Effect of milling process on local structure and lithium ion dynamics in lithium tantalate and lithium niobate

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Lithium transition-metal oxides have driven intensive studies in the field of solid state ionics in the past few decades. In special, many lithium transition-metal oxides such as $LiCoO_2$ and $LiNiO_2$ have been studied to use as the positive electrode for lithium secondary batteries. It is well known that in the charge/discharge process, $LiCoO_2$ and $LiNiO_2$ exhibit a complicated phase transition with decreasing lithium content. It is strongly connected with the Li^+ ion conduction in delithiated $LiCoO_2$ and $LiNiO_2$.

On the other hand, it is known that Li^+ ions diffuse with a high activation energy of around 1.5 eV at high temperatures in single crystalline samples of piezoelectric oxides, $LiMO_3$ (M=Nb, Ta) [1,2]. In $LiNbO_3$, the motional narrowing in ^7Li NMR spectra arising from the Li^+ ionic diffusion was observed in amorphous and fine particles of $LiNbO_3$. The ionic diffusion is dependent strongly on local changes in the crystal structure of $LiNbO_3$, and the activation energy for ionic diffusion becomes lower with structural changes caused by mechanical force [3-5], while structural changes due to milling degrades electrochemical performance in $LiCoO_2$ and $LiNiO_2$ [6,7]. Thus, the Li^+ ion dynamics is strongly related to the structural changes in Li^+ ion conductors. In this study, we discuss milling effects on structural changes and ion dynamics in $LiMO_3$ (M=Ta, Nb) prepared by ball milling method from results of NMR, electrical resistivity, and X-ray diffraction measurements.

Polycrystalline $LiNbO_3$ (p-LNO) and congruent single crystalline samples of $LiTaO_3$ (c-LTO) and $LiNbO_3$ (c-LNO) were used as starting materials. Ball milling was carried out using a planetary ball milling machine premium line P-7 (Fritsch Co.), and a P-6 (Fritsch Co.) also was used for milling p-$LiNbO_3$. MAS- and static-NMR spectra of ^7Li nucleus were measured using a Bruker Avance 300wb spectrometer at 116.4 MHz. Complex impedance measurements were performed using a computer-controlled HP-4192A in the frequency range from 50 Hz to 5 MHz and the temperature range of 300 to 500 K.

Fig. 1 shows ^7Li static NMR spectra of c-LTO and c-LNO. Broad shoulders lying at both sides of the central line get smeared out with increasing milling time. In milled samples, a narrow line appears in the broad central line and grows up at around 0 ppm with increasing milling time. The narrow line is attributed to mobile Li^+ ions, while the broad one is attributed to immobile Li^+ ones in the rigid lattice. Such an increase in the narrow line area means that the number of mobile Li^+ ions increases with increasing milling time. The number of mobile Li^+ ions in c-LNO is relatively larger than that in c-LTO as shown in Fig. 2. The shoulders of c-LNO become smaller than those of c-LTO with increasing milling time. This indicates that a larger distribution of the electric field gradient is caused by an increase in imperfections such as defects and lattice disorder induced

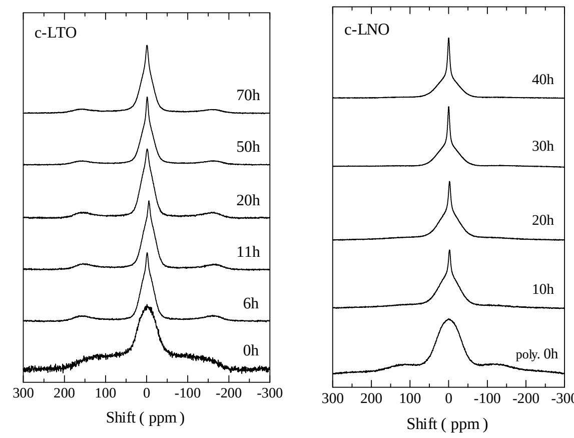

Fig. 1. ^7Li static NMR spectra of c-LTO and c-LNO samples milled for different milling times.

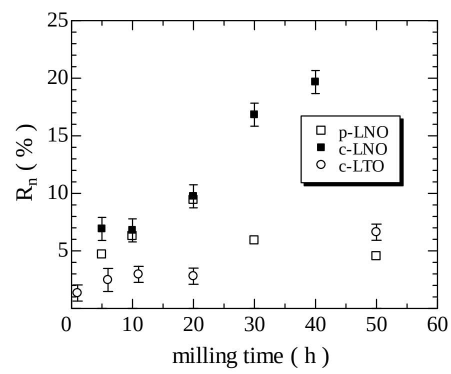

Fig. 2. Ratio of the narrow line area to the total line one of LTO and LNO.

by milling in LNO. The small activation energy of around 0.3 eV was evaluated from the temperature dependence of electrical resistivity in the milled LTO. These results suggest that the local structure of the milled samples is disordered and the effective activation energy is largely depressed.

The induced imperfections give different milling effect on local structure and ion diffusion in the milled LTO and LNO. Easier disruption in crystal structure would occur in the milled LNO in comparison to the milled LTO, although LTO is isostructure crystal of LNO.

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