Crystal structure, ionic conductivity and lithium-ion diffusion pathway in a La–Li–Co–O system

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Oxide electrolytes are a growing topic in battery research, but their full potential has not yet been realized owing to the lack of new materials. As opposite to the traditional design strategy that relies on $d^0$ or $d^{10}$ systems, we focus our attention on $3d^1$ systems, oxygen-excess La$_2$Li$_x$Li$_{1-x}$Co$_y$O$_{4.25}$ and oxygen-deficient La$_{x+y}$Li$_{1-x}$Co$_{1+y}$O$_{3.23}$. Among them, we achieve lithium-ion conduction in La$_{1.24}$Li$_0.73$Li$_{0.5}$Co$_{0.73}$O$_{3.15}$. A quasi-one dimensional pathway for lithium diffusion or distortion of lithium nuclear density is confirmed to be present at 100 °C by analyzing neutron powder diffraction data in combination with the maximum entropy method.

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1. Introduction

The development of lithium (Li)-ion batteries is being driven by an ever-increasing demand to shift from fossil fuels to electricity, along with the use of more renewable energy on the grid. Enhancing the energy density remains a central objective of research on cathode, electrolyte and anode materials. For example, Li$_x$FeS$_2$ (2 < $x$ < 10) is one of the most important cathodes owing to eight transferrable Li ions. Furthermore, our previous study revealed a pronounced influence of the type of electrolyte on the specific capacity. Progress in the field of oxide electrolytes has been severely hampered due to the lack of new families of candidate compounds besides the classic $d^0$ and main-group element systems (for example, Ti$^{4+}$, Ge$^{4+}$ and Zr$^{4+}$). On the other hand, cobalt oxides have attracted great interest in recent years because of the observations of huge thermoelectric power, superconductivity and a variety of peculiar physical properties reported by our group. Such properties are generally considered to be associated with the valence/spin states of Co ions and strong Coulomb interactions between 3$d$ electrons.

Two prerequisites for high-performance electrolytes, namely, a low electronic conductivity and a high ionic conductivity, should be achieved in an oxide. The ability of Co$^{3+}$ to form the low-spin (LS) configuration ($t_{2g}^6e_g^4$) may suppress electronic conduction through the filled $t_{2g}$ orbitals. Furthermore, Li injection in the void space between the stacked layers can facilitate Li-ion conduction.

In this study, we target two-dimensional La$_{2}$Li$_{0.5}$Co$_{0.5}$O$_{4}$ as a model system to expand the horizon in exploring oxide electrolytes. In a first step, we conducted a systematic study on the crystal structure, the magnetic properties and the ionic conductivity on oxygen-excess La$_{2}$Li$_{0.5}$Co$_{0.5}$O$_{4.25}$ with varying $x$ up to 4, maintaining the relation $x = 3y + 0.5$. Owing to its mixed ion/electron conductive behaviour, we next investigated oxygen-deficient La$_{x+y}$Li$_{1-x}$Co$_{1+y}$O$_{3.23}$. In our previous study, we investigated La$_{1.24}$Li$_{0.44}$Li$_{0.5}$Co$_{0.5}$O$_{1.08}$ (x = 0.09, y = 0.17) and La$_{1.24}$Li$_{0.73}$Li$_{0.5}$Co$_{0.5}$O$_{3.23}$ (x = 0.09, y = 0.46). Thus, we prepared La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$, in which the Li content is between 0.44 and 0.73. By combining the neutron powder diffraction (NPD) data and the maximum entropy method (MEM), a pathway for Li diffusion in the crystal was clearly visualized.

2. Experimental procedure

Polycrystalline La–Li–Co–O samples were prepared by solid-state reaction in oxygen, air or argon. The details of the crystal structure analysis, sample characterization and...
ionic/electronic conductivity measurements were reported elsewhere. The synchrotron-radiation spectra were accumulated at room temperature at the BL28XU beamline at SPring-8, Hyogo, Japan. A wavelength of 0.5 Å, quartz glass capillary tubes and an imaging plate as the detector were employed. The neutron time-of-flight diffraction data at room temperature and 100°C were obtained using a high-resolution neutron powder diffractometer at the BL09 (SPICA) beamline in the Materials and Life Science Experimental Facility of J-PARC, Tokai, Japan. For the high-temperature measurements, the temperature was calibrated using the lattice constant of silicon. The powder samples were sealed in a VNi cell (6 mm radius; approximately 25 mm height) using a silicon ring. The structural parameters were refined using the Z-Rietveld program. The MEM calculations were performed using the Z-MEM algorithm in the Z-code software package. The crystal structure and nuclear density distribution were visualized using the VESTA program.

