

*Supplementary Information for*

## **Highly Efficient Li<sub>2</sub>O<sub>2</sub> Oxidation System in Li-O<sub>2</sub> Batteries**

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### **1. Instruments.**

Battery characteristics were determined using charge-discharge cycling apparatus (ASKA electronic) at 25 °C, and the current density was 0.02 or 0.1 mA/cm<sup>2</sup>. Cyclic voltammograms were acquired using a IviumStatXR (Hokuto Denko) with a three-electrode cell (WE: glassy carbon (3 mm diameter), CE: Pt wire, RE: Li/Li<sup>+</sup>) at 25 °C. Scanning Electron Microscopy (SEM) images were obtained using SEM system (Hitachi high-technologies, S-4300) at an acceleration voltage of 1 kV. The samples were transferred from a glove box to the SEM chamber using a closed vessel to avoid exposure to the air.

### **2. Materials.**

All materials were used as purchased without further purification and stored under argon. Lithium foil (0.4 mm) and conditioned electrolyte containing 1 M LiTFSI in the mixed solvent of ethylene

carbonate and diethyl carbonate (3/7, v/v) were purchased from Honjo Metal (Osaka, Japan) and Kishida Chemical Co., Ltd. (Osaka, Japan), respectively. Lithium bis(tetrafluoromethanesulfonyl)imide (LiTFSI) (99.8%, water content < 0.01%) and 1-methoxy-2,2,6,6-tetramethylpyridine-1-oxyl (MeO-TEMPO) were obtained from Tokyo Kasei (Tokyo, Japan). *N,N*-Diethyl-*N*-methyl-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl) imide (DEME-TFSI) (water content < 0.02%) and acetonitrile (water content < 0.001%) were purchased from Kanto Chemical (Tokyo, Japan), and Wako (Osaka, Japan), respectively. Ketjen black (ECP600JD) and PTFE binder (F104) were obtained from Mitsubishi Chemical (Tokyo, Japan) and Daikin Industries (Osaka, Japan), respectively. Separator film (25  $\mu\text{m}$  of thickness, E25MMS) and carbon paper (TGP-H-060) were purchased from Tonen Chemical (Tokyo, Japan) and Toray Industries, Inc. (Tokyo, Japan), respectively. Li ion conducting glass ceramics (LIC-GC, 0.15 mm of thickness) was obtained from Ohara Inc. (Kanagawa, Japan). Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) was prepared and its Nitroxide (NO•) concentration was determined according to the previously reported method.<sup>1,2</sup> The nitroxide concentration and the specific capacity of PTMA used in this report was 91.6 %, 102.2 mAh/g (based on PTMA), respectively.

### 3. Battery test.

A typical experimental procedure is described below. Sheet type cathodes (**KB**) were prepared by mixing uniformly Ketjen-black (90 wt%) and PTFE binder (10 wt%) in a mortar, and stretched with a thickness of 80  $\mu\text{m}$  and a diameter of 18 mm. Carbon paper cathodes (**CP**) with a thickness of 190  $\mu\text{m}$  was used in a diameter of 20 mm. 200  $\mu\text{L}$  of 0.5 M LiTFSI in DEME-TFSI with or without 0.02 mmol of MeO-TEMPO (0.1 M) was added into the cell as electrolyte and O<sub>2</sub> or Ar gas (0.15 MPa) was introduced into a 50 mL cylinder which was attached to the cell. Li metal and 1 M LiTFSI in the mixed

solvent of ethylene carbonate and diethyl carbonate (3/7, v/v) were used as the anode and its electrolyte, respectively. Li ion-conducting glass ceramics (LIC-GC) (Ohara) with a 0.15 mm of thickness were used as the separators and were located between the cathode and anode chambers. The voltage range for cycling is 2.0 – 4.0 V and a current density is 0.02 and 0.1 mA/cm<sup>2</sup> for **CP** and **KB**, respectively.

#### **4. Preparation of the samples for SEM measurement.**

**CP** extracted from the cells were immersed in anhydrous acetonitrile for 24 h and washed with acetonitrile for 3 times to remove electrolytes, and then dried in vacuo at room temperature for 5 h. After the preparation, the samples were stored under Ar until the measurement.

