Electrochemical Characteristics of Co-Substituted $\alpha$- and $\beta$-Li$_5$AlO$_4$ as High-Specific Capacity Positive Electrode Materials

Daisuke Okuda, Hiroaki Kobayashi,* and Masashi Ishikawa*

**ABSTRACT:** Electric vehicles and hybrid electric vehicles require batteries with higher energy densities than conventional batteries. Anion redox-type active materials have been proposed as new high-capacity positive electrode materials for Li-ion batteries with high-energy densities. Co-substituted Li$_5$AlO$_4$ is a novel and promising high-capacity positive electrode material for Li-ion batteries. In this study, we investigated the influence of different synthesis conditions on the enhancement of the specific capacity. The material prepared via mechanical alloying of $\beta$-Li$_5$AlO$_4$ with LiCoO$_2$ at 300 rpm for 24 h exhibited a higher specific capacity than that prepared from $\alpha$-Li$_5$AlO$_4$ and LiCoO$_2$. Co-substituted $\beta$-Li$_5$AlO$_4$ demonstrated a specific capacity of approximately 250 mA h g$^{-1}$. The specific capacity of Co-substituted $\alpha$ and $\beta$-Li$_5$AlO$_4$ increased with increasing Co content in the samples. According to X-ray absorption near edge structure measurements, the irreversible oxygen redox reaction and a reversible reaction involving the formation and consumption of peroxide were responsible for the charge compensation of Co-substituted $\beta$-Li$_5$AlO$_4$ and $\alpha$-Li$_5$AlO$_4$, respectively.

## INTRODUCTION

Lithium-ion batteries are used as reliable power sources in modern equipment such as electric and hybrid electric vehicles and laptops. However, modern and future high-performance products require energy storage devices with higher energy densities. Active materials with relatively high capacities and reaction potentials have been investigated for enhancing the energy density of energy storage devices. Spinel-type lithium manganese oxides such as LiNi$_{0.5}$Mn$_{1.5}$O$_4$ have been developed as high-reaction potential materials. Previously, we developed Co-substituted Li$_5$AlO$_4$ (CSLA) as a stable and high specific capacity material, with a specific capacity of approximately 140 mA h g$^{-1}$. It was revealed that the redox reaction involving the formation and consumption of peroxide and super oxide was utilized in the charge compensation of CSLA. However, the specific capacity was still lower than the theoretical capacity of CSLA. It was hypothesized that this low specific capacity may originate from the small amount of substituted Co. Li$_5$AlO$_4$ has multiple crystalline structures such as $\alpha$-Li$_5$AlO$_4$ ($\alpha$-LA, orthorhombic, Pbca) and $\beta$-Li$_5$AlO$_4$ ($\beta$-LA, orthorhombic, Pcca) (Figure 1). The electrochemical characteristics and charge–discharge mechanisms of $\alpha$- and $\beta$-CSLA are investigated in this study.

However, Co-substituted Li$_2$O decomposes according to eq 2 when overcharged.

$$2\text{Li}_2\text{O} \rightarrow \text{Li}_2\text{O}_2 + 2\text{Li}^{+} + 2\text{e}^{-}$$ (1)

$$\text{Li}_2\text{O} \rightarrow 0.5\text{O}_2 + 2\text{Li}^{+} + 2\text{e}^{-}$$ (2)

Previously, we developed Co-substituted Li$_5$AlO$_4$ (CSLA) as a stable and high specific capacity material, with a specific capacity of approximately 140 mA h g$^{-1}$. It was revealed that the redox reaction involving the formation and consumption of peroxide and super oxide was utilized in the charge compensation of CSLA. However, the specific capacity was still lower than the theoretical capacity of CSLA. It was hypothesized that this low specific capacity may originate from the small amount of substituted Co. Li$_5$AlO$_4$ has multiple crystalline structures such as $\alpha$-Li$_5$AlO$_4$ ($\alpha$-LA, orthorhombic, Pbca) and $\beta$-Li$_5$AlO$_4$ ($\beta$-LA, orthorhombic, Pcca) (Figure 1). The electrochemical characteristics and charge–discharge mechanisms of $\alpha$- and $\beta$-CSLA are investigated in this study.

