

Mechanism Analysis of Charge-discharge Cathode Reaction with Anion Redox

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New materials for high energy density battery are developed for recent equipment. It was reported that Co-doped Li_2O showed about 450 mAh g^{-1} of reversible capacity [1]. However, Co-doped Li_2O was decomposed when it was overcharged. In this study, we developed Li_5AlO_4 as solid solution of Li_2O and Al_2O_3 for making electrochemical stability of Li_2O higher. Moreover, Li_5AlO_4 was substituted by Co^{3+} using mechanical alloying for enhancing its electroconductivity. As results of electrochemical measurements, it was turned out that Co-doped Li_5AlO_4 showed about 140 mAh g^{-1} of reversible capacity. XAFS measurement was conducted for analyzing the partial structure of Co-doped Li_5AlO_4 at BL-3, 10 and 11 during a charge-discharge cycle test. Fig. 1(a) and (b) show O and Al K-edge XANES spectra of Co-doped Li_5AlO_4 . It was turned out that the shoulder at 528 eV is increased in the charge process in O K-edge XANES spectrum. This is attributed to a redox reaction of oxygen. This result suggests that charge compensation is attained by a redox reaction of oxygen in Co-doped Li_5AlO_4 . Furthermore, the peaks attributed to tetrahedral and hexagonal Al were respectively present at 1565 and 1567 eV in Al K-edge XANES spectra. The peak attributed to hexagonal Al increased after the charge process. This result indicates that charge products of Co-doped Li_5AlO_4 have crystal structure similar to Li_2O_2 . Then after the discharge process, the peak decreased to the same as it in pristine. This result means that the charge-discharge reaction is reversible. Fig. 2(a) and (b) show O and Al K-edge XANES spectra of charged Co-doped Li_5AlO_4 at 1, 2 and 10th cycles. It is turned out that the shoulder attributed to a charge-state of O and the peak assigned to hexagonal Al decreased by cycles in XANES spectra. These results exhibit that charge products become hard to generate during the charge-discharge cycles. Fig. 3 shows pseudo radial distributions of Co in Co-doped Li_5AlO_4 calculated from EXAFS spectra. These results show that partial structure of Co changes every cycle. From these results, capacity degradation of Co-doped Li_5AlO_4 would be caused by decrease in charge-products due to Co-O change during its charge-discharge cycles.

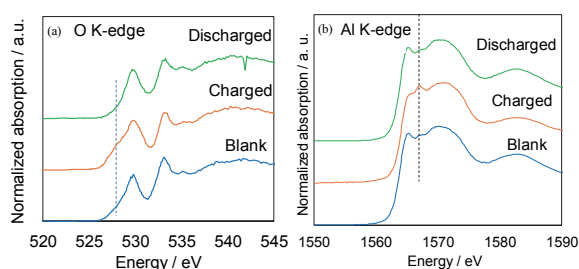


Fig. 1 Observed (a) O and (b) Al K-edge XANES spectra of Co-doped Li_5AlO_4 during charge-discharge cycle.

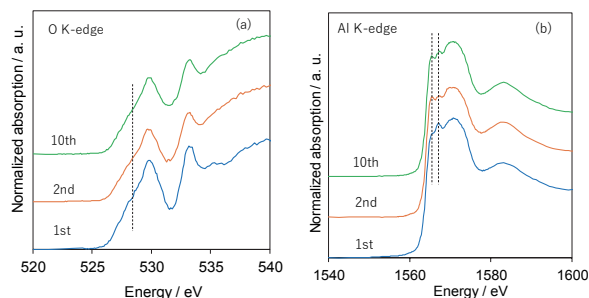


Fig. 2 Observed (a) O, (b) Al K-edge XANES spectra of charged Co-doped Li_5AlO_4 at 1st, 2nd and 10th cycles.

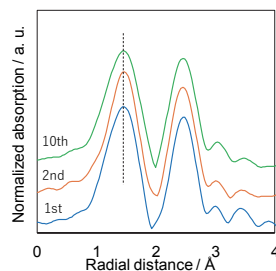


Fig. 3 Observed pseudo radial distribution function of Co in charged Co-doped Li_5AlO_4 at 1st, 2nd and 10th cycles.

References

- [1] H. Kobayashi, M. Hibino, Y. Ogasawara, K. Yamaguchi, T. Kudo, S. Okuoka, K. Yonehara, H. Ono, Y. Sumida, M. Oshima, N. Mizuno J. Power Sources, 306, 567-572 (2016).