#### **5. Chemical regeneration of the discharged cathode.**

Following experimental procedure was performed in the glove box. After the first discharge of Li-O<sub>2</sub> cell, the electrolyte was exchanged with the electrolyte including 0.006 mmol of MeO-TEMPO<sup>+</sup> which was prepared using the other cell under Ar in advance. The cell was allowed to stand at 25 °C for 3 hr. After that, the electrolyte was exchanged and rinsed twice with the electrolyte not including MeO-TEMPO<sup>+</sup>. The second discharge of Li-O<sub>2</sub> cell was performed under O<sub>2</sub> with the newly introduced electrolyte.

#### **6. Estimation of discharge capacity.**

2-Electron reduction is observed with MeO-TEMPO<sup>+</sup> in DEME-TFSI at the voltage range of 2.0 – 4.0 V vs. Li/Li<sup>+</sup> as shown in Fig. S3. Therefore, the discharge capacity of Li-O<sub>2</sub> battery and the 2-electron reduction capacity of MeO-TEMPO<sup>+</sup> were overlapped in Fig. S4. The independent discharge capacities of the Li-O<sub>2</sub> battery were estimated as described below. The capacities of the first plateau at

3.4 V (MeO-TEMPO<sup>+</sup> → MeO-TEMPO) were estimated from the obtained capacities in the voltage range of 2.5 – 3.6 V and the twice the values of these capacities were estimated as the 2-electron reducing capacity of the MeO-TEMPO which was active in the cell. The discharge capacities of Li-O<sub>2</sub> battery shown in Fig. 4A were estimated by subtracting the 2-electron reducing capacity assigned to MeO-TEMPO<sup>+</sup>.

### 7. Estimation of the activity of MeO-TEMPO before and after *chemical regeneration*.

100 μL of the electrolyte including 0.05 M MeO-TEMPO was introduced into the cathode rooms of the cells, which have the same constitution used for the battery tests, before and after chemical regeneration. After the charging to 4.0 V, the discharge tests were performed to estimate the activity of MeO-TEMPO in the each cells. These series of discharge and charge operations were performed at the current density of 0.01 mA/cm<sup>2</sup> under Ar.

### 8. Investigation of the deactivation of TEMPO structures.

For the further investigation of the deactivation of MeO-TEMPO during discharge-charge cycles in the Li-O<sub>2</sub> batteries, the retention rate of redox activity of TEMPO structure was monitored after discharge and charge. In this experiment, **KB** including 20 wt% of PTMA were applied because PTMA, which have TEMPO structure in the side chain, was insoluble in the electrolyte and enables to be anchored in **KB**. PTMA is also rechargeable with specifically high reversibility and efficiency in the potential range of 3.0 – 3.85 V under Ar or O<sub>2</sub> atmosphere (Fig. S8). However, in the case of Li-O<sub>2</sub> battery cycles, the area of the PTMA reduction was completely disappeared in the 2nd discharge curve (Fig. S9(b)). This result indicates that the deactivation of PTMA was accompanied with the discharge or charge reaction of Li-O<sub>2</sub> battery in a similar way of the deactivation of MeO-TEMPO in the

