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# A Study on Reaction Mechanism of $Li_2MoO_3$ as a Positive Electrode Material for Lithium-ion Batteries by X-ray Absorption Spectroscopy

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## 1 Introduction

Li-rich layered transition metal oxides are promising candidates as high capacity positive electrode materials for Li-ion batteries. However, the operation voltage decreases during cycles, which originates from irreversible structural change from layered to cation-disordered phase. Recently, structure of layered $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ was reported to almost completely changes from layered to a cation-disordered phase at an initial cycle but exhibits reversible capacity of more than 250 mAh $g^{-1}$ even after the irreversible phase transition.[1] In this study, we focus on $Li_2MoO_3$ as an end member of the $Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ solid solution to understand the role of Mo in the electrode performance as a fundamental study. According to the literatures, $Li_2MoO_3$ shows low electric conductivity.[2] To improve the electric conductivity, $Li_2MoO_3$/carbon composite is prepared by mixing and heating with acetylene black. $Li_2MoO_3$ composite with 1 wt% carbon delivered approximately 230 mAh $g^{-1}$ of initial discharge capacity much higher than that of $Li_2MoO_3$ without carbon composite. Reaction mechanism of $Li_2MoO_3$ without carbon composite has been already revealed[3]. In this report, to elucidate reaction mechanism of $Li_2MoO_3$ composite with 1 wt% carbon, we have examined the electric state of Mo in $Li_{2-x}MoO_3$ composite with 1 wt% carbon accompanied by the structural change during charge/discharge by X-ray absorption spectroscopy.

## 2 Experiment

Composite positive electrodes consisted of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVdF). An aluminum foil is used as a current collector. Electrolyte solution used was 1 mol $dm^{-1}$ $LiPF_6$ dissolved in propylene carbonate (Kishida Chemical Co.Ltd., Japan). Electrochemical tests were conducted using R2032-type coin cells with Li metal as a negative electrode. The coin cells were assembled in an Ar-filled glovebox and cycled at a rate of C/20 (16 mAh $g^{-1}$). After the electrochemical tests, composite electrodes were taken out from the cells, and the electrodes were rinsed with diethyl carbonate (DMC) and dried then sealed with a water-resistant polymer film in the Ar-filled glovebox.

## 3 Results and Discussion

*Ex-situ* XANES spectra at Mo K-edge of $Li_2MoO_3$/1 wt% C at various charging and discharging state are shown in Figure 1. Mo K-edge spectra of pristine sample is similar to that of $MoO_2$, suggesting that molybdenum is tetravalent in the pristine sample. Mo K-edge shifts to high energy by charging, reflecting oxidation of molybdenum. And pre-edge peak also appears by charge, which is assigned to an electric dipole transition from *s* to *p* orbital in the O2*p*-Mo4*d* hybridization state derived from the distortion of the $MoO_6$ octahedra or migration of Mo ions from octahedral to tetrahedral sites. Finally, Mo K-edge of fully charged sample to 4.4 V is similar to that of $MoO_3$, suggesting that Mo is oxidized from 4+ to 6+ by Li extraction. During discharge, on the other hand, Mo K-edge shifts back to low energy but does not reach back to that of as-prepared sample and $MoO_2$. Moreover pre-edge peak appeared by charging is still observed after fully discharge to 1.5 V. In conclusion, oxidation of Mo is observed from 4+ to 6+ on charge, but Mo does not reversibly reduces to 4+ on discharge. The irreversible behavior would be not only from irreversible capacity but also irreversible structural change into cubic phase at 1st cycle.

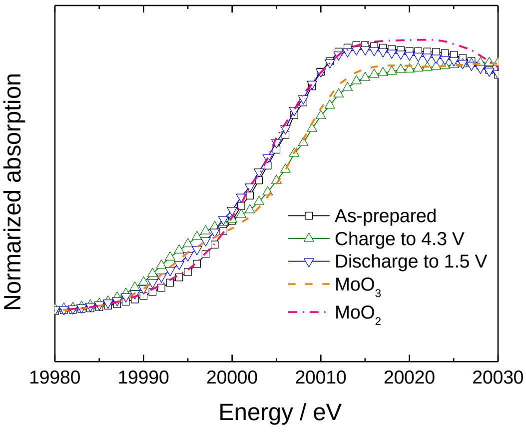

Fig. 1. XANES spectra at Mo K-edge of electrodes for $Li_2MoO_3$/1 wt% C.

## References

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