

Supplementary Information for

**Reaction and degradation mechanism in all-solid-state lithium-air
batteries**

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Ideal reaction mechanism.

Lithium ions and electrons produced from lithium anode move through the electrolyte and the external circuit, respectively, and meet again together with oxygen from the air at the cathode reactive sites, where they are stored in the form of compounds composed of lithium and oxygen, which are expected to be Li_2O_2 , during the discharge process. Then, the discharge products are decomposed and the opposite reaction takes place during the following charge process.

Preparation of $\text{Li}_{1+x}\text{Al}_y\text{Ge}_{2-y}\text{P}_3\text{O}_{12}$ (LAGP) solid electrolyte.

The LAGP powder for the air electrode and the LAGP pellet for the electrolyte layer were prepared by the conventional solid-state reaction. Reagent-grade chemicals of Li_2CO_3 (Wako Pure Chemical Industries, Ltd., 99 %), Al_2O_3 (Kojundo Chemical lab. Co., Ltd, 99.999 %), GeO_2 (Kojundo Chemical lab. Co., Ltd, 99.995 %) and $(\text{NH}_4)\text{H}_2\text{PO}_4$ (Wako Pure Chemical Industries, Ltd., 99 %) were used as starting materials. The starting materials was mixed by using a planetary ball milling apparatus (Pulverisette 5, Fritsch). The mixed powder was heated at 600 °C for 1 h in an oxygen atmosphere. The heated powder was pulverized by ball milling and then heated again at 900 °C for 6 h in an oxygen atmosphere. The heated powder was pulverized again. All the milling was wet type milling using ethanol media. The obtained LAGP powder was used for the air electrode. The LAGP pellet for the solid electrolyte layer was prepared from LAGP powder. LAGP powder was pressed

into pellets and sintered at 900 °C for 6 h in an oxygen atmosphere. The thickness of the obtained LAGP pellets was about 1 mm. The lithium ion conductivity is about $2 \times 10^{-4} \text{ S cm}^{-1}$. The temperature dependence of the conductivity is shown in Fig. S2. The calculated activation energy was 30.9 kJ mol^{-1} , which is consistent with the reported value. (Ref: X. Xu et al., *J. Am. Ceram. Soc.* **2007**, *90*, 2802-2806.)

All-solid-state Li-O₂ cell assemble

The air electrodes were fabricated on the LAGP pellet by the following procedure. 2 mg of CNT and 40 mg of LAGP powders were mixed in an agate mortar. The mixture was dispersed in 600 mg ethanol solution. A drop of the solution was put on the LAGP pellet and dried at room temperature. The air electrode deposited on the LAGP pellet was heated at 700°C for 10 min in an Ar atmosphere. After sintering, the air electrode combined with the solid electrolyte layer was obtained. The mass and area of the air electrode were about 0.5 mg and \varnothing 6 mm. On the other side of the LAGP pellet, a Li anode was put into contact with the LAGP pellet by a thermal adhesion process. A Li disc was melted on the LAGP pellet and a well contacted Li anode with the LAGP pellet was obtained. Then the Li anode was sealed with a plastic film to avoid the exposure to the air atmosphere. An Al mesh and a Cu mesh were used as current collectors for the cathode and the anode, respectively. The

laminate-type cell was sandwiched by two plastic plates and held by a screw clamp. All processes were performed in an Ar-filled glove box.

Electrochemical tests.

Electrochemical tests were conducted at room temperature using a charge-discharge measuring device (HJ1001SD8; Hokuto Denko Co.). The current density and cell capacity were normalized by the weight of CNT calculated from the weight of air electrode after sintering and the mixing ratio of LAGP and CNT.

Wet oxygen condition.

The cell was put into a bottle with electrical cables and connectors for the gas flow channels, and then the bottle was sealed. The cell set-up is illustrated in Fig. S3 (ESI). Pure oxygen gas was flowed through ultrapure water, which was first bubbled with nitrogen gas for 2 hours to remove CO₂ as much as possible. The oxygen flow rate was adjusted to 100 ml min⁻¹. The relative humidity (RH) was about 80-90 %.

Analysis.