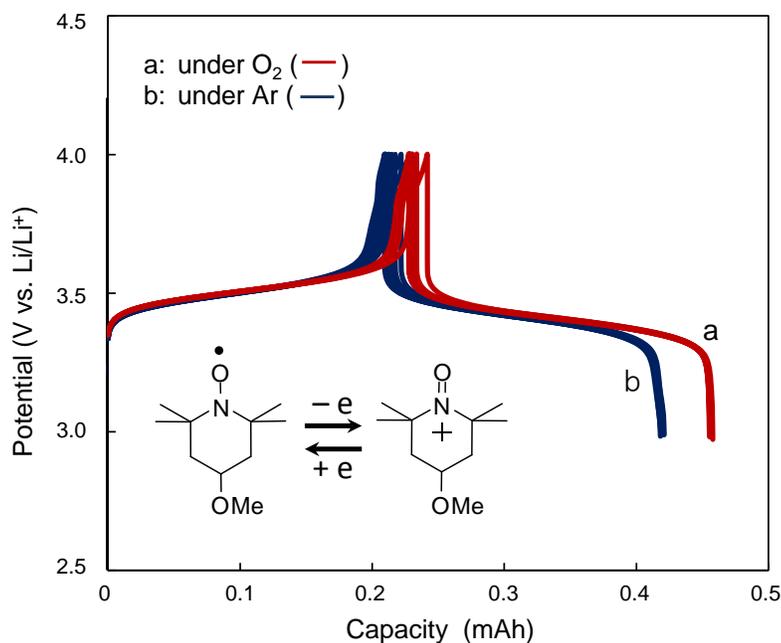
conventional Li-O<sub>2</sub> battery system. In the following investigation, we explored whether discharge or charge was the trigger process of the deactivation as described below. The discharged **KB** including PTMA were immersed in water for 1 h and washed with acetonitrile for 3 times to remove the discharge product and electrolytes from the **KB**, and then dried in vacuo at room temperature for 20 h. After the preparation, the cathode, which experienced the 1st discharge process, was constructed into another cell to evaluate the activity of PTMA. The discharge curve of PTMA obtained under Ar indicated that 80 % of the original capacity was retained (Fig. S9(c)). The difference between sample (b) and (c) was that the sample (b) experienced the 1st discharge-charge cycle and the sample (c) was used only for the 1st discharge process. These results clearly show that the deactivation of TEMPO structure is mainly associated with the charge process of Li-O<sub>2</sub> batteries.

The subsequent investigation revealed that this deactivation occurs when TEMPO structures are directly contacted with the cathode of Li-O<sub>2</sub> batteries. The **KB** including PTMA was placed in the Li-O<sub>2</sub> cell separately from the cathode for Li-O<sub>2</sub> battery reactions with separator film. After the first discharge-charge cycle, the **KB** including PTMA was taken off from the cell and placed in a newly constructed cell. The charge-discharge curves of the new cell indicated that the activity of TEMPO structures retained even though the sample experienced both of discharge and charge process of Li-O<sub>2</sub> battery in the electrolyte (Fig. S10). These results reveal that the parasitic reactions of the charge process, which induces the deactivation of TEMPO structures, surely occurs on the surface of the carbon cathode.

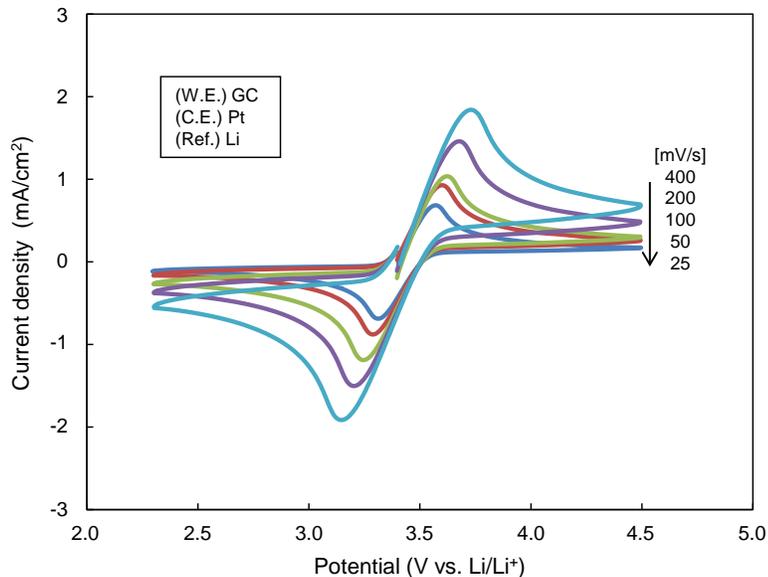
## 9. References.