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1. **INTRODUCTION**

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RESULTS AND DISCUSSION

Morphologies and Crystal Structures of α- and β-CSLA. The morphologies of α- and β-CSLA were observed using SEM. Both materials had average particle sizes of approximately 5 μm, as shown in Figure 2.

XRD analyses were conducted to investigate the crystal structures of α-LA, β-LA, α-CSLA, and β-CSLA, as shown in Figure 3. In the patterns for the as-prepared α- and β-LA, most peaks can be attributed to α- and β-Li5AlO4, respectively. After mechanical alloying of these materials with LCO, broad peaks at approximately 18, 38, 45, 58, 66, and 69° attributable to

EXPERIMENTAL METHODS

Synthesis of α- and β-CSLA. Li2AlO3 was synthesized using a sol–gel method. LiOH·H2O, Al(OH)3, and C2H4(NH2)2 purchased from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan) were dispersed in a 6:1:9 molar ratio in 100 cm3 of deionized water and stirred for 24 h to form a sol. The gel was obtained by heating the sol for 6 h. Subsequently, α- and β-LA were obtained by heating the gel at 750 and 950 °C, respectively, for 20 h under Ar flow. α- and β-CSLA were prepared via mechanical alloying of LiCoO2 (LCO) with α- and β-LA, respectively, in a 1:1 molar ratio. The mixture was sealed in a tungsten carbide (WC) pod with WC balls in an Ar-filled glovebox (Pure box, Yamato Co., Ltd., Osaka, Japan), and then, planetary ball milling (Premium Line P-7, Fritsch) was conducted at 300 rpm for 36 h to pulverize the oxides. To investigate the effect of ball-milling time, ball milling was also performed for 12 and 24 h using β-LA and LCO in a 1:1 molar ratio. The resultant materials were denoted as β-12 and β-24, respectively.

Structural and Morphological Characterization of α- and β-CSLA. The morphologies of the active materials were observed by scanning electron microscopy (SEM, Hitachi SU-1500) at an accelerating voltage of 15 kV. The crystal structures of α-LA, β-LA, α-CSLA, and β-CSLA were determined by X-ray diffraction (XRD, Rigaku ultima-IV) conducted at 4° min⁻¹ from 10 to 80° using Cu Kα1 radiation. Ex situ X-ray absorption spectroscopy (XAS) was performed at BL-10 and BL-11 of the Synchrotron Radiation Center, Ritsumeikan University to acquire X-ray absorption near edge structure (XANES) spectra of the O and Al K-edges of α- and β-CSLA during charge–discharge cycling. KTP (011) was used as the monochromator, and an unequally spaced diffraction grating was employed. The XANES spectra of the O and Al K-edges were analyzed using the Athena program.11

