



## Special Feature: Materials Analysis Using Quantum Beams

Review

### Ion Diffusion in Solids Detected with Muon-spin Spectroscopy

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**■ABSTRACT■** In this paper, we will give an introduction to the method itself but also summary of our muon-spin rotation and relaxation ( $\mu^+$ SR) work on Li-diffusion in battery positive electrode materials. Furthermore, we will show that the method is not limited to studying only Li-diffusion but can also be extended to other physical and/or electrochemical properties in transition metal oxides. Finally, we will compare our method to other available macroscopic and microscopic techniques that are able to study ion diffusion in solids, and provide an outlook towards future developments.

**■KEYWORDS■** Muon-spin Relaxation, Nuclear Magnetic Field, Diffusion, Li, Na

#### 1. Introduction

In order to store electric energy in a compact package, huge number of batteries have been under intense investigation since 1800, i.e. the discovery of a voltaic cell. Among them, Li-ion batteries are thought to be the most promising one,<sup>(1-4)</sup> particularly for the energy storage device for electric vehicles mainly due to its high energy density. Back to the basic principle behind the operation of such batteries, ion-diffusion in solids is one of the essential factors to govern the total performance of batteries, because the charge carrier in batteries should be ion. And, the speed and density of an ion flow provide the overall current.

According to Fick's first law, a diffusion behavior of ions in solids is expressed by;

$$J = -\tilde{D} \times \partial\phi/\partial x, \quad (1)$$

where  $J$  is the diffusion flux,  $\tilde{D}$  is the chemical diffusion coefficient,  $\phi$  is the concentration, and  $x$  is the position. Although  $\tilde{D}$  is usually determined by electrochemical measurements, it is very difficult to estimate  $\tilde{D}_{\text{Li}}$  accurately due to absence of knowledge on the reactive surface area of a porous electrode in a liquid electrolyte.<sup>(1)</sup>

On the other hand, a self diffusion coefficient or a jump diffusion coefficient ( $D$ ) of  $\text{Li}^+$  ions ( $D_{\text{Li}}$ ) in solids is usually evaluated by  $^7\text{Li}$ -NMR.<sup>(5)</sup> Here,  $D_{\text{Li}}$  is connected with  $\tilde{D}_{\text{Li}}$  by the relationship;

$$\tilde{D}_{\text{Li}} = \Theta D_{\text{Li}}, \quad (2)$$

where  $\Theta$  is a thermodynamic factor. However, for materials containing magnetic ions, Li-NMR provides very limited information on  $D_{\text{Li}}$ , because of the effect of electron spins on the spin-lattice relaxation rate ( $1/T_1$ ).<sup>(6)</sup> Hence, there is no optimal way to correctly determine  $D_{\text{Li}}$  for positive electrode materials of Li-ion batteries, since they all include transition metal ions to compensate charge neutrality during the  $\text{Li}^+$  intercalation and deintercalation reaction. This is a highly unsatisfactory situation, since  $D_{\text{Li}}$  is one of the primary parameters that govern the charge and discharge rate of a Li-ion battery, particularly in the case of future solid state batteries.

We have, therefore, attempted to measure  $D_{\text{Li}}$  for lithium-transition-metal-oxides (LiMO) with muon-spin rotation and relaxation ( $\mu^+$ SR) since 2005.<sup>(7-16)</sup> The other group also measured  $D_{\text{Li}}$  for Li ionic conductors with  $\mu^+$ SR.<sup>(17,18)</sup> More correctly, the first  $\mu^+$ SR work for studying dynamics in battery materials was, to author's knowledge, reported in 2000 for  $\text{Li}_x(\text{Mn}_{1.96}\text{Li}_{0.04})\text{O}_4$ ,<sup>(19)</sup> in which the authors concentrated the change in the average nuclear magnetic field (the field distribution width) with temperature. A similar experimental approach was also reported for  $\text{Li}_{0.6}\text{TiO}_2$ ,<sup>(20)</sup> although  $D_{\text{Li}}$  was not obtained in these work.