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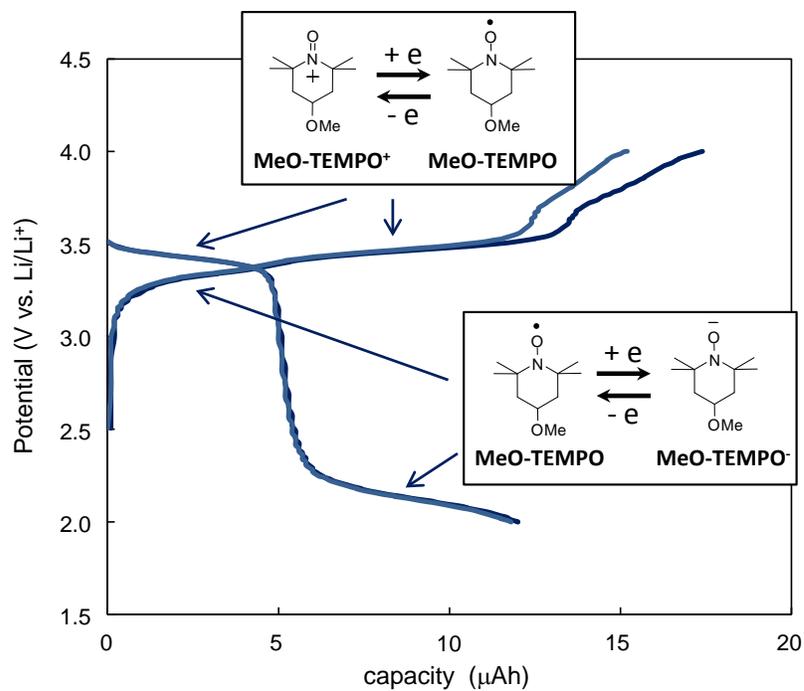
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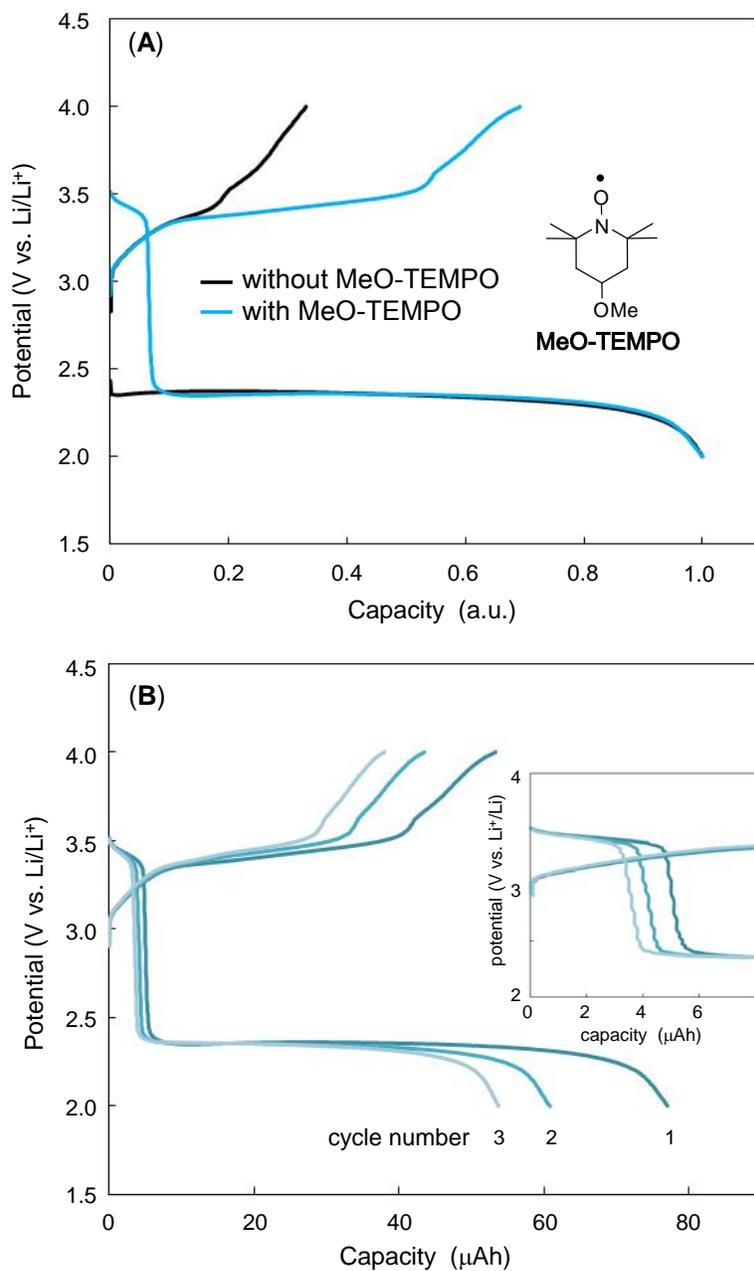
**Fig. S1.** Discharge-charge curves of the solution of MeO-TEMPO (0.1 M, 200 mL) in 0.5 M LiTFSI /DEME-TFSI obtained under Ar (a) and O<sub>2</sub> (b) at 25 °C (0.05 mA/cm<sup>2</sup>). **CP** was used as the cathode.