Electrochemical Characterization of α- and β-CSLA. The electrochemical characteristics were evaluated by charge–discharge cycling tests. The active material (α- or β-CSLA) was mixed with acetylene black (Denka black, Denka Co., Ltd., Tokyo, Japan) and polyvinylidene difluoride (#1100, Kureha Co., Ltd., Tokyo, Japan) in a 70:20:10 ratio by weight to form a paste, which was then applied to an Al foil using a doctor blade casting method and dried under vacuum at 60 °C for 12 h to obtain a working electrode. The electrolyte consisted of 1 mol dm⁻³ LiPF₆ in a 50:50 volume ratio of ethylene carbonate (EC) and methyl carbonate (DMC) (Kishida Chemical Co., Ltd., Osaka, Japan). The working electrode, a Li metal sheet (the counter electrode), the electrolyte, and a polyolefin film separator (NDS25, Asahi Kasei Co., Ltd.) were assembled in a demountable coin-type cell (Hosen Corp., Osaka, Japan). Charge–discharge cycle tests were conducted at 20 mA g⁻¹ at 25 °C. For the charge process, a voltage of 3.5 V was applied and maintained until the current density decreased to 2 mA g⁻¹. For the discharge process, the cells were discharged to 1.5 V.
XAS was conducted to investigate the partial structure around Al and O in \( \alpha \)- and \( \beta \)-CSLA. Figure 4a,b shows the Al and O K-edge XANES spectra, respectively, of \( \alpha \)- and \( \beta \)-CSLA obtained using partial fluorescence yield spectroscopy. In the Al K-edge XANES spectra of both \( \alpha \)- and \( \beta \)-CSLA, the pre-edge peak and shoulder at approximately 1564 and 1567 eV are attributable to Al\(^{3+}\) ions with tetrahedral and octahedral coordination, respectively. The hexacoordinated Al could be formed by the substitution of Co in LCO for Al in \( \alpha \)- and \( \beta \)-LA. Analysis of these spectra (Figure S1 in the Supporting Information) revealed that the pre-edge peak at 1567 eV had a higher absorption intensity in the \( \beta \)-CSLA spectrum than in the \( \alpha \)-CSLA spectrum. This indicates that more hexacoordinated Al was formed in \( \beta \)-CSLA than in \( \alpha \)-CSLA during mechanical alloying. In the O K-edge spectra of both \( \alpha \)- and \( \beta \)-CSLA, the shoulder and peak at 528 and 529.9 eV, respectively, could be assigned to the new bonding state formed by the substitution of Co in LCO for Al in \( \alpha \)- and \( \beta \)-LA and Co\(^{3+}\)–O bonding in LCO.\(^{10}\) The shoulder at 528 eV had a higher absorption intensity in the \( \beta \)-CSLA spectrum than in the \( \alpha \)-CSLA spectrum, while the peak at 529.8 eV had a lower absorption intensity in the \( \beta \)-CSLA spectrum than in the \( \alpha \)-CSLA spectrum. Analysis of these spectra (Figure S2 in the Supporting Information) revealed that the ratios of the intensities of the 528 and 529.8 eV peaks were 0.32 for \( \alpha \)-CSLA and 0.49 for \( \beta \)-CSLA. The proportions of substituted Co \( (P_{Co}) \) to the total amount of Co in \( \alpha \)- and \( \beta \)-CSLA were 0.24 and 0.33, respectively, as calculated using eq 3.

\[
P_{Co} = \frac{A_{528}^{\alpha}}{A_{528}^{\alpha} + A_{529}^{\beta}}
\]

where \( A_{528}^{\alpha} \) and \( A_{529}^{\beta} \) are the areas of the peaks at 528 and 529 eV, respectively, as calculated using curve fitting (Table S2 in the Supporting Information). These calculations indicate that 24 and 33\% of Co in LCO were substituted into \( \alpha \)- and \( \beta \)-CSLA, respectively, and that the molecular ratios of \( \alpha \)-CSLA to LCO in the active materials were 1:0.76 and 1:0.68, respectively.

### Charge–Discharge Mechanisms of \( \alpha \)- and \( \beta \)-CSLA.

Figure 5a,b shows the charge–discharge curves of \( \alpha \)- and \( \beta \)-CSLA. As observed in these curves, \( \alpha \)- and \( \beta \)-CSLA had reversible capacities of 200 and 250 mA h g\(^{-1}\), respectively. The plateau of the discharge curves was approximately 3 V longer for \( \beta \)-CSLA than for \( \alpha \)-CSLA. It has been reported previously that the charge compensation of \( \alpha \)-CSLA mostly originates from the redox reaction of oxygen, which is activated by the substitution of Co for Li or Al in Li\(_3\)AlO\(_4\).\(^{10}\) Combined with the fact that the resistances of these materials in powder form are on the same order of magnitude (Table S1 in the Supporting Information) and would therefore not contribute to the observed difference in electrochemical characteristics, these results suggest that the higher specific capacity of \( \beta \)-CSLA compared to that of \( \alpha \)-CSLA might originate from the higher oxygen activity of \( \beta \)-CSLA resulting from the greater amount of substituted Co (Figure 4b). Figure 5c shows the changes in specific capacity of \( \alpha \)- and \( \beta \)-CSLA over 10 charge–discharge cycles. \( \beta \)-CSLA showed a higher specific capacity than \( \alpha \)-CSLA at each cycle. However, the capacity of \( \beta \)-CSLA decreased steeply from the first to the fourth cycle. This rapid