3. Results and discussion

Figure 1 displays the synchrotron X-ray diffraction (XRD) patterns of La2−xLi1xLi0.5Co0.5O4.25. As can be seen, no apparent impurity peaks were observed with changing x. The single phase was obtained up to approximately x = 4 in La2−xLi1xLi0.5Co0.5O4.25. La2−xLi1xLi0.5Co0.5O4.25 had an orthorhombic lattice in the Ammm space group (No. 65). Table 1 summarizes the lattice constants of La2−xLi1xLi0.5Co0.5O4.25. Here, the lattice constants were estimated by the general extrapolation method based on a lattice constant vs cos²θ plot. The a- and b-axis lengths exhibited no noticeable change with changing x, while the c-axis length increased from 12.619(3) Å (x = 1) to 12.625(1) Å (x = 4). As a result, the volume increased with x.

The magnetic susceptibility for La2−xLi1xLi0.5Co0.5O4.25 was investigated to confirm the valence state and spin configuration of Co ions. As shown in Fig. 2(a), there was no magnetic transition and hysteresis between the data under zero-field cooling (ZFC) and field cooling (FC) conditions for all compositions. The susceptibility was small in magnitude, on the order of 10⁻⁷–10⁻⁸ emu mol⁻¹, indicating that the effective magnetic moment derived from the susceptibility curve was quite small. This nonmagnetic behaviour at least up to 300 K demonstrates that the LS state of Co³⁺ makes electron transfer improbable.

The x variation of conductivity is summarized in Fig. 2(b). The data at 25 and 140°C showed a dome-shaped relation, in which the conductivity took a maximum for 2 ≤ x ≤ 3. The highest conductivity (1.5 × 10⁻⁴ S cm⁻¹) was observed at 140°C for x = 2. However, a low-frequency spike characteristic of electrode polarization in the Nyquist plot was not observed for x = 2, which indicates that ionic and electronic conduction coexist. Electronic conduction would appear at high temperature probably owing to a spin-state crossover from the LS state to higher spin states.

We next turn our attention to the oxygen-deficient system, La1.24Li0.57Li0.5Co0.5O3.15. The structural analysis

![Figure 1](image1.png)

**Table 1.** Lattice constants for La2−xLi1xLi0.5Co0.5O4.25 at 300 K

| composition | a (Å)     | b (Å)     | c (Å)     |
|-------------|-----------|-----------|-----------|
| x = 1, y = 1/6 | 5.353(3)  | 5.353(5)  | 12.619(3) |
| x = 4/3, y = 5/18 | 5.353(5)  | 5.353(4)  | 12.621(2) |
| x = 2, y = 0.5 | 5.352(4)  | 5.353(5)  | 12.622(1) |
| x = 8/3, y = 13/18 | 5.352(1)  | 5.353(2)  | 12.623(2) |
| x = 4, y = 7/6 | 5.352(1)  | 5.353(2)  | 12.625(1) |

![Figure 2](image2.png)

**Fig. 2.** (a) Temperature dependence of magnetic susceptibility under the ZFC (closed symbols) and FC (open symbols) conditions for La2−xLi1xLi0.5Co0.5O4.25. (b) Total conductivity at 25 and 140°C as a function of x in La2−xLi1xLi0.5Co0.5O4.25.
Table 2. Refined crystal parameters for La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ at 100 °C. $g$, occupancy; $B$, atomic displacement parameter

| atom | site | $g$   | $x$  | $y$  | $z$  | $B$ (Å$^2$) |
|------|------|-------|------|------|------|-------------|
| La1  | 4i   | 0.62  | 0    | 0    | 0    | 0.1340(1)   |
| La2  | 4i   | 0.62  | 0.5  | 0    | 0    | 0.3650(1)   |
| Li1  | 2d   | 1     | 0    | 0    | 0    | 0.5         |
| Li2  | 4i   | 0.12  | 0    | 0    | 0    | 0.1340(5)   |
| Li3  | 4j   | 0.12  | 0.5  | 0    | 0    | 0.3650(5)   |
| Li4  | 4i   | 0.33  | 0    | 0    | 0    | 0.25        |
| Co1  | 2b   | 1     | 0.5  | 0    | 0    | 0.25        |
| O1   | 8o   | 0.88  | 0.2585(5) | 0.2472(7) | 0 | 0.97(8) |
| O2   | 4i   | 0.55  | 0    | 0    | 0    | 0.3214(5)   |
| O3   | 4j   | 0.80  | 0    | 0    | 0    | 0.1630(6)   |

