Advanced neutron diffraction researches on the NCM electrode and oxide-based solid-state electrolyte materials for rechargeable batteries

Korea Atomic Energy Research Institute, Seongsu Lee

1. Introduction

Neutron diffraction techniques have been widely used to investigate the crystal and magnetic structure of energy storage materials which are composed of light elements (i.e. H, Li, Na, O). Because neutron interacts with the atomic nucleus, coherent neutron scattering length does not depend on the atomic number, so, the response of neutrons from light elements is much higher than X-rays. Furthermore, quantitative analysis on neighborhood elements in the periodic table such as Mn, Fe, Co, and Ni is comparably easy.

In this research, we discovered atomic position and ionic conduction mechanism of Li in oxide-based solid-state electrolyte materials (i.e. $Li_{7-x}Al_xLa_3Zr_{1.9}Ta_{0.1}O_{12}$ (LLZO)) series by using neutron diffraction and bond valence sum energy landscape. Also, the atomic migration of Li and transition metals (Ni, Co, Mn) in $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) upon charge/discharge was investigated. A large amount of powder samples (2~3g) were measured and analyzed. We believe that neutron diffraction studies on electrode and solid state electrolyte materials will give a hint to understand electrochemical properties of battery materials and give a way to design new promising energy storage materials.

2. Experiment

We measured $Li_{6.7}Al_{0.3}La_3Zr_2O_{12}$ and $Li_{6.9}Al_{0.3}La_3Zr_{1.9}Ta_{0.1}O_{12}$ powder samples and W-doped series of $Li_xNi_{0.88}Co_{0.095}Mn_{0.025}Al_{0.005}O_2$ (4 samples) at room temperature by using SuperHRPD in J-PARC. Neutron diffraction data were analyzed by Z-Rietveld and Fullprof program (Bondstr) to investigate atomic position and Li conduction mechanisms.

Planned experiment:

Beamtime limit: SuperHRPD (measurement time of 2hour for NCM samples (#2), 5hour for LLZO (#2) and LATP (#2) samples; total 24 hours) / NOVA (measurement time of 6hour for LSTP (#2) samples; total 12 hours)

Due to the crystallinity and the limit of the beamtime, we conducted neutron diffraction experiment on 4 samples of NCM and 2 samples of LLZO.

3. Results

i) Neutron diffraction analysis on LLZO samples

Structural characterization of LLZO neutron diffraction data were conducted by Z-Rietveld program. Atomic sites and occupancies of each atom were investigated, and especially, partially occupied Li atoms in the lattice were carefully analyzed. We discover that Ta doped LLZO sample has expended Li diffusion channel compared to as-prepared LLZO. We conducted bond valence sum energy landscape analysis to ensure the expanded Li channel with low activation energy (est.) and visualize Li conduction pathes as shown in Figure 1. The analyzed data is under preparation of the manuscript and will be published soon in SCI journals.

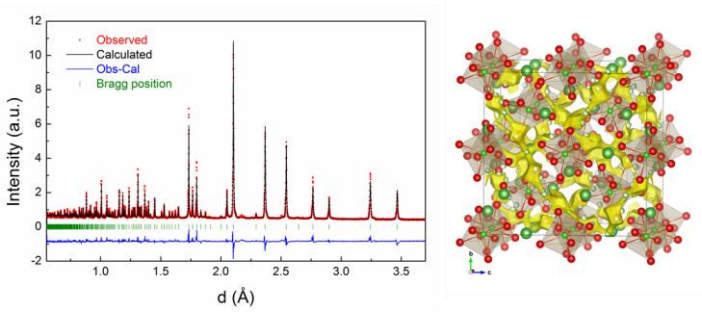

Figure 1. Rieveld refinement of neutron diffraction patterns of Ta doped LLZO sample

ii) Neutron diffraction studies on Ni-rich NCM materials

To investigate transition and Li migration in Ni-rich NCM electrode materials, structural characterization of NCM series of neutron diffraction data were conducted by Z-Rietveld program. Ni migration from transition metal layer to Li layer was confirmed from neutron diffraction analyses, and we found that only ~1% of Ni migrate into Li layer as shown in Figure 1 and 2. W doping enhances structural stability upon electrochemical cycling and the the analyzed data is under preparation of the manuscript and will be published soon in SCI journals.

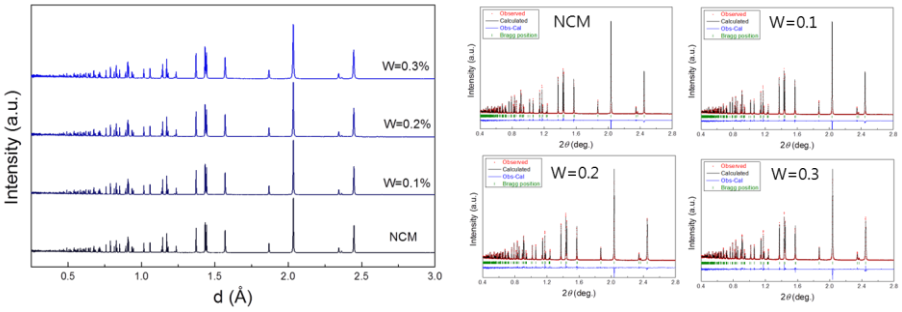

Figure 2. Rieveld refinement of neutron diffraction patterns of NCM series

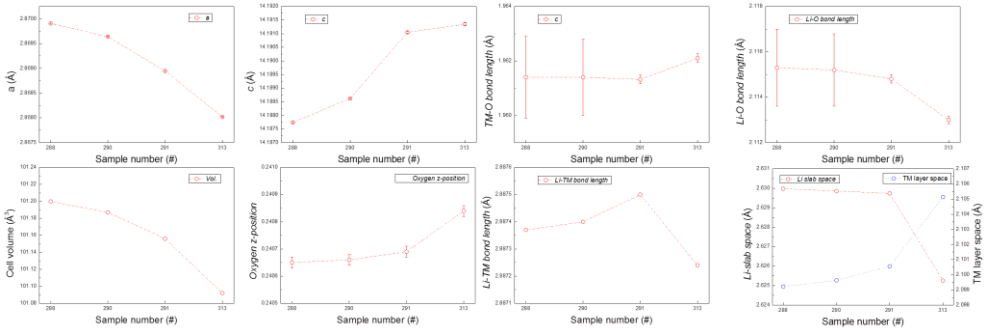

Figure 3. Structural information from Rieveld refinement of neutron diffraction patterns of NCM series

4. Conclusion

In summary, we conducted neutron diffraction experiment in SuperHPRD in J-PARC to investigate detailed structure of LLZO solid electrolyte and NCM electrode materials. We found the clues of the enhanced electrochemical properties of doped samples of electrodes and solid-state electrolyte materials compared to as-prepared samples by Rietveld refinement. We believe that these results can give a hint to develop better next generation energy storage materials for rechargeable batteries.