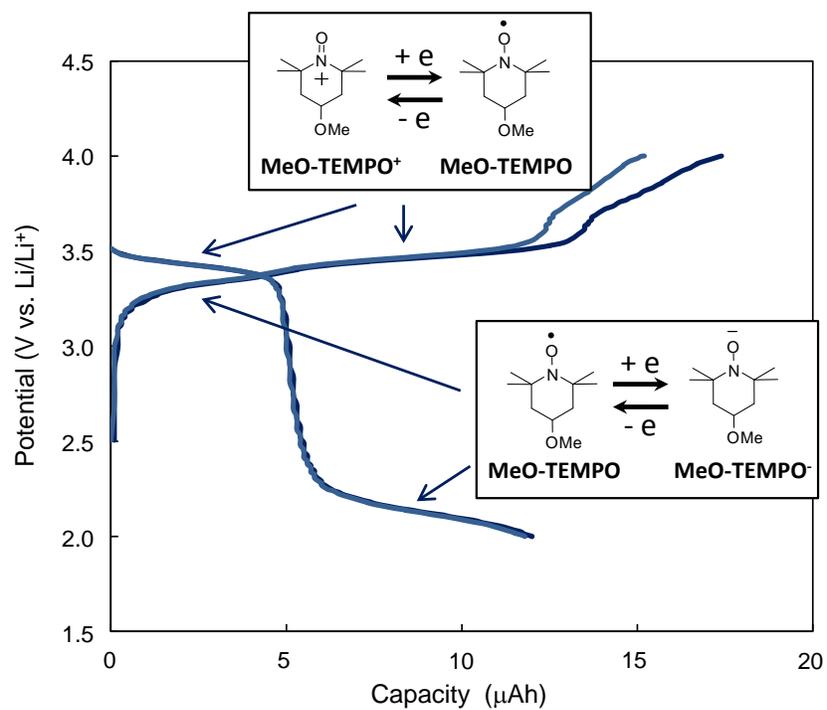
**Fig. S2.** Cyclic voltammograms of 0.1 M MeO-TEMPO in 0.5 M LiTFSI /DEME-TFSI with a glassy carbon electrode at 25 °C measured under Ar. The voltage range was 2.3 V to 4.5 V (vs. Li/Li<sup>+</sup>) and the sweep rates were 25, 50, 100, 200 and 400 mV/s.