Fourier transform infrared (FT-IR) measurements were conducted with the KBr pellet method by using a JASCO instrument of FT/IR-6200. The air electrode powder was scraped from the cell and

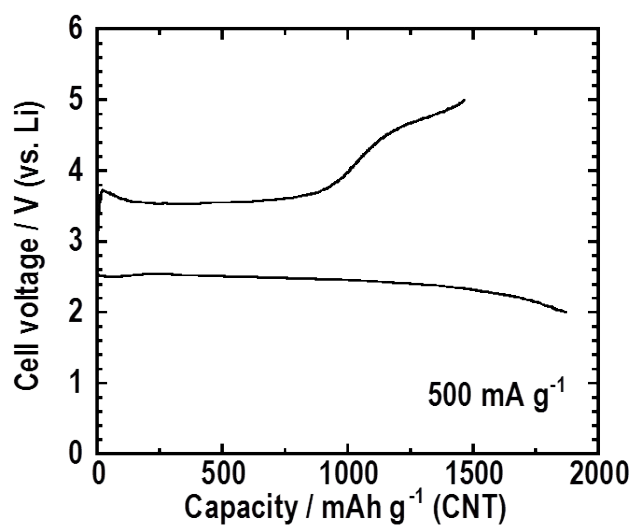
mixed with KBr in the glove box. As the reference data, reagents of Li_2O_2 , Li_2CO_3 , and LiOH were used. The mixture of the objective substance and KBr was pressed into pellet under vacuum. X-ray diffraction (XRD) patterns were measured by using a device (Bruker D8 Advanced diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation). The samples, which should be avoided from the exposure to the ambient air, were covered with a Kapton® film. Raman spectra were obtained by using a Raman spectrophotometer (Ventuno21, JASCO). The cross-sectional images of the air electrode on LAGP pellet were obtained by using field emission scanning electron microscopy (FE-SEM : Gemini Supra). Transmission electron microscopy-electron energy-loss spectroscopy (TEM-EELS) and high-angle annular dark field-scanning TEM (HAADF-STEM) measurements were performed by using Tecnai G2 F20. The air electrode particles were scraped from the cell and mounted on a Cu grid.

Discussion about TEM-EELS

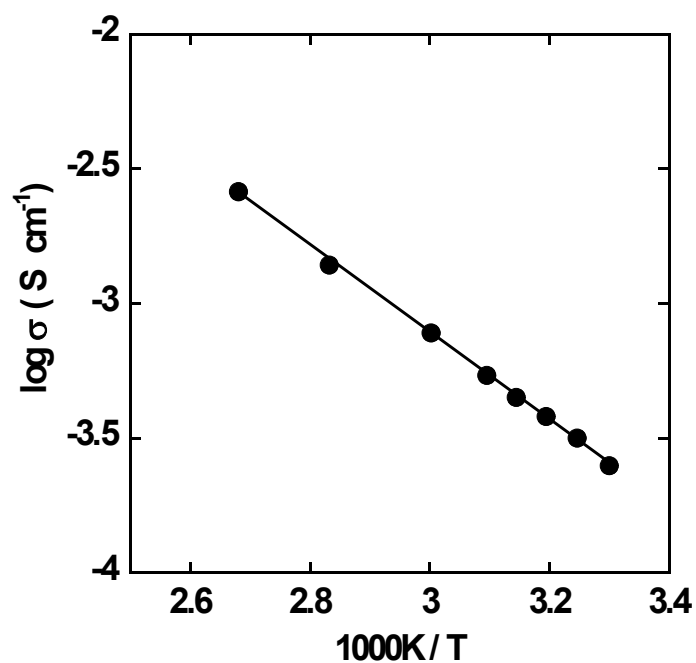
Fig. 3a and b show the high-angle annular dark field-scanning TEM (HAADF-STEM) images of the particles scraped from the air electrode before and after discharging. The clear white particles of LAGP and the gray particles of the CNTs were observed in both images before and after discharging. Areas 1-4 denote the areas monitored by EELS and each Li K-edge EELS spectra is shown in Fig. 3c. The EELS spectra of the LAGP and CNT particles before discharging were collected from Area

1 and Area 2, respectively. No peak was observed for both Area 1 and Area 2. The reason that there was no peak even for the LAGP particles containing a lithium constituent before discharging is due to the weak intensity of the Li K-edge peak and the too large size of the LAGP particles for transmission-type EELS. After discharging, substances covering the LAGP particles with a different contrast to the LAGP particles were observed. EELS spectra of this substance and CNT particles after discharging were measured from Area 3 and Area 4, respectively. Two peaks derived from the discharge products were observed for both areas. This indicates that the discharge products were formed on both the LAGP and CNT particles.