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.<sup>(21)</sup> Here, we summarize our  $\mu^+$ SR work on Li diffusion and compare the  $\mu^+$ SR method to other available experimental techniques in terms of accuracy, flexibility as well as time window.

## 2. Basic Principle

Among several methods to detect ion diffusion in solids, the muon-spin relaxation ( $\mu^+$ SR) technique provides unique information on Li diffusion, mainly because of its characteristic time and spatial resolutions.<sup>(22)</sup> Muons are  $S = 1/2$  particles with a very large gyromagnetic ratio  $\gamma/2\pi = 13.553$  kHz/Oe. Therefore, the implanted muons into a material act as an extremely sensitive and local probe of static as well as dynamic magnetic/dipole fields. Furthermore, when using muons with momentum  $p_\mu = 29.8$  MeV/c and kinetic energy  $K_\mu = 4.1$  MeV, – i.e. *surface muons*, the initial muon-spin direction is perfectly antiparallel to its momentum due to parity violation. This is a significant advantage over NMR and other resonance techniques, since such 100% *spin polarized* muons sense the local magnetic field under zero applied field (ZF).

### 2.1 How to Detect Li-diffusion by $\mu^+$ SR

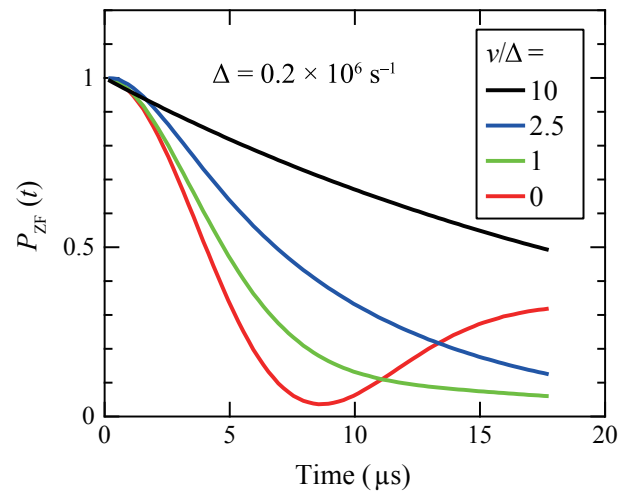
Positive muons are identified as an ideal point charge with a positive elementary charge. Thus, the implanted muons into LiMO are located in the vicinity of oxygen anions, i.e. typically 1-1.2 Å away from  $O^{2-}$  ions so as to make a stable  $\mu^+-O^{2-}$  bond. In other words, the muon in LiMO is stationary in the vicinity of  $O^{2-}$  ions and is able to sense the local magnetic field of nuclear origin ( $H_{int}^{Nu}$ ), when LiMO is in a paramagnetic state. If we assume a static and isotropic Gaussian field distribution around the muon, the ZF- $\mu^+$ SR time-spectrum is expressed by a static Gaussian Kubo-Toyabe (KT) function<sup>(22)</sup> ( $G_{zz}^{KT}(\Delta, t)$ , see the curve with  $v/\Delta = 0$  in Fig. 1);

$$P_{ZF}(t) = G_{zz}^{KT}(\Delta, t) = \frac{1}{3} + \frac{2}{3}(1 - \Delta^2 t^2) \exp\left(-\frac{1}{2} \Delta^2 t^2\right). \quad (3)$$

Here,  $P_{ZF}(t)$  is the muon-spin depolarization function in ZF and  $\Delta$  is the static width of the local field distribution at the muon site. Note that  $\Delta$  corresponds to the linewidth of Li-NMR, while  $\nu$  corresponds to  $1/T_1$ .