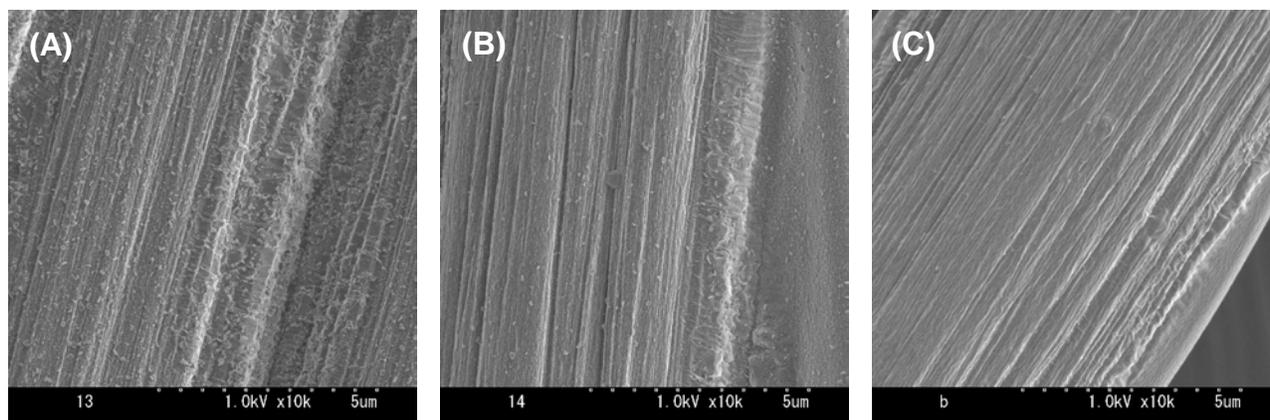
**Fig. S3.** Discharge-charge curves ( $0.02 \text{ mA/cm}^2$ ) of  $0.005 \text{ M}$  MeO-TEMPO in  $0.5 \text{ M}$  LiTFSI /DEME-TFSI ( $200 \text{ mL}$ ) at  $25 \text{ }^\circ\text{C}$  under Ar.



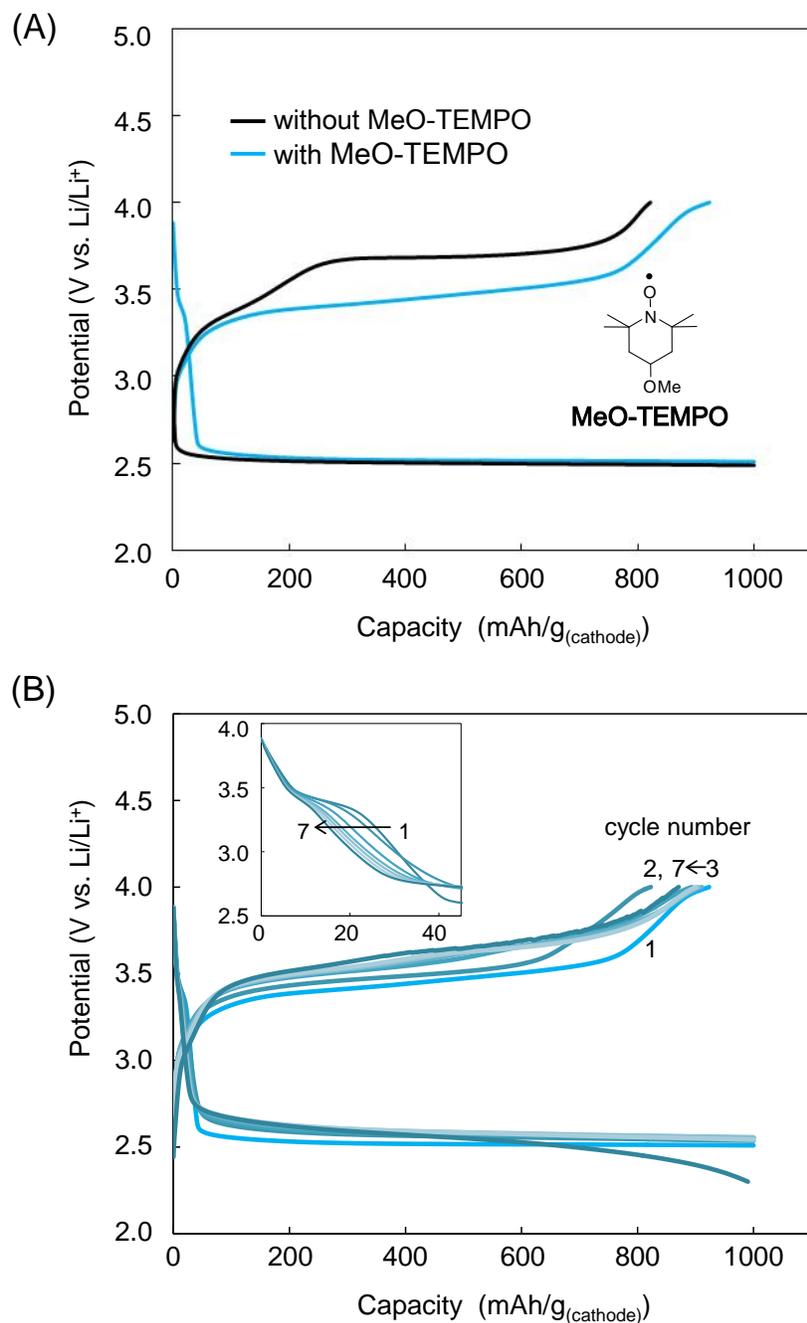
**Fig. S4.** Discharge-charge curves ( $0.02 \text{ mA/cm}^2$ ) of Li-O<sub>2</sub> cell with and without 0.005 M MeO-TEMPO in 0.5 M LiTFSI / DEME-TFSI at 25 °C. (A) The discharge-charge curves of the first cycle. (B) The discharge-charge curves with MeO-TEMPO. The inset figure is the extended version of (B).