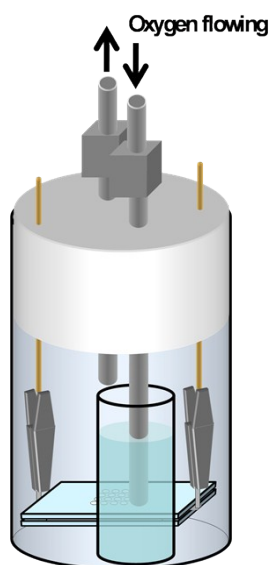
Supplementary Figures



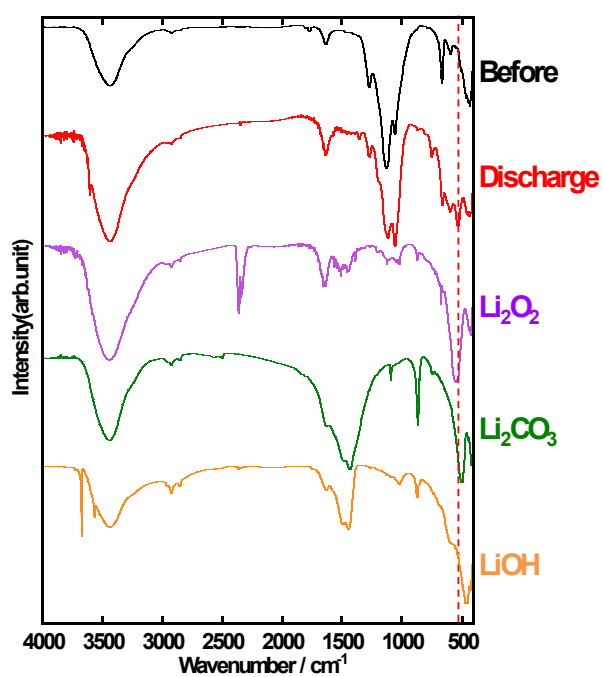
Supplementary Figure S1 Discharge-charge curves of the all-solid-state Li-air cell at a current density of 500 mA g^{-1} in a laboratory atmosphere.



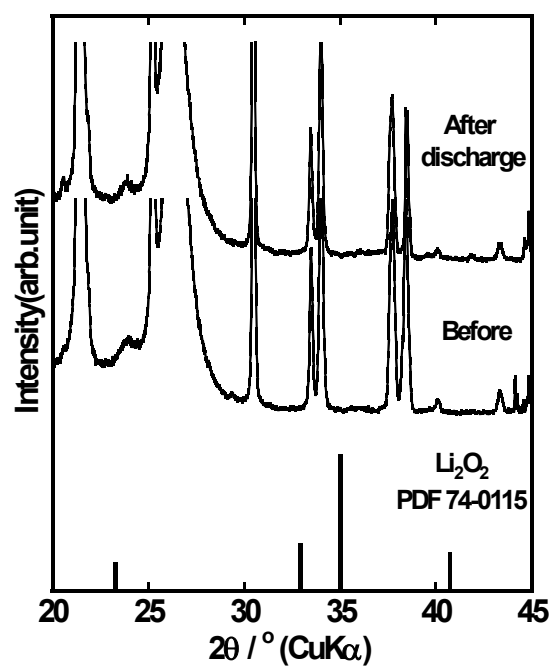
Supplementary Figure S2 Temperature dependence of the conductivity for the prepared LAGP pellet.



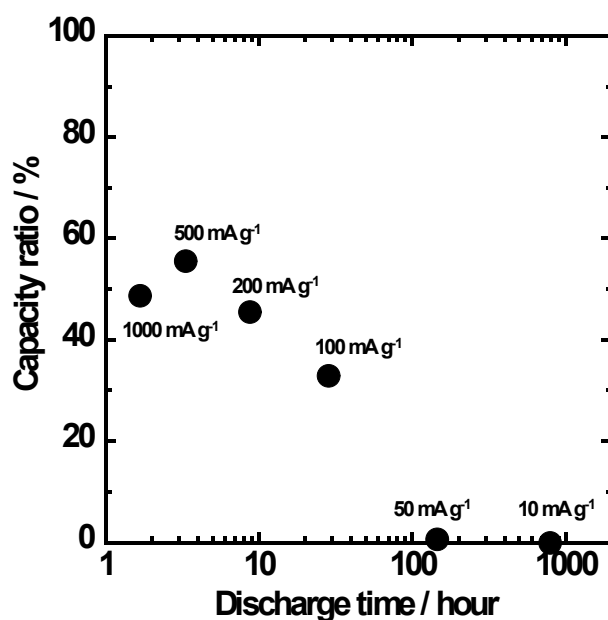
Supplementary Figure S3 Illustration of the cell set-up for the wet oxygen condition.