LCO were observed, along with small peaks at approximately 22, 24, 33, and 35° attributable to \( \alpha \)-Li\(_2\)AlO\(_4\) for \( \alpha \)-CSLA and 19, 34, and 57° attributable to \( \beta \)-Li\(_2\)AlO\(_4\) for \( \beta \)-CSLA. These results suggest that \( \alpha \)- and \( \beta \)-CSLA comprised low-crystallinity \( \alpha \)- and \( \beta \)-LA phases and LCO after the mechanical alloying process.

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**Figure 4.** (a) Al and (b) O K-edge XANES spectra of \( \alpha \)- and \( \beta \)-CSLA.

**Figure 5.** Charge–discharge curves of (a) \( \alpha \)-CSLA and (b) \( \beta \)-CSLA between 1.5 and 3.5 V at 20 mA g\(^{-1}\) with 1 mol dm\(^{-3}\) of LiPF\(_6\) in a 50:50 volume ratio EC and DMC mixture. (c) Relationship between fi capacity of \( \alpha \)- and \( \beta \)-CSLA and cycle number.
A decrease in specific capacity could be due to the difference between the charge–discharge mechanism of $\alpha$- and $\beta$-CSLA.

The charge–discharge mechanisms of $\alpha$- and $\beta$-CSLA were investigated using XAS. Figure 6a,b shows the Al K-edge XANES spectra of pristine, charged, and discharged $\alpha$- and $\beta$-CSLA for the first charge–discharge cycle. In the $\alpha$-CSLA spectra, the intensities of the peak and shoulder at 1565 and 1567 eV, respectively, increased (decreased) after the charge (discharge) process, and the pristine and discharged material produced similar spectra. The increase in absorption intensities in the charged state was attributed to the structural disorder caused by the oxygen redox reaction. Furthermore, similar spectra in the pristine and discharged states indicated that the electrochemical reaction in $\alpha$-CSLA was reversible. In contrast, for $\beta$-CSLA, the peak and shoulder had higher intensities in the discharged state than in the pristine state. This suggests that the charged $\beta$-CSLA could not revert to its as-prepared crystal structure during the discharge process. Therefore, the electrochemical reaction of $\beta$-CSLA would be irreversible.

Figure 6c,d exhibits the O K-edge XANES spectra of pristine, charged, and discharged $\alpha$- and $\beta$-CSLA for the first charge–discharge cycle. In the charged $\alpha$-CSLA spectrum, the shoulder at 528 eV is higher than that for pristine $\alpha$-CSLA. In addition, the pristine and discharged $\alpha$-CSLA spectra have very similar shapes. These results indicate that the electronic state of the bonding between oxygen and substituted Co in $\alpha$-CSLA changed reversibly during the charge–discharge process. Meanwhile, the shoulder at 528 eV in the discharged $\beta$-CSLA spectrum is lower than that in the pristine $\beta$-CSLA spectrum. This result shows that the electronic state of the bonding between oxygen and substituted Co in $\beta$-CSLA changes irreversibly during the charge–discharge process. This further indicates that the electrochemical reaction of $\beta$-CSLA is irreversible. The irreversible electrochemical reaction would cause a rapid decrease in the capacity of $\beta$-CSLA during the initial stages of charge–discharge cycling (Figure 5c).