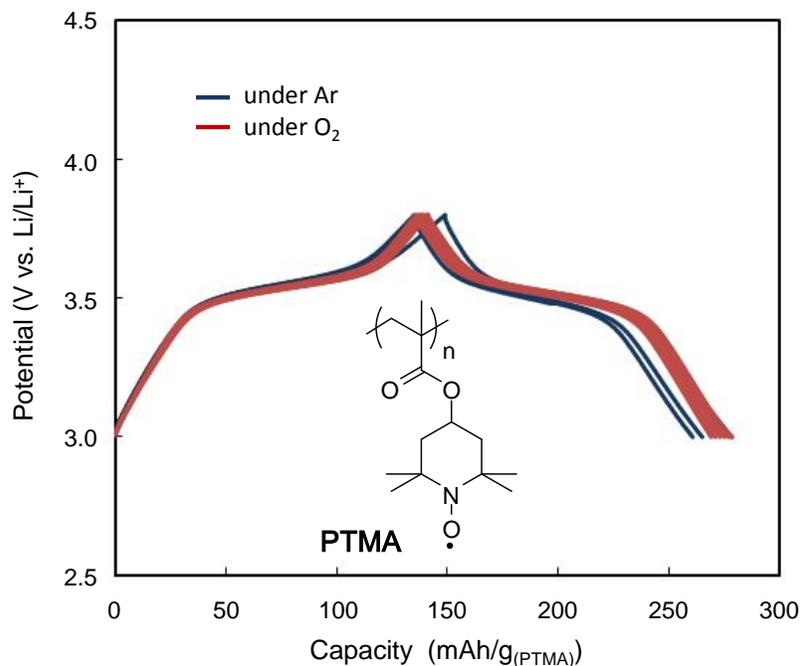
**Fig. S5.** Discharge-charge curve of Li-O<sub>2</sub> cell with 0.005 M MeO-TEMPO in 0.5 M LiTFSI / DEME-TFSI at 25 °C. Applied current densities were 0.02 and 0.005 mA/cm<sup>2</sup> for discharge and charge, respectively.



