

# Na diffusion in $\text{Na}_x\text{CoO}_2$ prepared with an electrochemical reaction technique (2017A0190)

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## 1. Introduction

Lithium-ion batteries have become a leading part as a power storage device for portable electronics and electric vehicles. Nevertheless, due to uneven distribution of lithium resources in the world and future demand for Li-ion batteries in hybrid and electric vehicles, sodium-ion batteries would be one of the significant alternatives for the Li-ion batteries [1], since Na is more abundant than Li. Here, diffusion of  $\text{Na}^+$  ions in solids is a basic principle behind the operation of Na-ion batteries, as in the case of Li-diffusion for Li-ion batteries. Here,  $\mu^+$ SR is known to provide reasonable  $D_{\text{Li}}$  for  $\text{Li}_x\text{CoO}_2$  [2],  $\text{LiNiO}_2$  [3],  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$  [4], and  $\text{LiMPO}_4$  [5]. This situation should be the same for Na-diffusion in solids [6].

In fact, we measured  $\mu^+$ SR spectra for  $\text{Na}_{0.7}\text{CoO}_2$ , which was prepared by a solid-state reaction technique, at high temperatures and found that the field fluctuation rate ( $\nu$ ) starts to increase at a certain temperature, above which the spin-lattice relaxation rate of Na-NMR also starts to increase [7]. Such behavior is also consistent with the result of a neutron scattering experiment [8]. For  $\text{Na}_{0.5}\text{CoO}_2$ , a diffusive behavior was suppressed until  $\sim 400$  K by a Na-ordering [9], as expected, but  $\nu$  starts to increase with  $T$  above  $\sim 400$  K, above which electron diffraction observations indicate the occurrence of displacement of the  $\text{Na}^+$  ions [9]. This also confirms the power of  $\mu^+$ SR for detecting  $D_{\text{Na}}$  in solids.

Recently, R. Berthelot and coworkers [10] reported another way to prepare  $\text{Na}_x\text{CoO}_2$  samples with wide  $x$  range. That is, an electrochemical reaction between Na and  $\text{Na}_{0.7}\text{CoO}_2$  in a  $\text{NaClO}_4$  electrolyte (1M PC solution). As a result, the stable phase of NCO was found to be  $x = 1/2, 4/7, 2/3, 0.72, 0.76, 0.79,$  and  $0.85$ . On the contrary, the samples with the other compositions are, more or less, a mixture of two phases.

This leads to a question on the reliability of the past measurements for the samples prepared by a solid-state reaction technique. We have, therefore, re-measured  $D_{\text{Na}}$  in the  $\text{Na}_x\text{CoO}_2$  samples prepared by an electrochemical reaction.

## 2. Experiment

Two  $\text{Na}_x\text{CoO}_2$  samples with  $x = 0.33$  and  $0.85$  were prepared by the above-mentioned electrochemical reaction in CNRS-Bordeaux. Since the samples are very sensitive to moisture in air, they were packed in a Ti cell in an Ar filled glove-box. The Ti cell has a Ti window with the diameter of 10 mm and was sealed with gold O-ring. The Ti cell was then set into a cryo-furnace on the S1 muon beamline. The  $\mu^+$ SR spectra were measured in zero field (ZF), weak transverse field (wTF) and longitudinal field (LF) in the temperature range between 50 and 500 K. All the  $\mu^+$ SR data were analyzed with **musrfit**.

## 3. Results

Figure 1 shows the variation of the ZF- and LF- $\mu^+$ SR spectra for  $\text{Na}_{0.33}\text{CoO}_2$  with temperature. The ZF- $\mu^+$ SR spectrum at 150 K exhibits a typical static Kubo-Toyabe (KT) relaxation. Indeed, the applied LF with 10 Oe almost suppresses (decouples) the relaxation, meaning that a random field distribution width is comparable to 10 Oe. This indicates that the KT behavior is caused by a nuclear magnetic field formed by  $I = 3/2$  of  $^{23}\text{Na}$  and  $I = 7/2$  of  $^{59}\text{Co}$ . As temperature increases from 150 K, the ZF spectrum becomes dynamic due to Na diffusion. The

ZF-, wTF, and LF- $\mu^+$ SR spectra were fitted with a combination of a KT signal, an exponential relaxation signal, and a time-independent background signal. Such fit provided the field distribution width ( $\Delta$ ) and the field fluctuation rate ( $\nu$ ), which directly lead to  $D_{\text{Na}}$ .

