First-principles Study of K-edge XANES for Li-rich layered cathode material

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Recent research has focused on the Li-rich solid-solution layered cathode materials Li₂MnO₃-LiMO₂ (M=Co, Ni etc), which exhibit a discharge capacity of more than 200mAh/g when operated above 4.6V. However, the mechanism of the charge-discharge reaction, which is the origin of the discharge capacity, has not been clarified. In order to reveal the change in valence state of transition metals (TM), TM K-edge XANES was measured and it was found that one part of the Mn K-edge moves in the opposite direction of the other parts during charge-discharge, near the inflection point of the spectra. [1] It thus appears to be somewhat complicated to discuss the reaction mechanism from only the experimental results. In this study, we performed first-principles calculations of TM K-edge XANES spectra for Li-rich layered cathode materials and investigated effects of Li-extraction on XANES spectra.

Recently, the computational function of XANES/ELNES spectra has been installed to QMAS (Quantum MAterials Simulator) code [2] based on the first-principles projector augmented-wave (PAW) method. In the calculation of spectra, the core-hole effects are included with the use of excited PAW pseudopotentials, and the threshold energies are calculated as the total energy difference between ground-state and excited-state supercells with the correction term for contributions of core-orbitals. The DFT calculations are performed with GGA+U approach (U_{eff}=5.0 eV for Mn-d).

Li₂MnO₃ belongs to the space group C2/m (No 12) and the experimental structural parameters are a= 4.925, b=8.522, c=5.025, β=109.4. [3] The calculated parameters a= 4.976, b=8.560, c=5.059, β=109.5 are in good agreement with the experimental ones. For the calculation of XANES spectra, 2x1x2 supercell was used in order to reduce an artificial interaction between excited atoms. Figure 1 shows the experimental and theoretical Mn K-edge XANES spectra for bulk Li₂MnO₃ in comparison with MnO₂ and MnO. In the experimental spectrum for Li₂MnO₃, pre-edge peaks, two shoulders A and B, and main peak C can be seen, and the present calculation reproduces those spectral features. Experimental spectra for MnO₂ and MnO are also well reproduced. The estimated threshold energy values are in good agreement with the experimental ones within the difference of 0.3%.

Next, we investigated effects of Li-extraction from Li₂MnO₃ on Mn K-edge spectra. We simulated two cases, extraction of all Li atoms (i) from Mn-rich layers and (ii) from Li layers. In the case of Li-extraction from Mn-rich layers, the intensity of shoulder B increases while apparent changes can not be seen in the other peaks. On the other hand, in the case of Li-extraction from Li-layers, the intensity of shoulder A decreases drastically and the peak C splits into two parts while the intensity of shoulder B does not change. In both cases, spectral changes for shoulder B are smaller than those experimentally observed. Thus, not only atomic relaxations with Li-extractions but also...
phase transitions should be taken into account. We propose the structural changes from 
Mn$^{4+}$ in Li$_2$MnO$_3$ to Mn$^{4+}$ in spinel LiMn$_2$O$_4$.

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References

FIG. 1. Theoretical and experimental Mn K-edge for Li$_2$MnO$_3$ in comparison with MnO and MnO$_2$ [1].