When the muon sees a local field that fluctuates randomly with an average rate, i.e. the field fluctuation rate ( $\nu$ ) due to Li-diffusion,  $G_{zz}^{KT}$  is replaced by a dynamic Gaussian KT function ( $G_{zz}^{DGKT}(\Delta, \nu, t)$ ). Although the strict analytical expression for  $G_{zz}^{DGKT}$  is unavailable, the variation of the  $\mu^+$ SR spectrum with  $\nu/\Delta$  is given by numerical calculations (see Fig. 1). If  $Li^+$  ions start to diffuse above a certain temperature ( $\equiv T_{diffu}$ ), such diffusive motion induces additional fluctuation in the local field, resulting in the increase of  $\nu$  with temperature above  $T_{diffu}$ , and we can know the change in  $\nu$  from the ZF- $\mu^+$ SR measurements, and, as a result, evaluate  $D_{Li}$ , if we assume that  $\nu$  corresponds to the jump rate of the  $Li^+$  ions between the neighboring sites. This is the basic principle how to measure  $D_{Li}$  in solids by  $\mu^+$ SR.

Note that, when  $\nu \gg \Delta$ ,  $G_{zz}^{DGKT}(\Delta, \nu, t)$  is equivalent to  $\exp(-\lambda^{nu}t)$  (see Fig. 1 with  $\nu/\Delta = 10$ ). Here,  $\lambda^{nu}$  is the exponential relaxation rate due to fluctuating nuclear magnetic moments. For such situation, we can not extract  $\nu$  from the  $\mu^+$ SR data. This leads to the upper limit for detecting Li-diffusion in solids with  $\mu^+$ SR, as shown in Section 5.



**Fig. 1** Muon-spin depolarization in ZF expressed by a dynamic Gaussian Kubo-Toyabe function with four different  $\nu/\Delta$ . Here,  $\Delta$  is fixed at  $0.2 \times 10^6$  s<sup>-1</sup>, which corresponds to about 2.3 Oe.

## 2.2 How to Separate Electronic Contribution from Nuclear Contribution

For the case that the ZF- $\mu^+$ SR spectrum shows a KT-type relaxation, longitudinal field (LF) measurements are very useful to study  $\Delta$  and  $\nu$  in detail.<sup>(21)</sup> Here, LF means the external field applied parallel to the initial muon-spin direction. When  $H_{LF} > \Delta$ , the nuclear field contribution is quenched by  $H_{LF}$ . As a result, the muon-spin is held its original direction with increasing  $H_{LF}$ , leading to a decrease in relaxation (see Fig. 2(a)). Such behavior is called “decoupling” with LF. Since  $\Delta$  of nuclear origin usually ranges below 10 Oe in LiMO, the decoupling behavior is observed even with an LF of a few Oe.

When the muon-spin is depolarized by both  $H_{int}^{Nu}$  and  $H_{int}$  originated by electron ( $H_{int}^{Ele}$ ), the total depolarization function is given by the product of the two polarization functions (see Fig. 2(b)).<sup>(23)</sup>

