

Local Chemical Ordering in Li₃NbO₄-Based Positive Electrode Material with Disordered Rock Salt Structure

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As is well known, lithium transition-metal oxides with the layered rock salt structure, such as LiCoO₂, have been used as a positive electrode material of the lithium-ion battery in last few decades, whereas similar oxides with the “disordered” rock salt structure have been believed not to be able to act as the positive electrode since they seem not to have Li⁺ diffusion path apparently. In recent years, however, some of “lithium-rich” transition-metal oxides with the “disordered” rock salt structure have come to draw much attention because of the high discharge capacities around 250 mAh g⁻¹ with high coulombic efficiencies. From such background, many research groups have devoted their efforts to investigate electronic structures of the materials, and then have tried to interpret their electrochemical properties from the viewpoint of electronic structures, especially electronic states of oxygens. However, atomic configurations of the materials have not been clarified yet since it is quite difficult to visualize the “disordered” average structures.

In this work, we focus on a Li₃NbO₄-based oxide, i. e. Li_{1.3}Nb_{0.3}Fe_{0.4}O₂, as an example of the positive electrode materials with the disordered rock salt structure [1], and investigate an atomic configuration of the oxide by the pair distribution function (PDF) analysis in the same way as our previous work on LiNi_{0.5}Mn_{0.5}O₂ [2]. On the basis of the analytical result, we try to reveal local chemical ordering underneath the apparent disordered structure of Li_{1.3}Nb_{0.3}Fe_{0.4}O₂.

The sample with the disordered average structure (S. G.: *Fm-3m*) was prepared by a conventional solid-state reaction method according to the previous work [1]. A metal composition of the synthesized oxide was determined by an ICP spectroscopy. In order to uncover local chemical ordering in the sample, we performed a neutron total scattering measurement with NOVA installed at J-PARC, Japan. We also measured X-ray diffraction/total scattering patterns with BL19B2 and BL04B2 at SPring-8, Japan. By using all the collected data simultaneously, we conducted the reverse Monte Carlo (RMC) modelling using a RMCProfile program [3] and then analyzed the atomic-configuration snapshot.

Figure 1 shows a part of results of the RMC simulation. As can be seen, all the experimental data can be explained well by the simulation. From the obtained atomic-configuration snapshot, we analyzed a coordination environment around each cation. As a result, it is found that Nb⁵⁺ tends to be surrounded by a cation with lower valence, i. e. Li⁺, in the disordered average structure.

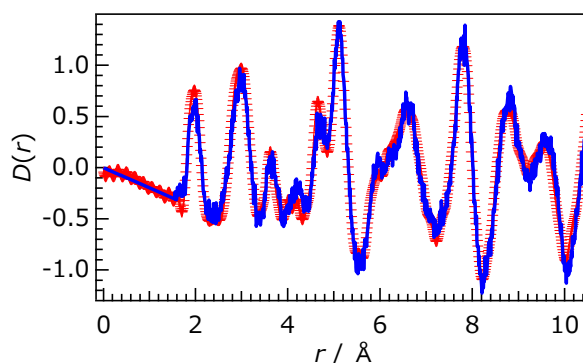


Fig. 1 Neutron $D(r)$ of Li_{1.3}Nb_{0.3}Fe_{0.4}O₂. The red marks and the blue solid line represent the experimental data and the RMC model, respectively.

References: [1] N. Yabuuchi et al., *Proc. Natl. Acad. Sci. USA*, **112** (2015) 7650. [2] N. Kitamura et al., *Electrochemistry*, **84** (2016) 789. [3] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin, Q. Hui, *J. Phys.: Condens. Matter*, **19** (2007) 335218.