

Na diffusion in Na_xCoO_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 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, μ^+ SR is known to provide reasonable D_{Li} for Li_xCoO_2 [2], LiNiO_2 [3], $\text{Li}_x(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ [4], and LiMPO_4 [5]. This situation should be the same for Na-diffusion in solids [6].

In fact, we measured μ^+ 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 (ν) 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 ~ 400 K by a Na-ordering [9], as expected, but ν starts to increase with T above ~ 400 K, above which electron diffraction observations indicate the occurrence of displacement of the Na^+ ions [9]. This also confirms the power of μ^+ SR for detecting D_{Na} in solids.

Recently, R. Berthelot and coworkers [10] reported another way to prepare Na_xCoO_2 samples with wide x range. That is, an electrochemical reaction between Na and $\text{Na}_{0.7}\text{CoO}_2$ in a 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_{Na} in the Na_xCoO_2 samples prepared by an electrochemical reaction.

2. Experiment

Two Na_xCoO_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 μ^+ 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 μ^+ SR data were analyzed with **musrfit**.

3. Results

Figure 1 shows the variation of the ZF- and LF- μ^+ SR spectra for $\text{Na}_{0.33}\text{CoO}_2$ with temperature. The ZF- μ^+ 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}Na and $I = 7/2$ of ^{59}Co . As temperature increases from 150 K, the ZF spectrum becomes dynamic due to Na diffusion. The

ZF-, wTF, and LF- μ^+ 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 (Δ) and the field fluctuation rate (ν), which directly lead to D_{Na} .

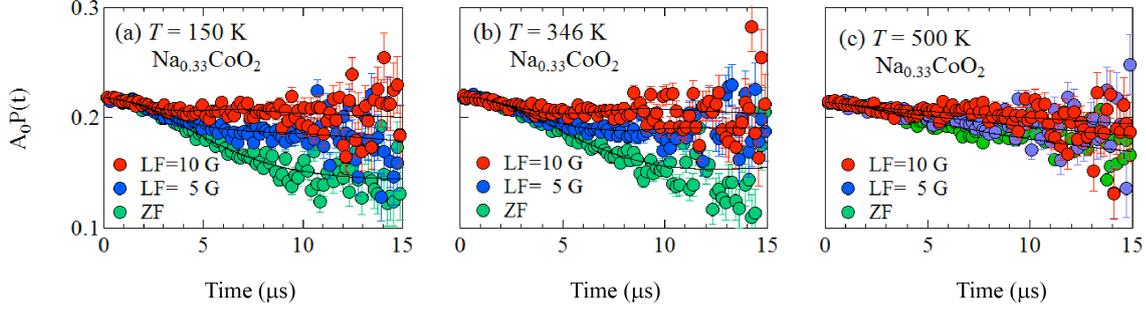


Fig. 1 ZF- and LF- μ^+ SR spectra for $\text{Na}_{0.33}\text{CoO}_2$ recorded at (a) 150, (b) 346, and (c) 500 K.

Figure 2 shows the relationship between D_{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_{Na} is strongly affected by chemical order particularly at $x = 0.5$, D_{Na} is most likely to exhibit a maximum at $x \sim 0.8$. This is consistent with the result of Li_xCoO_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_{Na} changes with the Na content (x) and temperature in Na_xCoO_2 . This would affect the total performance of the Na-ion battery using Na_xCoO_2 .

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

References

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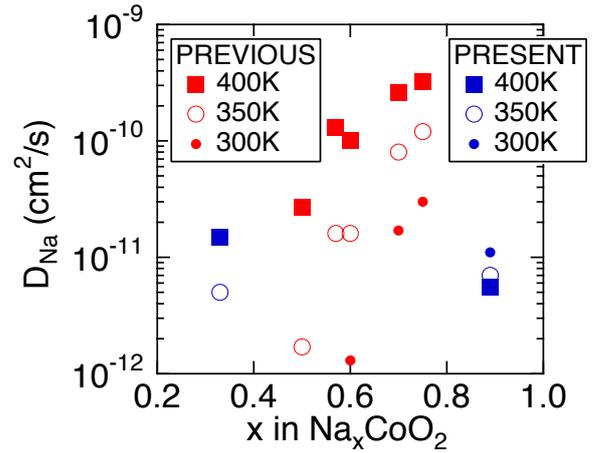


Fig. 2 The relationship between D_{Na} and the Na content (x) in Na_xCoO_2 . For the $x=0.85$ sample, Na is most likely to be static even at 400 K, for reasons currently unknown.