$$P_{ZF}(t) = G_{zz}^{DGKT}(\Delta, \nu, t) \exp(-\lambda t). \quad (4)$$

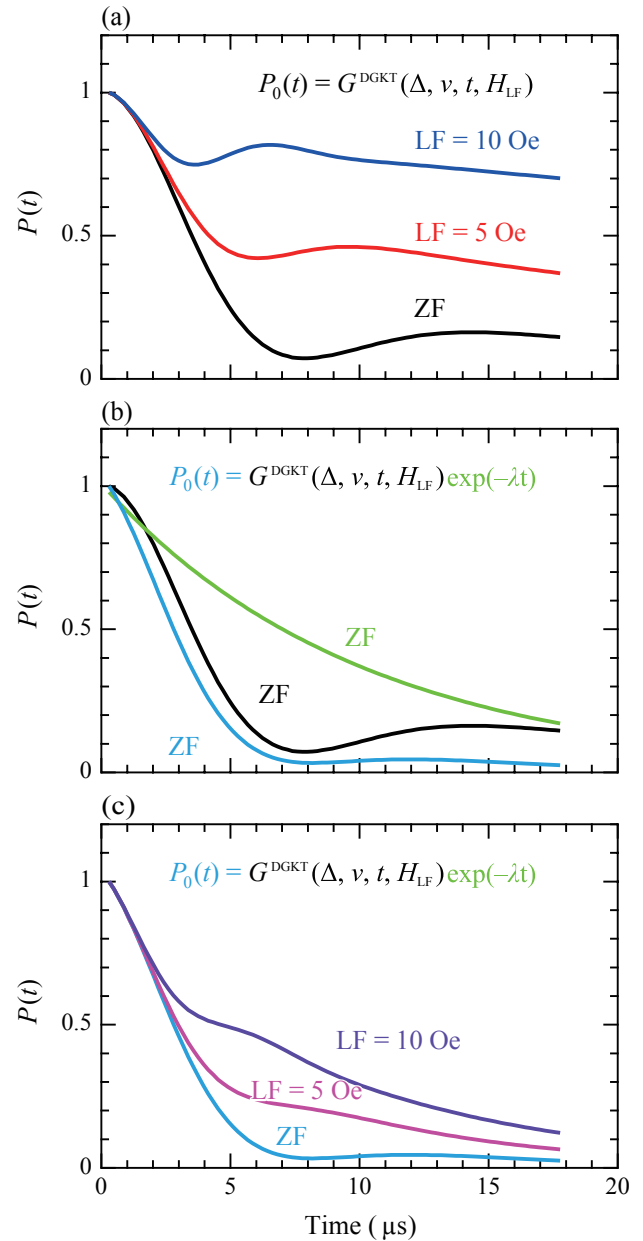
Since  $H_{int}^{Ele} \gg H_{int}^{Nu}$ , the electronic contribution is distinguishable from the nuclear contribution by LF measurements.<sup>(21)</sup> This is because a weak LF decouples the nuclear contribution but does not affect the stronger electronic contribution (see Fig. 2(c)). As a result, we can know  $\Delta$  and  $\nu$  originated by  $H_{int}^{Nu}$  under the coexistence of  $H_{int}^{Ele}$ . This makes  $\mu^+$ SR a significant technique for detecting  $D_{Li}$  in LiMO and other magnetic materials. We wish to emphasize that such characteristic feature is caused by the fact that the initial muon-spin is polarized even in ZF.

## 3. Experiment

Powder samples of LiMO were used for the  $\mu^+$ SR measurements. Since some samples are unstable in air, the sample was usually packed into a sealed powder cell made of titanium. The  $\mu^+$ SR spectra were mainly measured at the surface muon beam lines in pulsed-muon facilities, i.e., ISIS at Rutherford Appleton Laboratory in UK and MUSE of Materials and Life Science Facility at J-PARC in Japan, because of their higher counting rate than that of continuous-muon facilities.

## 4. Results

Figure 3 shows the ZF- $\mu^+$ SR spectrum for the  $Li_{0.73}CoO_2$  sample recorded at 100, 225, and 275 K. At 100 K, the ZF-spectrum exhibits a typical KT



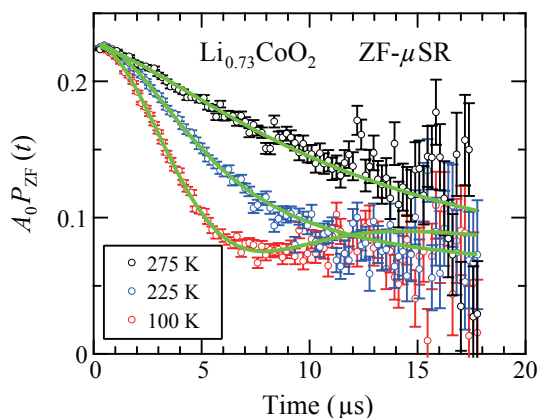
**Fig. 2** (a) Muon-spin depolarization in ZF and LF represented by a dynamic Kubo-Toyabe function ( $G_{zz}^{DGKT}$ ), which corresponds to the relaxation due to a nuclear magnetic field, (b) the depolarization represented by  $G_{zz}^{DGKT}$ , by an exponential relaxation function ( $\exp(-\lambda t)$ ), and by a product of the two functions, and (c) the depolarization in ZF and LF represented by  $G_{zz}^{DGKT} \exp(-\lambda t)$ . In (a)-(c),  $\Delta = 2.8$  Oe =  $0.24 \times 10^6$  s<sup>-1</sup> and  $\nu = 0.08 \times 10^6$  s<sup>-1</sup>. In (b) and (c),  $\lambda = 0.2 \times 10^6$  s<sup>-1</sup>.

