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# Reversibility of Anionic Redox Reaction in Lithium-rich Co-based Positive Electrodes with Cation Disordered Rocksalt Structure

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Li-excess electrode materials potentially boost the energy density of Li-ion batteries, but the origin of activation of anionic redox in these electrode materials is still under debate. To study the anionic redox reversibility in  $\text{Li}_3\text{NbO}_4\text{-CoO}$  binary system, Co L-edge and O K-edge XAS spectra are collected for  $\text{Li}_{7/6-y}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$  at different charge states. XAS study reveals that partially reversible anionic redox is achieved for  $\text{Li}_{7/6-y}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$ , which is theoretically predicted by the formation of linear Co-O-Co environment for a cation disordered system.

**Keywords:** lithium-ion batteries, positive electrode material, anionic redox, Co L-edge spectra, O K-edge spectra

## 背景と研究目的 (Introduction)

In recent years, towards fossil fuel-free society, a shift from internal combustion engine vehicles to electric vehicles is accelerating. To further increase its speed, it is necessary to develop high-energy density positive electrode materials. Research on positive electrode materials using anionic redox with higher energy density, when compared with classical layered materials with cationic redox, is expanding in recent years. However, many materials with anionic redox are composed of Mn ions, and therefore the knowledge of anionic redox with other transition metal ions is limited. Most recently, soft XAS study at the SR center reveals that anionic redox is activated in materials with Ni ions, which originates from structural disordering coupled with the formation of linear Ni-O-Ni environment[1]. Therefore, in this study, to deepen our understanding on anionic redox with different transition metal ions with a disordered rocksalt structure, soft XAS study is conducted with electrode materials with Co ions. For this purpose,  $\text{Li}_{7/6}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$  with a disordered rocksalt structure is synthesized using a solid-state calcination reaction from precursors containing Li, Co, and Nb ions. For comparison of charge compensation mechanism and reversibility of anionic redox, lithium-rich system,  $\text{Li}_{4/3}\text{Co}_{2/9}\text{Nb}_{4/9}\text{O}_2$  was also synthesized, and both samples,  $\text{Li}_{7/6}\text{Co}_{4/9}\text{Nb}_{4/9}\text{O}_2$  and  $\text{Li}_{4/3}\text{Co}_{2/9}\text{Nb}_{4/9}\text{O}_2$ , are found for solid solution oxides in  $\text{Li}_3\text{NbO}_4\text{-CoO}$  binary system.

## 実験 (Experimental)

$\text{Li}_{7/6}\text{Co}_{4/9}\text{Nb}_{4/9}\text{O}_2$  was synthesized by solid-state calcination.  $\text{Li}_2\text{CO}_3$  (98.5%, Kanto Kagaku),  $\text{CoCO}_3\cdot\text{Co}(\text{OH})_2\cdot 4\text{H}_2\text{O}$  (Wako Pure Chemical Industries), and  $\text{Nb}_2\text{O}_5$  (99.9%; Wako Pure Chemical Industries) were mixed by wet ball-milling at 300 rpm for 6 h with ethanol. The obtained powder was then pressed into a pellet under a pressure of 20 MPa. The pellet was transferred into a quartz tube and calcined in Ar at 1000 °C for 2 h. The electrode performance of samples was tested using two-electrode cells (TJ-AC, Tomcell Japan). The composite positive electrode consisted of 80 wt% active material, 10 wt% acetylene black (HS-100, Denka) and 10 wt% poly(vinylidene fluoride) (#1100, Kureha), pasted on an aluminum foil, then the slurry was dried in vacuum, and before assembling cells a positive electrode was further dried at 120 °C for 2 h in vacuum. Metallic lithium (Honjo Metal) was used as a negative electrode. The electrolyte solution used was 1.0 mol  $\text{dm}^{-3}$   $\text{LiPF}_6$  dissolved in ethylene carbonate:dimethyl carbonate (3:7 by volume) (battery grade, Kishida Chemical). A polyolefin microporous membrane was used as separator. A constant current charge-discharge test was conducted. Regarding the change in the charge compensation mechanism, Co L-edge and the O K-edge XAS spectra of the samples were collected at the SR Center, BL-11, in Ritsumeikan University.