The difference spectra were analyzed to further investigate the charge–discharge mechanism of $\alpha$- and $\beta$-CSLA. The difference spectra of the O K-edge XANES spectra for $\alpha$-CSLA are plotted in Figure 7a. The peaks at 528, 530.5, and 532.5 eV can be attributed to increasing/decreasing amounts of tetrahedrally coordinated Co$^{3+}$–O bonding, super oxides, peroxides, and tetrahedrally coordinated Al$^{3+}$–O bonding.10,12 The difference spectrum obtained by subtracting the spectrum of the pristine state from that of the charged state (i.e., charged—pristine) showed good symmetry with that obtained...
by subtracting the spectrum of the charged state from that of the discharged state (i.e., discharged−charged). However, the peak at 528 eV decreased slightly in the difference spectrum calculated by subtracting the spectrum of the pristine state from that of the discharged state (i.e., discharged−pristine). This was due to a decrease in the amount of tetrahedrally coordinated Co$^{3+}$. This is further evidence of a reversible electrochemical reaction occurring in α-CSLA.

On the other hand, for β-CSLA, the charged—pristine difference spectrum showed poor symmetry against the discharged—charged difference spectrum. The peaks at 528 and 532.5 eV are attributed to the increase/decrease in tetrahedrally coordinated Co$^{3+}$ and Al$^{3+}$−O, respectively. These peaks were obviously more negative in the discharged—pristine difference spectrum for β-CSLA than that for α-CSLA. This is further evidence of an irreversible electrochemical reaction occurring in β-CSLA. We propose that the irreversible charge−discharge process of β-CSLA originates from the excess Co content.

To verify the relation between the amount of substituted Co and irreversibility of the charge−discharge process in β-CSLA, XAS analysis and charge−discharge tests were conducted on β-12 and β-24, which were mechanically alloyed with LCO for less time than β-CSLA, namely, 12 and 24 h, respectively, versus 36 h. Their average particle sizes were approximately 5 μm, regardless of the ball-milling time (Figure S3). Thus, the oxides were completely pulverized after 12 h of ball-milling. Figure 8 shows the XRD patterns of β-12, β-24, and β-CSLA. The peaks attributed to LCO and β-LA broadened with the increase in ball-milling time, which suggests that mechanical alloying decreases the crystallinity of these phases.
Figure 9a,b shows the Al and O K-edge XANES spectra of $\beta$-12, $\beta$-24, and $\beta$-CSLA. In the Al K-edge XANES spectra, the shoulder at 1567 eV increased slightly with the ball-milling time. Furthermore, the shoulder at 527 eV in the O K-edge XANES spectra clearly increased with the ball-milling time. These results indicate that the mechanochemical reaction between $\beta$-LA and LCO proceeded further as the ball-milling time increased. The changes in the XRD patterns with the increase in ball-milling time (Figure 8) further prove that the mechanochemical reaction between $\beta$-LA and LCO proceeds as ball milling continues.

Figure 10a,b shows charge–discharge curves of (a) $\beta$-12 and (b) $\beta$-24 between 1.5 and 3.5 V at 20 mA g$^{-1}$ with 1 mol dm$^{-3}$ of LiPF$_6$ in a 50:50 volume ratio EC and DMC mixture. (c) Relationship between discharge capacity for the first cycle (blue diamonds), capacity retention after 10 cycles (orange squares), and ball-milling time.

Figure 10. Charge–discharge curves of (a) $\beta$-12 and (b) $\beta$-24 between 1.5 and 3.5 V at 20 mA g$^{-1}$ with 1 mol dm$^{-3}$ of LiPF$_6$ in a 50:50 volume ratio EC and DMC mixture. (c) Relationship between discharge capacity for the first cycle (blue diamonds), capacity retention after 10 cycles (orange squares), and ball-milling time.

Figure 11. Relationship between specific capacity and area of the peak at 528 eV in O K-edge XANES spectra of $\alpha$- and $\beta$-CSLA synthesized under various conditions.

