

Charge Compensation Mechanism of Oxygen Release from Li-ion Battery Cathode Material Li(Ni,Co,Mn)O₂

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High energy density batteries are developing for the wide utilization of renewable energies, the electrification of transportations and the establishment of reliable energy grids [1]. For those applications, developing high energy density and highly reliable cathode materials is one of the most important issues. To develop such advanced cathode materials, it is important to prevent oxygen release from cathode active materials which causes safety problems such as gas generation, heat generation and thermal runaway [2]. Although the oxygen vacancy formation energy and the binding energy of lattice oxygen were calculated based on density functional theory [3, 4], systematic investigations by experimental approaches on oxygen release have not been reported. We recently reported the oxygen release behavior and its influences on electrochemical performance of Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ by coulometric titration technique [5]. In this work, charge compensation during oxygen release from Li(Ni,Co,Mn)O₂ were investigated by the combination of coulometric titration and soft X-ray absorption spectroscopy.

LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (NCM523) was synthesized by solid state reaction route from LiOH·H₂O and the (Ni,Co,Mn)CO₃ precursor prepared by coprecipitation. 2 mol% and 3 mol% oxygen-deficient NCM523 was prepared by using the electrochemical cell composed of the oxide-ion conducting Ytria stabilized zirconia tube [5]. Ni L-, Co L- and Mn L-edge spectra of the oxygen-deficient NCM523 were recorded by total electron yielding, partial electron yielding and (inverse) partial fluorescence yielding modes at BL-11, the SR Center, Ritsumeikan University.

It was confirmed that the 2 mol% and 3 mol% oxygen-deficient NCM523 kept the original layered rock salt structure after the oxygen extraction treatment, meaning that the mechanism of charge compensation due to oxygen release can be discussed from X-ray absorption spectra. Figure 1 shows Ni L_{III}-, Co L_{III}- and Mn L_{III}-edge spectra of the oxygen-deficient NCM523. 1 mol% of oxygen release induced the decrease in the area intensity of higher peak in Ni L_{III}-edge spectra, and the generation of peaks at the shoulder part of the lower energy side of

the Co L_{III}-edge spectra. On the contrary, no clear changes were not observed in Mn L_{III}-edge spectra. These spectral changes indicate that the charge balance due to oxygen release was maintained by the cooperative reduction of Ni and Co while Mn did not contribute to the charge compensation. These are important clues to understand the function of each transition metal elements, and design advanced battery materials.

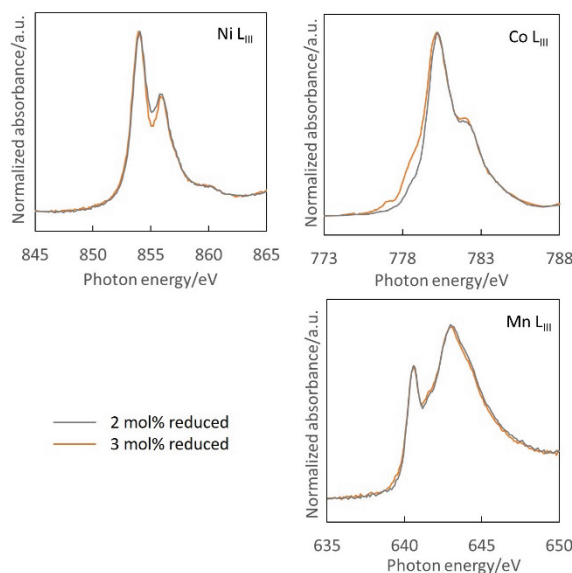


Figure 1. Ni L_{III}-, Co L_{III}- and Mn L_{III}-edge spectra of the oxygen-deficient LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂.

References

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