Fig. 3. NPD pattern of La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$. The measured spectra are displayed with the marker ○, and the calculated spectra (black lines) are superimposed on the measured ones. The differences between the measured and calculated spectra are plotted underneath (blue lines) along with the allowed Bragg positions (vertical green bars).

carried out for La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ is the Rietveld refinement for the NPD profile. The NPD data are essential to refine light elements such as Li and O because their scattering ability of the nucleus is relatively large. Figure 3 shows the NPD spectrum of La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ together with the refined and differential spectra. The orthorhombic $Ammm$ (No. 65) symmetry was applied. Table 2 summarizes the refined structure parameters of La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$. The lattice was refined as $a = 5.352(5) \text{Å}$, $b = 5.355(6) \text{Å}$ and $c = 12.632(1) \text{Å}$, with $R_w = 8.84\%$. The crystal structure of La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ is displayed in Fig. 4(a). The interstitial Li ions together with vacancies are located at $(0, 0, 0.25)$ for oxygen-deficient La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{4.73}$. The structural difference between La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{4.15}$ and La$_{1.24}$Li$_{0.73}$Li$_{0.5}$Co$_{0.5}$O$_{3.23}$ is the Li fraction in the $4i$ interstitial sites. On the other hand, the interstitial Li ions are probably located at $8m(0.25, 0.25, 0.25)$ for oxygen-excess La$_{2.2}$Li$_{1.5}$Co$_{0.5}$O$_{4.25}$, as in the case for oxygen-excess La$_{1.8}$Li$_{0.5}$Co$_{0.5}$O$_{4.02}$.

The ionic conductivity of La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ was $1.5 \times 10^{-5} \text{ S cm}^{-1}$ at 100 °C. Understanding ion diffusion is of fundamental importance in solid state ionics. The MEM using the NPD data was applied to determine the precise nuclear densities. In the MEM analysis, the entropy is given by

$$S = - \sum_{j=1}^{N} \rho_j \ln \left( \frac{\rho_j}{\tau_j} \right).$$

where $N$, $\rho_j$ and $\tau_j$ are the number of grids, normalized nuclear density and default nuclear density, respectively.

Figure 4(b) shows nuclear density distribution at $z \approx 0.25$ calculated using the MEM with the NPD data. The displayed position corresponds to $(0, 0, 0.25)$ [orange spheres in Fig. 4(a)]. Li cations diffused throughout a quasi-one-dimensional pathway along the $b$-axis direction via exchange between interstitial Li and vacancies, as well as La$_{1.24}$Li$_{0.73}$Li$_{0.5}$Co$_{0.5}$O$_{3.23}$. On the other hand, for La$_{1.24}$Li$_{0.44}$Li$_{0.5}$Co$_{0.5}$O$_{3.08}$, a clear diffusion pathway was not visible owing to a small occupancy of Li in the interstitial site. Instead, nuclear density distribution was obscured, in agreement with lower conductivities than La$_{1.24}$Li$_{0.57}$Li$_{0.5}$Co$_{0.5}$O$_{3.15}$ and La$_{1.24}$Li$_{0.73}$Li$_{0.5}$Co$_{0.5}$O$_{3.23}$.

Oxide solid electrolytes have been developed in a span of 15–20 years. We have explored a novel strategy for the design of Li-ion conductors based on a transition-metal oxide, which is strikingly against our common belief that $3d$-electron systems are not suitable materials for solid electrolytes. The conventional design strategy relies on $d^0$ systems, where the $d$ orbitals are empty (zero $d$-electron...
count). As opposite to this view, the most significant difference between our targeted material (3d⁶ band insulator) and general oxide electrolytes is the existence of occupied d orbitals. Paired electrons in the t₂g orbitals are difficult to delocalize, resulting in a reduction in electronic conductivity, as is established for band insulators. Furthermore, Li-ion conduction was achieved by the defect chemistry approach, maintaining the electronic insulating state.

4. Conclusion

Systematic study was performed on Laₓ₋₁LiₓLiₓ₀.₅Co₀.₅O₄₋₀.₂₅, but unfortunately, the system was a mixed ion/electron conductor. We next discovered the Laₓ₋₁₋₂Liₓ₀.₅Liₓ₀.₅Co₀.₅O₄₋₀.₁₅ electrolyte as a leading contender. We applied the MEM to the NPD data. As a result, atomic-scale lithium diffusion along the b-axis direction was clearly visualized at 100 °C for the oxygen-deficient system. Our achievements will play a seminal role in expanding the frontiers of late transition-metal oxide electrolytes. Also, the MEM approach is expected to be effective for three-dimensional visualization of diffusional pathways of anions in next-generation batteries such as fluoride-ion batteries, which is currently underway.

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