Investigation of the synthesis conditions for CSLA showed that $\beta$-CSLA contained approximately twice the amount of substituted Co as $\alpha$-CSLA. The Co content was dependent on the structure of the materials. Furthermore, $\beta$-CSLA had an approximately 25% higher specific capacity and lower capacity time. The relationships among the ball-milling time, discharge capacity at the first cycle, and capacity retention after 10 charge–discharge cycles are plotted in Figure 10c. The discharge capacity at the first cycle and capacity retention of $\beta$-CSLA after 10 charge–discharge cycles, respectively, increased/decreased with increasing ball-mill time owing to the ball-milling time dependence of the Co content for $\beta$-CSLA, as shown in Figure 9b.

The specific capacity of $\alpha$- and $\beta$-CSLA depended on synthesis condition. The difference of specific capacity of the samples would come from the Co content. The relationship between the amount of Co in $\alpha$- and $\beta$-CSLA synthesized under various conditions and their specific capacity could be estimated from the relationship between the specific capacity and the peak area of tetrahedrally coordinated Co at 528 eV in Co K-edge XANES spectra of the samples. This is because the area of the peak attributed to the tetrahedrally coordinated Co is proportional to the amount of Co in the samples showing similar shapes of O K-edge XANES spectra. Figure 11 shows the relationship between the specific capacity and the area of the peak at 528 eV. It was found that the specific capacity of the samples is proportional to the area of the peak at 528 eV. This result indicates that the specific capacity of $\alpha$- and $\beta$-CSLA increases with the increasing Co content in the samples. Furthermore, this correlation was observed among all samples regardless of the raw material crystal structure.

■ CONCLUSIONS

Investigation of the synthesis conditions for CSLA showed that $\beta$-CSLA contained approximately twice the amount of substituted Co as $\alpha$-CSLA. The Co content was dependent on the structure of the materials. Furthermore, $\beta$-CSLA had an approximately 25% higher specific capacity and lower capacity
CSLA increased as the ball-milling time increased. However, discharge process. This irreversible decomposition reaction of the active material during the charge—discharge process. This irreversible decomposition reaction caused the capacity to decrease. The specific capacity of β-CSLA increased as the ball-milling time increased. However, the capacity retention of β-CSLA after 10 charge—discharge cycles decreased with increasing ball-milling time. This relationship between the electrochemical characteristics and ball-milling time originates from differences in the Co content. β-CSLA is suitable as a new positive electrode material for lithium-ion batteries due to its high specific capacity.

**ASSOCIATED CONTENT**

Supporting Information

Results of curve fitting analysis for XANES spectra of α- and β-CSLA, resistances of α- and β-CSLA in powder form, and SEM images of β-12, β-24, and β-CSLA (PDF)

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**Author Contributions**

D.O. and H.K. conceived the idea. D.O. conducted the experiments and wrote the paper. M.I. supervised the research. H.K. and M.I. proofread a draft of the paper. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

CSLA, Co-substituted Li₅AlO₄; DMC, methyl carbonate; EC, ethylene carbonate; LA, Li₅AlO₄; LCO, LiCoO₂; PFY, partial fluorescence yield; XANES, X-ray absorption near edge structure; XAS, X-ray absorption spectroscopy

**REFERENCES**

(1) Kim, J.-H.; Myung, S.-T.; Yoon, C. S.; Kang, S. G.; Sun, Y.-K. Comparative Study of LiNi₀.₇Mn₀.₃O₄ and LiNi₀.₅Mn₁.₅O₄ Cathodes Having Two Crystallographic Structures: Fd3m and P432m. Chem. Mater. 2004, 16, 906–914.

(2) Lu, Y.; Lu, T.; Zhang, Y.; Yan, L.; Xie, J. Improving the Electrochemical Properties of High-Voltage LiNi₀.₇Mn₁.₃O₄ for Li-Ion Battery by Modified Current Collectors. J. Electrochem. Soc. 2017, 164, A1298–A1306.