behavior, meaning that the implanted muons see  $H_{\text{int}}^{\text{Nu}}$  due to the nuclear magnetic moments of  ${}^7\text{Li}$ ,  ${}^6\text{Li}$  and  ${}^{59}\text{Co}$ . Although the ZF-spectrum still shows a KT behavior that at 225 K, the relaxation rate is smaller than that at 100 K. At 275 K, the spectrum looks like an exponential relaxation behavior due to an increase in  $\nu/\Delta$  with  $T$ , as expected from Fig. 1. In order to estimate the KT parameters precisely, the ZF- and two LF-spectra recorded at 5 and 10 Oe were fitted simultaneously by a combination of Eq. (4) and an offset signal from the fraction of muons stopped mainly in the sample cell.

$$A_0 P(t) = A_{\text{KT}} G^{\text{DGKT}}(\Delta, \nu, t) \exp(-\lambda t) + A_{\text{BG}}, \quad (5)$$

where  $A_0$  is the empirical maximum muon decay asymmetry,  $A_{\text{KT}}$  and  $A_{\text{BG}}$  are the asymmetries associated with the two signals.

**Figure 4** shows the  $T$  dependencies of  $\Delta$  and  $\nu$  for  $\text{Li}_{0.73}\text{CoO}_2$ . As  $T$  increases from 10 K,  $\Delta$  slightly but linearly decreases until about 150 K, then decreases more rapidly up to 200 K, and levels off around 2.3 Oe up to 250 K, then, finally rapidly decreases again above 250 K. Making comparison with the line width of Li-NMR for  $\text{Li}_{0.6}\text{CoO}_2$ <sup>(24)</sup> and neutron diffraction measurements on  $\text{Na}_{0.7}\text{CoO}_2$ <sup>(25)</sup> it is found that  $\text{Li}^+$  ions start to diffuse along the  $a$ -axis above around 150 K ( $= T_{\text{diffu}}^{\text{1D}}$ ), whereas in the  $ab$ -plane above 275 K ( $= T_{\text{diffu}}^{\text{2D}}$ ). In fact, the ZF spectrum above 275 K shows a simple exponential decay (Fig. 3). On the other hand, the  $\nu(T)$  curve is almost  $T$ -independent up to 150 K, starts to increase at about 150 K, and exhibits a maximum at 275 K. Above 275 K, although



**Fig. 3** ZF- $\mu^+\text{SR}$  spectra for  $\text{Li}_{0.73}\text{CoO}_2$  measured at 100, 225, and 275 K. Solid lines represent the fit result using Eq. (5).

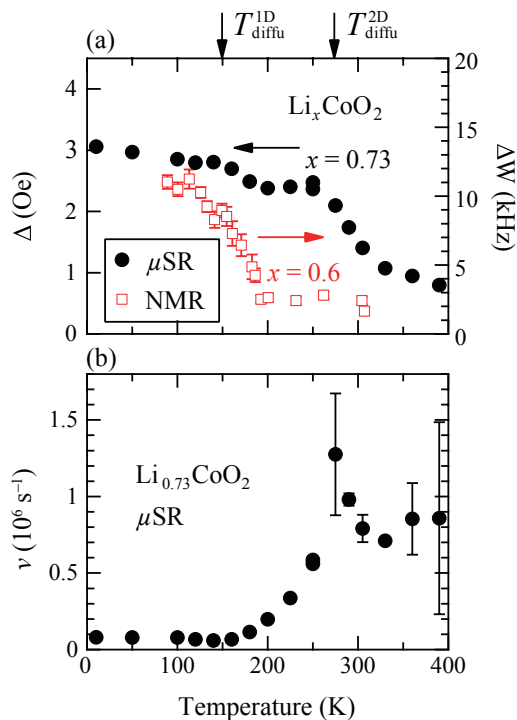
$\nu$  is likely to decrease down to  $0.7 \times 10^6 \text{ s}^{-1}$  at about 325 K, it is very difficult to estimate  $\nu$  accurately because of the fact that  $\nu \gg \Delta$ . The increase in  $\nu$  between 150 and 275 K is well explained by a thermal activation process (not shown),<sup>(9)</sup> which signals the onset of diffusive motion of  $\text{Li}^+$ .

