Electronic Supplementary Information

Operando structural study of non-aqueous Li–air batteries using synchrotron-based X-ray diffraction

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Section 1. LAB cell assembly and experimental set-up for operando SR-XRD measurements

Figure S1. Schematic view of Li-air battery cell assembly.

Figure S1 shows the schematic view of lithium-air battery (LAB) cell assembly. The LAB cell was designed to prevent any unintended exposure to the ambient environment during discharge/charge processes. LAB cell consists of top and bottom parts, (+) (-) electrodes, Teflon spacer, washer, curved washer as well as a conductive porous cathode, an electrolyte, a separator, and a Li foil anode. All gaps between top part, (-), (+) electrodes, and bottom part are sealed with O-rings, that guarantees air tightness. It was confirmed by checking no pressure change for 5 hours or more after filling an Ar gas up to 0.3 MPa in the LAB cell. The windows of top and bottom part were Al-coated Kapton. The bottom part was designed to provide oxygen.
Figure S2. Experimental set-up. (A) Synchrotron-based *operando* XRD study of a lithium–air battery cell under discharge/charge processes. (B) Enlarged view of Fig. S2(A).

Figure S2 shows the experimental set-up used for synchrotron-based *operando* XRD measurements, which was developed to allow time-resolved measurements without the requirements of a scattering angle (2θ) scan. Six one-dimensional detectors were asymmetrically arranged in the perpendicular line as shown in Fig. S2(A). A diffraction intensity profile can be simultaneously recorded in the 2θ angular range from 1.63° to 74.37° in a "one shot" measurement using this experimental set-up. The details of this set-up are described in Ref. S1. The water content in the gap space above the cathode, which was experimentally confirmed by measuring the dew point at the downstream of the LAB cell, was kept below 100 ppm by continuously flowing pure (dried) O₂ gas during the measurement.

Section 2. High quality XRD patterns and Rietveld refinement analysis for a discharge product

Figure S3. XRD profile for a fully discharged lithium–air battery (LAB) cell (blue line) and fresh LAB cell (red line). The inset is the XRD pattern obtained by subtracting the XRD profile of the fresh LAB cell, before a discharge process, from that of the fully discharged LAB cell.
Figure S4. Refinements results for a discharge product Li$_2$O$_2$ during (A) discharge and (B) charge processes. The black, red, and blue line represent the measured pattern ($I_{\text{obs}}$), the calculated pattern ($I_{\text{cal}}$), and the difference ($I_{\text{obs}}-I_{\text{cal}}$), respectively. The direction of the arrows represents the flow of time.

Figure S3 shows the collection process used to obtain the XRD pattern of discharge products from the XRD profiles for fully discharged and fresh LAB cells. The red line is the XRD profile for the fresh LAB cell before a discharge process, which includes peaks originating from carbon (current collector,
cathode) and aluminium (window material: Al-coated Kapton). The blue line is the XRD profile for a fully discharged LAB cell, which contained only Li$_2$O$_2$ peaks in addition to the same ones as the red line. Namely, the XRD patterns of crystalline Li$_2$O$_2$ for Rietveld refinement analysis, which is shown in the inset of Fig. S3, can be obtained by subtracting the red line from the blue line.

Figure S4 shows the results of the Rietveld refinement analysis for a discharge product Li$_2$O$_2$ during the operating process. The Bragg R factor ($R_B$), which shows the accuracy of the refinement procedure, is presented in Fig. S5. It is noted that peaks corresponding to the Li anode occasionally appear as indicated by “Li” in Fig. S4(B). In this case, the Rietveld refinement analysis was performed using the pseudo-Voigt (Li$_2$O$_2$) and split Pearson-VII (Li) functions. To compare with the crystalline Li$_2$O$_2$ XRD pattern after full discharge of the lithium-air battery (3.54 mAh/cm$^2$) in the Fig. 3, figure S4 was applied on the same scale (x and y axes) of Fig. 3. Notably, it is noted that no XRD peaks from other reaction products such as Li$_2$O, LiOH, and Li$_2$CO$_3$ with a crystalline phase were found during the operating process.

![Figure S5. $R_B$ factor for Rietveld refinement analysis on the operating process.](image)

**Figure S5. $R_B$ factor for Rietveld refinement analysis on the operating process.**

**Section 3. FWHM comparison of commercial bulk Li$_2$O$_2$ and discharge product Li$_2$O$_2$**

Figure S6 depicts the XRD patterns of commercial bulk Li$_2$O$_2$ and discharge product Li$_2$O$_2$ obtained from the LAB cell. Figure S6 reveals that the full width at half maximum (FWHM) of the XRD peaks of the discharge product in the c-direction are anisotropically broadened compared with those of commercial bulk Li$_2$O$_2$. FWHM and relative intensity ratio values are presented in Table S1.
**Figure S6.** XRD patterns for (A) commercial bulk Li$_2$O$_2$, and (B) discharge product Li$_2$O$_2$.