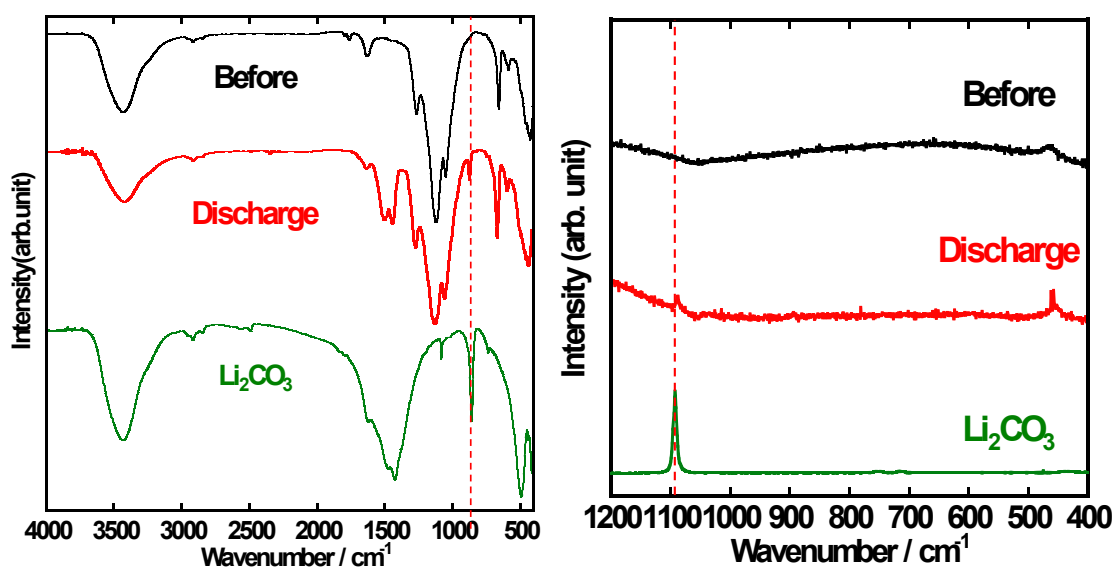
Supplementary Figure S4 FT-IR spectra of reagents (Li_2O_2 , Li_2CO_3 , LiOH) and the air electrodes before and after discharge in a wet oxygen condition (RH : 80-90%).



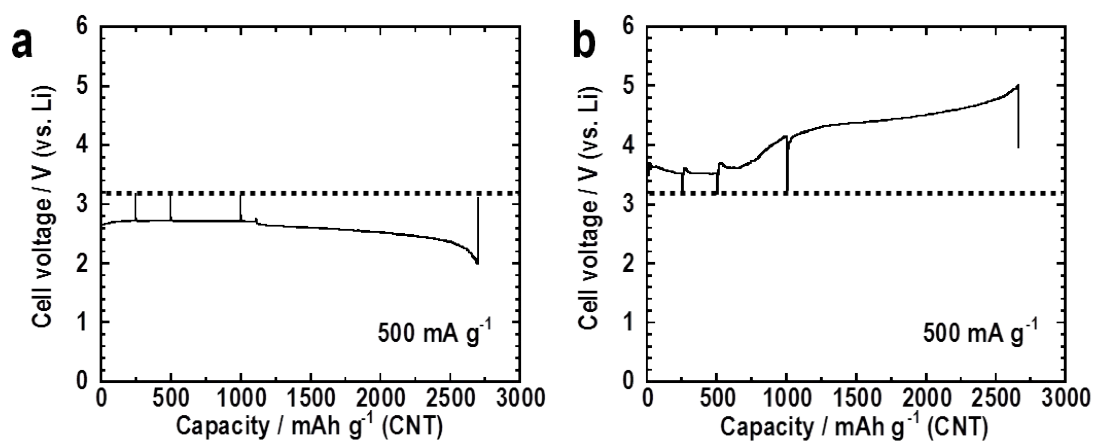
Supplementary Figure S5 XRD patterns of the air electrodes before and after discharge in a wet oxygen condition (RH : 80-90%).



