Average and Local Structure Change of $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ during First Discharge Process depend on Operating Temperature

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Recent years, applications of lithium ion secondary batteries have expanded, and thus it is required to improve energy density of batteries. In this regard, the solid solutions of Li_2MnO_3 and $LiMO_2$(M= Mn, Ni, Co) have attracted attention over the years because they deliver high discharge capacity of over 200 mAh/g. In our laboratory, we have focused on xLi_2MnO_3-$(1-x)LiMO_2$(M= Mn, Ni, Co) with x=0.4 and 0.5 because of the good electrochemical performance, and then performed average and local crystal structure analysis on the materials[1),2)]. However, the influence of operating temperature has not been studied. The present study investigated the temperature dependence of the average and local structure of $0.4Li_2MnO_3$-$0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ electrodes during the first discharge cycle, using neutron and synchrotron X-ray diffraction and total scatterings. In addition, the electrode by TEM, STEM/EDS and SAED were observed and compared the result with those of the crystal structure analysis, and examined the structural changes of the particle surface and inside.

Sample was synthesized by co-precipitation method. From the XRD data, it was found that a product can be attributed to a single phase of the layered structure with *C*2/*m*. In the cycle tests at room and high temperatures at 60 ºC, it was found that at 60°C, a capacity of more than 280 mAh/g could be achieved at a voltage of 2.5-4.8 V vs. Li/Li^+, which was larger than the capacity at room temperature. To clarify the reason for this, an analysis was carried out based on the pair distribution function for electrodes following their first charge and discharge cycles, and examined the average structure by Rietveld technique using neutron diffraction measurements at BL20, J-PARC and synchrotron X-ray diffraction measurements at BL02B2, BL19B2, SPring-8. As a result, it was found that the ordering of the transition metal might be changed by the operating temperature and Ni cation mixing might be increased at 60°C. We also investigated the cation-distribution uniformity within the particle by STEM/EDS, and confirmed that there was not significant variation in the cation distribution. In addition, we constructed local structure models by extending the refined unit cell, and then analyzed the local structure by PDF technique using neutron total scattering measurements at BL21, J-PARC and synchrotron X-ray total scattering measurements at BL04B2, SPring-8. The results showed a unique distortion of Ni-O_6 octahedra at higher temperature. In addition, an analysis using XAFS spectroscopy indicated a change in valence during charging and discharging based on a shift in the position of peaks associated with Mn, Ni, and Co. At 60°C, the shift was particularly large for the Ni peak. Thus, the operating temperature can have a large effect on the behavior of especially Ni, which can influence the battery characteristics.

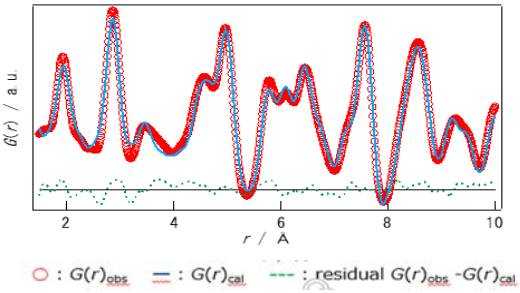

Fig. 1 PDF analysis of discharged sample at 2.5V in first discharge process using synchrotron X-ray total scattering data at 60ºC.

References:

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[2] Y. Idemoto, T. Sekine, N. Ishida N. Kitamura, *J. Materials Science*, **52**,(2017)8630-8649.