(3) Yabuuchi, N.; Takeuchi, M.; Nakayama, M.; Shiba, H.; Ogawa, M.; Nakayama, K.; Ohta, T.; Endo, D.; Ozaki, T.; Inamasu, T.; Sato, K.; Komaba, S. High-Capacity Electrode Materials for Rechargeable Lithium Batteries: LiₓNBO₃-Based System with Cation-Disordered Rocksalt Structure. Proc. Natl. Acad. Sci. U.S.A. 2015, 112, 7650–7655.

(4) Okuoka, S.-i.; Ogasawara, Y.; Suga, Y.; Hibino, M.; Kudo, T.; Ono, H.; Yonehara, K.; Sumida, Y.; Yamada, Y.; Yamada, A.; Oshima, M.; Tochigi, E.; Shibata, N.; Ikuhara, Y.; Mizuno, N. A New Sealed Lithium-Peroxide Battery with a Co-Doped LiO Cathode in a Superconcentrated Lithium Bi(S₃fluorosulfon)amide Electrolyte. Sci. Rep. 2015, 4, 5684.

(5) Ogasawara, Y.; Hibino, M.; Kobayashi, H.; Kudo, T.; Asakura, D.; Nanba, Y.; Hisonou, E.; Namagami, N.; Kitada, Y.; Honma, I.; Oshima, M.; Okuoka, S.-i.; Ono, H.; Yonehara, K.; Sumida, Y.; Mizuno, N. Charge/Discharge Mechanism of a New Co-Doped LiO Cathode Material for a Rechargeable Sealed Lithium-Peroxide Battery Analyzed by X-ray Absorption Spectroscopy. J. Power Sources 2015, 287, 220–225.

(6) Kobayashi, H.; Hibino, M.; Ogasawara, Y.; Yamaguchi, K.; Kudo, T.; Okuoka, S.-i.; Yonehara, K.; Ono, H.; Sumida, Y.; Oshima, M.; Mizuno, N. Improved Performance of Co-Doped LiO Cathodes for Lithium-Peroxide Batteries using LiCoO₂ as a Dopant Source. J. Power Sources 2016, 306, 567–572.

(7) Harada, K.; Hibino, M.; Kobayashi, H.; Ogasawara, Y.; Okuoka, S.-i.; Yonehara, K.; Ono, H.; Sumida, Y.; Oshima, M.; Mizuno, N. Electrochemical Reactions and Cathode Properties of Fe-Doped LiO for the Hermetically Sealed Lithium Peroxide Battery. J. Power Sources 2016, 322, 49–56.

(8) Kobayashi, H.; Hibino, M.; Makimoto, T.; Ogasawara, Y.; Yamaguchi, K.; Kudo, T.; Okuoka, S.-i.; Yonehara, K.; Ono, H.; Yonehara, K.; Mizuno, N. Synthesis of Cu-Doped LiO Cathodes and its Cathode Properties for Lithium-Ion Batteries. J. Power Sources 2017, 340, 365–372.

(9) Kobayashi, H.; Hibino, M.; Kubota, Y.; Ogasawara, Y.; Yamaguchi, K.; Kudo, T.; Okuoka, S.-i.; Ono, H.; Yonehara, K.; Sumida, Y.; Mizuno, N. Electrochemical Properties for Lithium-Ion Batteries Based on Oxi/Peroxide Redox Reactions. J. Power Sources 2017, 340, 365–372.

(10) Okuda, D.; Kobayashi, H.; Ishikawa, M. Electrochemical Characteristics and Charge-Discharge Mechanisms of Co-Substituted Li₅AlO₄ as a Novel Positive Electrode Material. Solid State Ion. 2020, 353, 115374.

(11) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using FEFFFIT. J. Synchrotron Radiat. 2005, 12, 537–541.

(12) Kato, Y.; Shimizu, K.-i.; Matsushita, N.; Yoshida, T.; Yoshida, H.; Satsuma, A.; Hattori, T. Quantification of aluminium coordinations in alumina and silica-alumina by Al K-edge XANES. Phys. Chem. Chem. Phys. 2001, 3, 1925–1929.