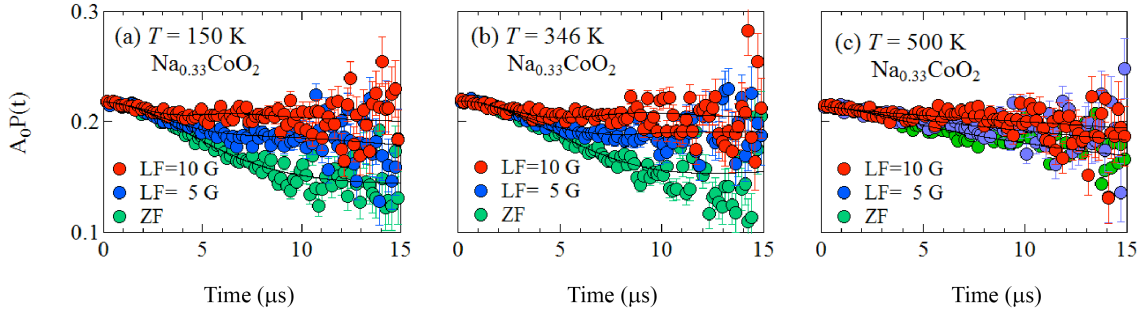


Fig. 1 ZF- and LF- $\mu^+$ SR spectra for  $\text{Na}_{0.33}\text{CoO}_2$  recorded at (a) 150, (b) 346, and (c) 500 K.

Figure 2 shows the relationship between  $D_{\text{Na}}$  and the Na content ( $x$ ) at 300, 350, and 400 K using the present result for  $x = 0.33$  and 0.85 together with the previous data obtained for the chemically prepared samples. Although  $D_{\text{Na}}$  is strongly affected by chemical order particularly at  $x = 0.5$ ,  $D_{\text{Na}}$  is most likely to exhibit a maximum at  $x \sim 0.8$ . This is consistent with the result of  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$  [2,4].

#### 4. Conclusion

We have found that  $D_{\text{Na}}$  changes with the Na content ( $x$ ) and temperature in  $\text{Na}_x\text{CoO}_2$ . This would affect the total performance of the Na-ion battery using  $\text{Na}_x\text{CoO}_2$ .

Therefore, we need additional experiments for the samples with  $x > 0.8$ .

#### References

- [1] S. P. Ong et al., Energy Environ. Sci. **4**, 3680 (2011).
- [2] J. Sugiyama et al., Phys. Rev. Lett. **103**, 147601 (2009).
- [3] J. Sugiyama et al., Phys. Rev. B **82**, 224412 (2010).
- [4] J. Sugiyama et al., Phys. Chem. Chem. Phys. **15**, 10402 (2013).
- [5] J. Sugiyama et al., Phys. Rev. B **84**, 054430 (2011); *ibid* **85**, 054111 (2012).
- [6] M. Mansson and J. Sugiyama, Physics Scripta **88**, 068509 (2013).
- [7] J.L.Gavilano et al., Phys. Rev. B **69**, 100404(R) (2004).
- [8] H. W. Zandbergen et al., Phys. Rev. B **70**, 024101 (2004); Q. Huang et al., Phys. Rev. B **70**, 184110 (2004).
- [9] H. X. Yang et al., Solid State Commun. **134**, 403 (2005).
- [10] R. Berthelot, D. Carrier, and C. Delmas, Nature Materials **10**, 74 (2011).

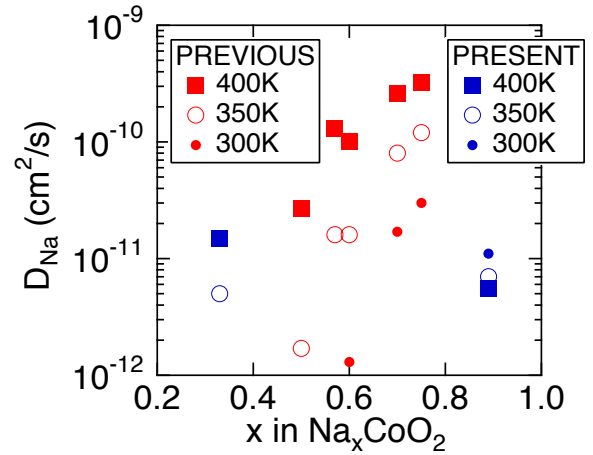


Fig. 2 The relationship between  $D_{\text{Na}}$  and the Na content ( $x$ ) in  $\text{Na}_x\text{CoO}_2$ . For the  $x=0.85$  sample, Na is most likely to be static even at 400 K, for reasons currently unknown.