**Table S1.** FWHM and relative intensity ratio of XRD peaks for commercial bulk Li$_2$O$_2$ and discharge product Li$_2$O$_2$

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<th>hkl</th>
<th>FWHM</th>
<th>Integrated intensity ratio (%)</th>
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<td>Discharge product Li$_2$O$_2$</td>
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<tr>
<td>100</td>
<td>0.100</td>
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Figure S7 shows the variation of relative intensity ratio for 100 and 004 peaks of discharge product Li$_2$O$_2$ on the charge process. The relative intensity ratios have no variation during the operation process, except for the beginning of discharge process.
Figure S7. Variation of relative intensity ratios for 100 and 004 peaks on the charge process

Section 4. FWHM and domain size of crystalline Li$_2$O$_2$ during LAB operation

Table S2. FWHM and domain size ($D$) of crystalline Li$_2$O$_2$ during discharge/charge processes.

<table>
<thead>
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<td>0.6</td>
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<td>(101)</td>
</tr>
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<td>(004)</td>
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<td>(100)</td>
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<tr>
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<td></td>
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</table>
Table S2 lists the FWHM and domain size of crystalline Li$_2$O$_2$ during the operation of the LAB cell. The FWHM of the 100 reflections are sharper than those of the 101 and 004 reflections. This result indicates that the crystalline Li$_2$O$_2$ has an anisotropic morphology.

Section 5. Integrated and normalised areas of crystalline Li$_2$O$_2$ during the discharge process

![Graph showing integrated and normalised areas of Li$_2$O$_2$ peaks during discharge](image)

Figure S8. Integrated and normalised areas of crystalline Li$_2$O$_2$ peaks during the discharge process.

Figure S8 shows the variation of the integrated and normalised areas of crystalline Li$_2$O$_2$ during the discharge process. The integrated and normalised areas of Li$_2$O$_2$ peaks increase linearly without a change of slope irrespective of current density (0.4, 0.6, and 0.8 mA/cm$^2$). From the extrapolation of the curves for the discharge process, the capacity is 0.114 mAh/cm$^2$ when the integrated and normalised area = 0.

Section 6. Estimation of the magnitude of instrumental broadening

Figure S9 shows the variation of the magnitude of instrumental broadening ($\beta_{\text{instrumental}}^2$) as a function of 2θ. In Fig. S5, each point represents the difference between the observed FWHM and theoretical FWHM for a standard powder crystal (CeO$_2$, NIST SRM 674a, 200 nm). From the fitting results obtained using the equation $(\Delta \text{FWHM})^2 = U \tan^2 \theta + V \tan \theta + W$, the magnitude of instrumental broadening was able to be evaluated.
Figure S9. Magnitude of instrumental broadening as a function of 2θ.

Section 7. Lattice constants of crystalline Li$_2$O$_2$ during the discharge/charge processes

Figure S10 illustrates the variation of lattice constants of crystalline Li$_2$O$_2$ during the operation. The lattice constant of the $a$-axis has no variation during the discharge process. However, the lattice constant of the $c$-axis looks to increase gradually from 2.28 mAh/cm$^2$ during the charge process. This tendency has not concluded because of the large error (Fig. S5) for Rietveld refinement analysis that originates from the weak XRD intensity for crystalline Li$_2$O$_2$ in this charge region.

Figure S10. Lattice constants of crystalline Li$_2$O$_2$ during the discharge/charge processes.
Section 8. $O_2$, $CO_2$ evolution during the charge process

Figure S1. $O_2$, $CO_2$ evolution versus (A) cell charge and (B) cell voltage during a charge process for a Li-air battery cell. (C) is the enlargement of $CO_2$ part in (B).

Figure S11 shows the typical data of differential electrochemical mass spectroscopy during a charge process (CC-mode, the operating current was 100 $\mu$A) for a tetraethylene glycol dimethyl ether (TEGDME)-based Li-air battery cell. Those data were measured using the same system as that described in Ref. S2. It is found from Fig. S11(A) that $O_2$ is dominantly exhausted almost in the whole range of charge process except of its end region. Fig. S11(B) is a graph chart replotted by converting amount of charge to voltage using the charge profile shown in Fig. S11(A) and rescaling the emission rate to logarithmic scale. At the beginning and middle of the charge process, the emission rate of $CO_2$ is in the order of one thousandth of $O_2$. The $CO_2$ in this region may be a background, irrelevant to the electrochemical reaction in Li-air battery cell, generated by a reaction of residual carbon and large
amount of oxygen introduced to an ionization chamber of a mass spectrometer. On the other hand, the emission rate of CO₂ drastically increases, in contrast to the decrease of O₂ above ~4 V. This fact is very clear when the CO₂ emission rate is replotted in linear scale and enlarged as shown Fig. 11S(C). This phenomenon must be originated from the electrochemical reaction in Li-air battery cell, in which decomposition of the solvent or carbon cathode is thought be involved. And thus, it is natural to think that such change in the way of the electrochemical reaction may be related to the nonlinear decrease with two steps of the peak intensity for the 100 reflection (Fig. 2D) during the charge process, the increase in the domain size for the 100 reflection (Fig. 5) and the lattice constant of the c-axis (Fig. S10) in the latter half of the charge process, although the side reaction product such as LiOH is not apparently detected.

Reference
