nu, H_{\rm LF})$ is the static Gaussian KT function $G^{\rm KT}_{zz}(t, \Delta)$ in ZF, namely, $G^{\rm KT}_{zz}(t, \Delta) = \{\frac{1}{3} + \frac{2}{3}(1 - \Delta^2t^2)\exp(-\frac{1}{2}\Delta^2t^2)\}$.

Figure 3 shows the temperature dependences of the field distribution width (Δ) and field fluctuation rate (ν) for powder and film samples of Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$. The overall result of the film sample is very similar to that of the powder sample, as expected. If we assume that ν corresponds to the jump frequency of Li$^+$ ions between the regular Li site (8*a* site) and the vacant octahedral site (16*c* site), as in the case for LiTi$_2$O$_4$ [3], $D_{\rm Li}$ is estimated as $\sim 5 \times 10^{-11}$ cm^2/s at 300 K and $\sim 8 \times 10^{-11}$ cm^2/s at 350 K and $\sim 14 \times 10^{-11}$ cm^2/s at 400 K, with thermal activation energy $E_a \sim 0.1$ eV. These values are found to be comparable to those for spinel Li$_4$Ti$_5$O$_{12}$, implying a balanced combination of $D_{\rm Li}$ between Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$ cathode and Li$_4$Ti$_5$O$_{12}$ anode in the future all solid state battery.

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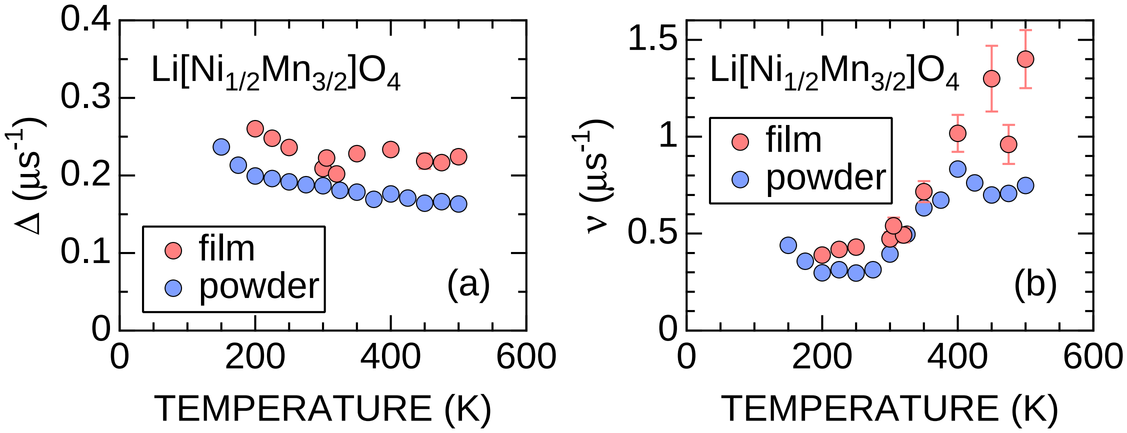

Fig. 3. The temperature dependences of (a) the field distribution width (Δ) and (b) field fluctuation rate (ν) for powder and film samples of Li[Ni$_{1/2}$Mn$_{3/2}$]O$_4$. The data were obtained by fitting the ZF- and LF-μ^+SR spectra with Eq. (1).

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