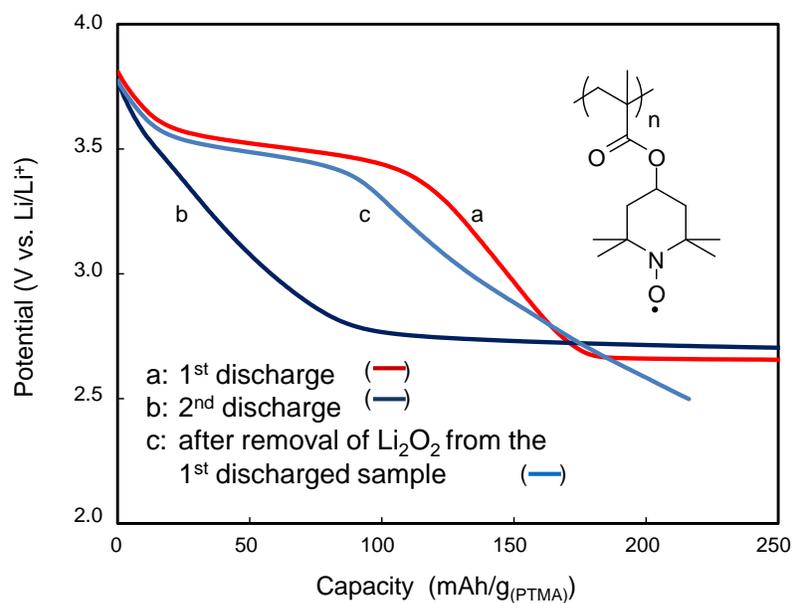
**Figure S6.** SEM images of discharged CP obtained before (A) and after *chemical regeneration* (B) and pristine state (C).



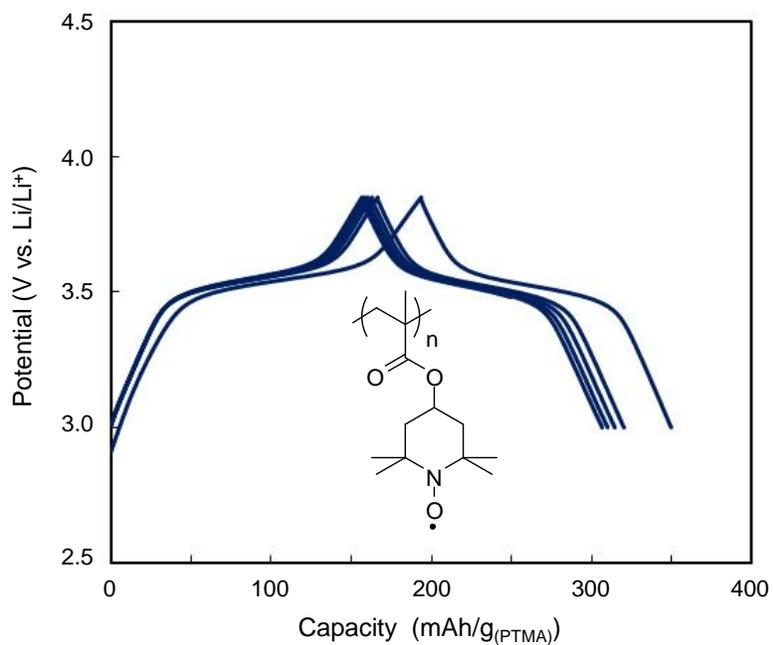
**Fig. S7.** Discharge-charge curves ( $0.1 \text{ mA/cm}^2$ ) of Li-O<sub>2</sub> cell with and without 0.1 M MeO-TEMPO in 0.5 M LiTFSI / DEME-TFSI at 25 °C. **KB** was used as the cathodes. (A) The discharge-charge curves of the first cycle. (B) The discharge-charge curves with MeO-TEMPO. The inset figure is the extended version of (B).



**Fig. S8** Discharge-charge curves of the **KB** including 20 wt% of PTMA obtained in 0.5 M LiTFSI / DEME-TFSI under Ar and O<sub>2</sub> at 60 °C (0.1 mA/cm<sup>2</sup>).



**Fig. S9.** The discharge curves of 20 wt% of PTMA in **KB** obtained in 0.5 M LiTFSI / DEME-TFSI at 60 °C (0.1 mA/cm<sup>2</sup>). 1st (a) and 2nd (b) discharge curves measured under O<sub>2</sub> and the discharge curve obtained under Ar after the removal of Li<sub>2</sub>O<sub>2</sub> with water from the 1st discharged sample (c).



**Fig. S10.** Discharge-charge curves of the sample including PTMA obtained in 0.5 M LiTFSI / DEME-TFSI under Ar at 60 °C (0.1 mA/cm<sup>2</sup>). Before this experiment, the sample experienced 1 cycle of discharge-charge under O<sub>2</sub> without any contact with the cathode of the cell.