Using a simple diffusion model through vacant Li sites,<sup>(29)</sup>  $D_{\text{Li}}$  was easily estimated as a function of the Li content  $x$  (see **Fig. 5(a)**). And, such  $D_{\text{Li}}$  is found to be more consistent with the prediction from first principles calculations<sup>(28)</sup> than  $D_{\text{Li}}$  estimated from Li-NMR, as expected. A very similar experiment on  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ <sup>(14,27)</sup> demonstrated that  $D_{\text{Li}}$  for  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$  is lower than  $D_{\text{Li}}$  for  $\text{Li}_x\text{CoO}_2$  by one order of magnitude in the whole  $x$  range measured (Fig. 5(b)). We also estimated  $D_{\text{Li}}$  for  $\text{LiNiO}_2$ ,<sup>(10)</sup>  $\text{LiFePO}_4$ ,<sup>(11)</sup>  $\text{LiCoPO}_4$ ,<sup>(12)</sup>  $\text{LiNiPO}_4$ ,<sup>(12)</sup> and  $\text{Li}_2\text{MnO}_3$ <sup>(13)</sup> with  $\mu^+\text{SR}$ .

Furthermore, the following properties have been obtained from  $D_{\text{Li}}$  estimated with  $\mu^+\text{SR}$ ;

(i) Reactive surface area<sup>(14)</sup>

When  $D_{\text{Li}}$  is clarified, a reactive surface area ( $A$ ) of a positive electrode in a liquid electrolyte is obtained by



**Fig. 4** The temperature dependences of (a) the field distribution width ( $\Delta$ ) and (b) the field fluctuation rate ( $\nu$ ) obtained with  $\mu^+\text{SR}$ . In (a), the line width ( $\Delta W$ ) obtained by Li-NMR<sup>(24)</sup> is also plotted for comparison.

comparison with  $D_{\text{Li}}^{\text{EC}}$  extracted from electrochemical measurements in a liquid electrolyte. Namely,  $D_{\text{Li}}^{\text{EC}}$  is known to be proportional to  $A^{-2}$ , although  $A$  was not clarified so far. However, if we assume that  $D_{\text{Li}} = D_{\text{Li}}^{\text{EC}}$ , we obtain correct  $A$ , as in the case for  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ .<sup>(14)</sup>

(ii) Carrier density, i.e. mobile Li content<sup>(30)</sup>

For ionic conductors, the relationship between  $D$  and ionic conductivity ( $\sigma$ ) is represented by a Nernst-Einstein equation;

$$D = \frac{\sigma RT}{nF^2 z^2}, \quad (6)$$

where  $R$  is the gas constant,  $F$  is the Faraday's constant,  $z$  is ionic valence, and  $n$  is the density of

mobile ions. Therefore, if we measure  $D_{\text{Li}}$  and  $\sigma_{\text{Li}}$  for  $\text{Li}^+$  ionic conductors, we can estimate the number density of the mobile  $\text{Li}^+$  ions, as in the case for garnet-type oxides,  $\text{Li}_{5+x}\text{La}_3\text{Zr}_x\text{Nb}_{2-x}\text{O}_{12}$  with  $x = 0-2$ .<sup>(30)</sup>

(iii) Diffusion pathway<sup>(13)</sup>

When  $\text{Li}^+$  ions start to diffuse very rapidly above  $T_{\text{diffu}}$ , the nuclear magnetic field of such  $\text{Li}^+$  becomes invisible by  $\mu^+\text{SR}$ , resulting in a step-like decrease in  $\Delta$  above  $T_{\text{diffu}}$ , i.e. so-called a motional narrowing behavior (see Fig. 4(a)).

