

The Relationship between Electrochemical Reaction and the Crystal Structure Change of Co-substituted Li_4SiO_4 during Charge-discharge Process

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Anion-redox cathode materials (ARCMs), which utilize the redox reaction of oxygen for charge compensation, have been investigated for Lithium-ion batteries with high energy density^[1]. The redox potential of oxygen varied depending on the crystal structure and composition. Based on the results of the investigation, Li_4SiO_4 (LS) was investigated as an ARCMs with high reaction potential. It was found that Co-substituted Li_4SiO_4 (CSLS) has a high specific capacity of about 230 mAh g^{-1} and a higher reaction potential (about 3.9 V) than conventional ARCMs. In this study, we will clarify the reaction mechanism.

Figure 1 (a), and (b) show the results of XAS measurements performed to clarify the local structural changes of CSLS with different Co/Si ratios before and after charge/discharge. In the O K-edge XANES spectra of the CSLSs after charging, a shoulder can be observed at about 528.5 eV, which cannot be seen in the spectra before charging and after discharge. Furthermore, the intensity of the shoulder of CSLS with Co/Si ratio of 2 (CSLS2) is larger than that with Co/Si ratio of 1 (CSLS1). The shoulder is considered to be derived from the charging products generated in the charging process. Furthermore, in the O K-edge XANES spectra of CSLS1, it can be seen that the spectra before charging and after discharge have similar shapes. From the results, the first charge-discharge process of CSLS1 is considered to be reversible. On the other hand, for the CSLS2, the shape of the spectrum is different before and after charging and discharging. This may be attributed to the low reversibility of the first charge-discharge reaction. For the detailed analysis of the charge-discharge reaction mechanism of CSLS, the difference spectra prepared by using the O K-edge XANES spectra before and after charging of CSLS with different Co/Si ratios are shown in Figure 2(a) and (b). Peaks at 527.0, 527.9, 528.5, and 530.5 eV can be observed in all spectra, and the peaks at 528.5 and 530.5 eV can be attributed to the formation of LiO_2 and Li_2O_2 , respectively^[2]. It can be found that the peak intensities at 527.0 and 528.5 eV of CSLS2 are larger than those with CSLS1. On the other hand, the peak intensities at 527.9 and

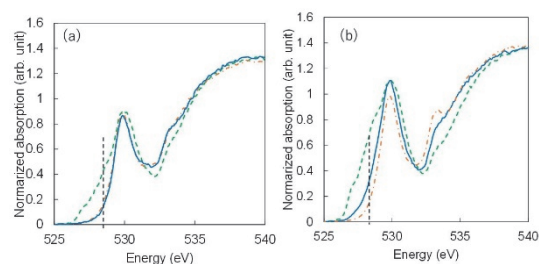


Fig. 1. O K-edge XANES spectra of pristine (solid-line), charged (blue dashed-line), and discharged (dashed-dotted-line) (a) CSLS1 and (b) CSLS2.

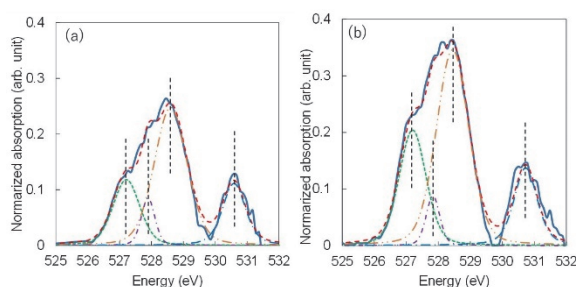


Fig. 2. Difference spectra of (a) CSLS1 and (b) CSLS2.

530.5 eV were similar regardless of the Co/Si ratio. From these results, it can be inferred that the Co contained in the active material contributes to the charging reaction with the formation of LiO_2 . On the other hand, the contribution of Co in the charging reaction with the formation of Li_2O_2 is considered to be small.

References

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- [2] D. Okuda et al., *Solid State Ion*, 353, 115374 (2020).