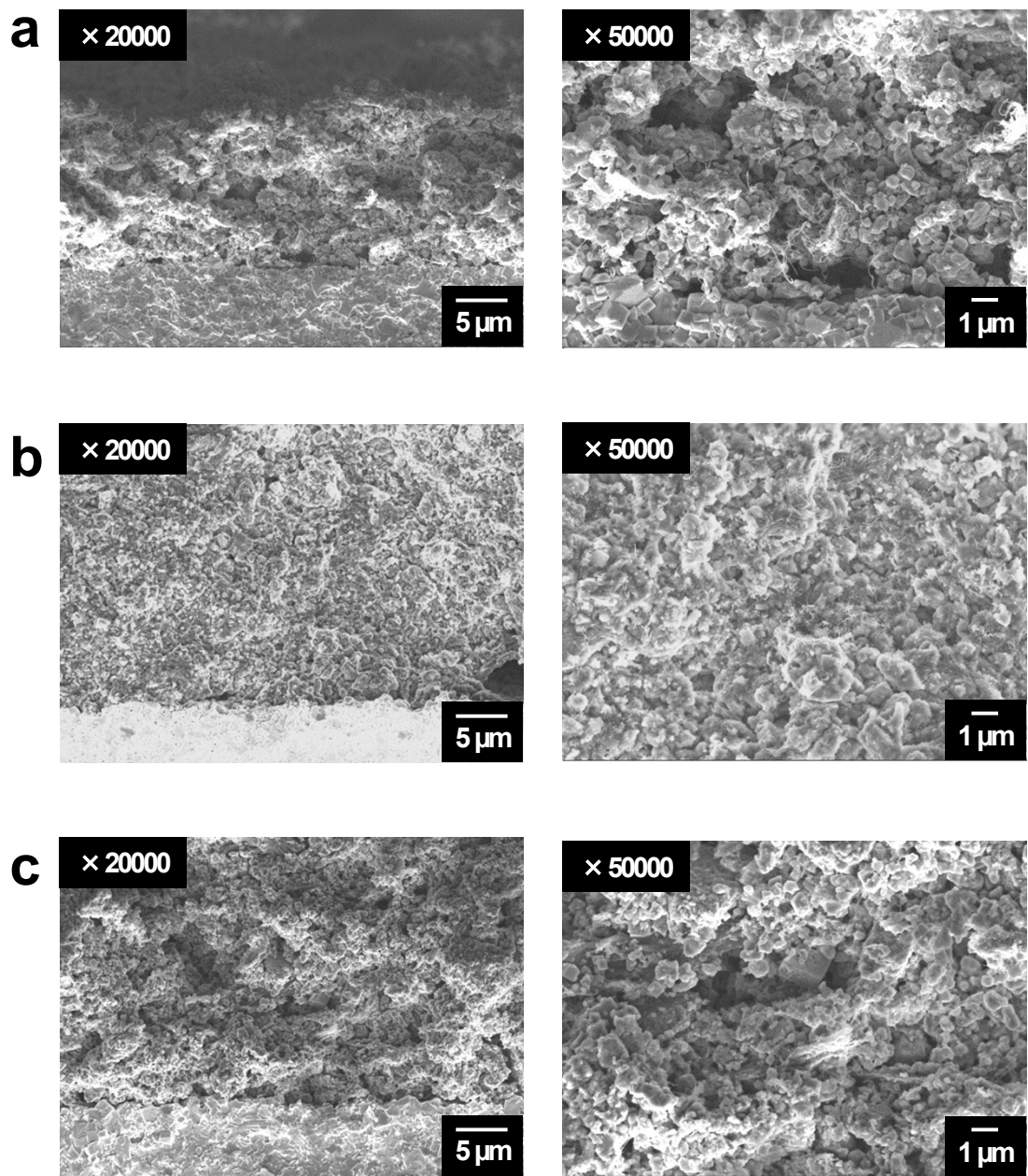
Supplementary Figure S6 The proportion of the charge capacity of the first plateau to the discharge capacity as a function of the discharge time at several current densities. The discharge-charge measurements were conducted in a laboratory atmosphere.



Supplementary Figure S7 FT-IR and Raman spectra of Li₂CO₃ reagent and the air electrodes before and after discharge in a laboratory atmosphere (RH : 20-30 %).



Supplementary Figure S8 OCV measurements of the all-solid-state Li-air cell during (a) discharging and (b) charging.



Supplementary Figure S9 Cross-sectional SEM images of the air electrode (a) before discharge, (b) after discharge and (c) after charge.