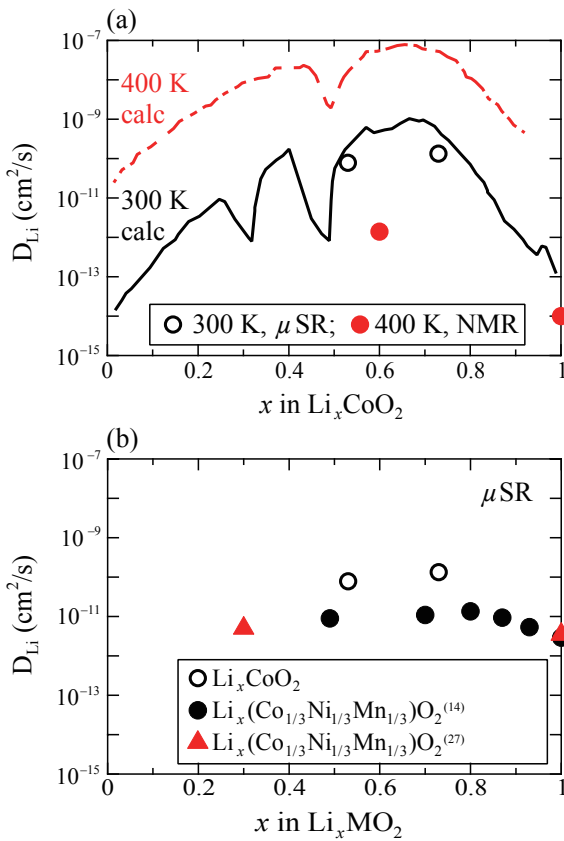
When there are multiple Li sites in the lattice, and some of them are diffusing, whereas the rest static, we can determine the Li sites responsible for Li-diffusion. As a result, we could determine the diffusion pathway, as in the case for  $\text{Li}_2\text{MnO}_3$ .<sup>(13)</sup>

(iv) Diffusion coefficient of Na ( $D_{\text{Na}}$ )<sup>(16,31)</sup>

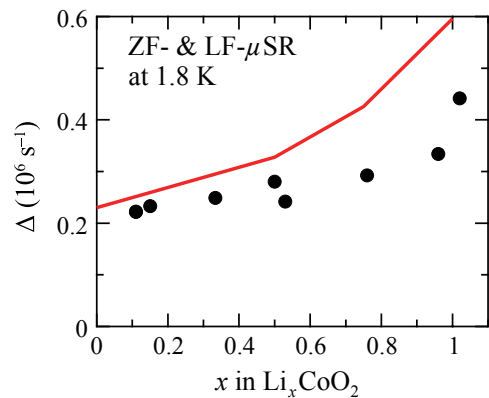
Not only Li-diffusion but also Na-diffusion is observed in  $\text{Na}_x\text{CoO}_2$ <sup>(16)</sup> and  $\text{Na}_x\text{FePO}_4$ ,<sup>(31)</sup> because  $^{28}\text{Na}$  has a nuclear magnetic moment as well as Li.

(v) Concentration of Li and Na

In a paramagnetic state, the field distribution width at the muon site ( $\Delta$ ) is determined by the dipole field created by nuclear magnetic moments, including  $^6\text{Li}$  and  $^7\text{Li}$ . In fact,  $\Delta$  increases with the Li content ( $x$ ) in  $\text{Li}_x\text{CoO}_2$  (see Fig. 6).<sup>(8)</sup> A very similar relationship between  $\Delta$  and  $x$  was also obtained for  $\text{Na}_x\text{CoO}_2$ . This means that we could deduce the Li and Na content from  $\Delta$ . Such measurements would become significant for the future solid state batteries, particularly at the interface between electrode and electrolyte, when  $\mu^+\text{SR}$  has a good depth resolution (see Section 5).