### 結果、および、考察 (Results and discussion):

To study the charge compensation mechanisms in  $\text{Li}_3\text{NbO}_4\text{-CoO}$  binary system, Co L-edge and O K-edge XAS spectra of  $\text{Li}_{7/6}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$  were measured at different charge states, and results are summarized in Fig. 1. For Co L-edge XAS spectra, the as-prepared  $\text{Li}_{7/6}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$  contains  $\text{Co}^{2+}$  with a high-spin  $d^7$  configuration (up-spin  $t_{2g}^3 e_g^2$ , down-spin  $t_{2g}^2$ ), similar to CoO with a disordered rocksalt structure[2]. After charge to  $80 \text{ mA h g}^{-1}$ , the oxidation state of Co is increased to the trivalent state as noticed from the energy shift of Co L-edge XAS spectra to a higher energy region. However, there is still a shoulder peak at lower energy, indicating divalent Co ions also remain. Upon further charge to  $160 \text{ mA h g}^{-1}$ , Co was oxidized to trivalent state, the shoulder peak corresponding to divalent state disappeared. There is no change of Co L-edge XAS spectra after fully charge.

Because the covalency of Co is increased, the energies of O K-edge XAS spectra are also gradually shifted to a lower energy region (from pristine to  $160 \text{ mA h g}^{-1}$ ). Noticeably, a small but clear peak appears at O K-edge XAS spectra at  $527 \text{ eV}$  upon charge, which is not observed for  $\text{LiCoO}_2$  and  $\text{LaCoO}_3$  with trivalent Co ions. Moreover, this peak is also observed for  $\text{SrCoO}_3$  synthesized by high-pressure method, and this peak for O K-edge XAS spectra is assigned to a ligand hole[2]. This fact suggests that ligand holes are partially formed in  $\text{Li}_{7/6-y}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$ . Our DFT study also supports that this trend and ligand holes are formed in oxygen, which have a linear Co-O-Co environment. This environment is only formed in the disordered rocksalt structure and not formed in layered structure. Moreover, such ligand hole cannot be stabilized in lithium-rich system and oxygen loss is evidenced for  $\text{Li}_{4/3-y}\text{Co}_{2/9}\text{Nb}_{4/9}\text{O}_2$  because Li enrichment results in the loss of linear Co-O-Co environment for oxygen.

These findings in this study, potentially contribute to a better understanding of anionic redox reversibility in Co-based oxides, leading to further development of high-energy electrode materials with anionic redox in the future.

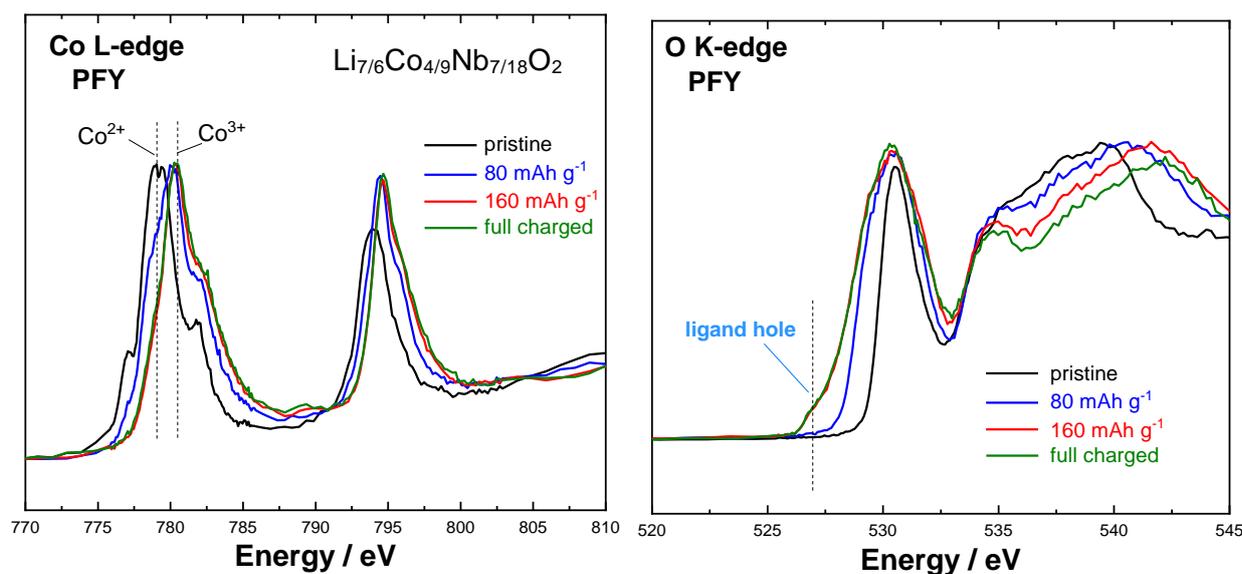


Fig. 1. (left) Co L-edge and (right) O K-edge XAS spectra of  $\text{Li}_{7/6-y}\text{Co}_{4/9}\text{Nb}_{7/18}\text{O}_2$  with different charged states.

### 参考文献

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### 研究成果公開方法 / 産業への応用・展開について

- This study has been published in JPCC as shown in reference [2].