**Fig. 5** The relationship between  $D_{\text{Li}}$  and  $x$  in (a)  $\text{Li}_x\text{CoO}_2$  estimated by  $\mu^+\text{SR}$ <sup>(9)</sup> and Li-NMR<sup>(24,26)</sup> and (b)  $\text{Li}_x\text{CoO}_2$ <sup>(9)</sup> and  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ <sup>(14,27)</sup> estimated by  $\mu^+\text{SR}$ . In (a), solid line represents the predictions by  $\mu^+\text{SR}$ . In (a), solid line represents the predictions by first-principles calculations<sup>(28)</sup> at  $T = 300$  K for  $\text{Li}_x\text{CoO}_2$ , when the effective vibration frequency is a typical value ( $10^{13} \text{ s}^{-1}$ ). Sharp minima in the predicted curve (at  $x = 1/3$  and  $1/2$ ) are caused by Li-ordering.



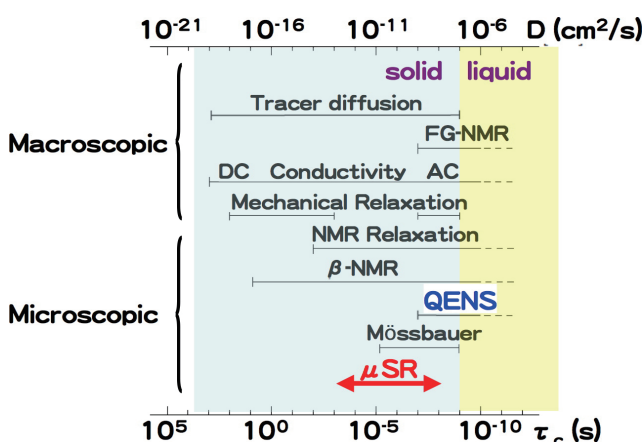
**Fig. 6** The relationship between  $\Delta$  and  $x$  in  $\text{Li}_x\text{CoO}_2$  at 1.8 K.<sup>(8)</sup> A solid line represents the prediction by dipole field calculations.



## 5. Summary and Future

We wish to compare  $\mu^+$ SR with the other techniques for detecting  $D_{\text{Li}}$  from a viewpoint of time window<sup>(5)</sup> (see Fig. 7). Here,  $D_{\text{Li}}$  for positive and negative electrode materials of the Li-ion battery are expected to range between  $10^{-12}$  and  $10^{-9}$  cm<sup>2</sup>/s. Furthermore, it is extremely difficult to measure  $D_{\text{Li}}$  by Li-NMR in the materials containing magnetic ions. Therefore,  $\mu^+$ SR is a very good complementary technique to quasi-elastic neutron scattering (QENS) in the research of Li-diffusion in solids.

For future investigations, we find a particularly interesting and versatile development using a  $\mu^+$ SR technique in combination with the unique low-energy muon available at the Paul Scherrer Institute (PSI) in Switzerland<sup>(32)</sup> or the upcoming ultra-slow muon (USM) at J-PARC in Japan.<sup>(33)</sup> With this technique, it is possible to tune the kinetic energy of the muons i.e. their implantation depth (1-250 nm) into the sample. As a result, it is possible to perform depth resolved studies of ion diffusion and to clarify both the effects of reduced dimensionality (nano) in the form of ultra-thin films, but also to study each of the individual components as well as their interfaces of an operational thin film solid state battery. There is no other technique currently available that allows for such studies and it is our estimate that  $\mu^+$ SR/LEM/USM will become crucial tools for materials development of future solid state energy devices.



**Fig. 7** The time range of  $\mu^+$ SR is added to the typical ranges of a diffusion coefficient ( $D$ ) and motional correlation time ( $\tau_c$ ) of some macroscopic and microscopic methods.<sup>(5)</sup>

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Figs. 1, 2 and 7

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Fig. 3

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Figs. 4 and 5(a)

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Fig. 6

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Sections 2 and 4

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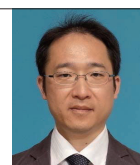
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