Supporting Information

Quantitation of Li_2O_2 Stored in Li-O_2 Batteries Based on Reaction with an Oxoammonium Salt

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1. Instruments.

IR spectra were taken on a FT-IR spectrometer (AVATAR 360, Nicolet) with diamond ATR prism. Absorption spectra were measured in a 1.0- or 5.0-mm quartz cell on a UV-3600·ISR-3100, Shimadzu spectrophotometer. Elemental analysis was performed by Toray Research Center, Inc. (Tokyo, Japan). Battery evaluation was carried out by charge-discharge cycling apparatus (ASKA electronics) at 60˚C, and the current density was 0.1 mA/cm^2. GC-MS measurements were performed with an Agilent GSLJ9810 gas chromatograph equipped with a thermal conductivity detector using an Agilent J&W HP-PLOT Q column and argon gas was used as the eluent at a flow rate of 18.5 mL/min.

2. Materials.

Li_2O (97%), Li_2O_2 (90%), Li_2CO_3 (> 99%), and LiOH (98%) were obtained from Aldrich and stored under argon. Anhydrous acetonitrile (water content < 0.001%), anhydrous dimethyl sulfoxide (DMSO, water content < 0.005%), and anhydrous chloroform (water content < 0.001%) were purchased from Wako (Osaka, Japan) and stored under argon. Diethyl ether and aqueous $HClO_4$ (60 wt%) were obtained from Wako. Lithium bis(tetrafluoromethanesulfonyl)imide ($LiNTf_2$) (99.8%, water content < 0.01%) and Lithium foil (0.4 mm) were purchased from Kishida (Osaka, Japan) and Honjo Metal (Osaka, Japan), respectively, and stored under argon. Aqueous NaOCl (8.5-13.5 wt%) and 2,2,6,6-tetramethylpyridine-1-oxyl were obtained from Nacalai tesque (Kyoto, Japan) and Tokyo Chemical Industry (Tokyo, Japan), respectively. *N*,*N*-Diethyl-*N*-methyl-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-NTf_2) (water content < 0.02%) was purchased from Kanto Chemical (Tokyo, Japan) and stored under argon. Ketjen black (ECP600JD) and PTFE binder (F104) were obtained from Mitsubishi Chemical (Tokyo, Japan) and Daikin Industries (Osaka, Japan), respectively. Separator film (25 μm of thickness, E25MMS) was purchased from Tonen Chemical (Tokyo, Japan). $TEMPO^+ClO_4^-$ was prepared according to the previously reported method.[1]

Spectroscopic data of $TEMPO^+ClO_4^-$. IR (ATR, cm^{-1}): 1624 ($\nu_{N=O}$). Anal. Calcd (%) for ($C_9H_{18}O_5NCl$): C, 42.28; H, 7.10; N, 5.48. Found (%): C, 42.22; H, 6.98; N, 5.46.

3. Cell construction.

Sheet type cathodes were prepared by mixing uniformly Ketjen-black (90 wt%) and PTFE binder (10 wt%) in a mortar, and stretched with a thickness of 80 μm and a diameter of 18 mm. Li foil, separator film, and a piece of cathode sheet were piled in the order and set with Swagelok type cells. 400

μL of $LiNTf_2$ in DEME-NTf_2 (0.32 mol/kg) was added into the cell as electrolyte and O_2 gas (2 kgf/cm^2) was introduced into a 50 mL cylinder which was attached to the cell.

4. Absorption spectra measurements.

A typical experimental procedure is described below. The absorption spectra of the solution of $TEMPO^+ClO_4^-$ in acetonitrile after the reaction with lithium compounds were measured in 5.0-mm quartz cell. A stock solution of $TEMPO^+ClO_4^-$ (20 mg/mL) in acetonitrile was prepared in a 20-mL flask equipped with a stopcock. 1.5 mL of the solution was transferred to an ampule, and appropriate amount of lithium compound was added under the Ar atmosphere. The ampule was sealed and thermostated at 25˚C on the temperature-controlled bath under shielded light. After the sample had been allowed to stand at 25˚C for 20 h, the residue was removed by filtration with PTFE filter (pore diameter: 0.5-μm) and then the solution was diluted with acetonitrile to keep $TEMPO^+ClO_4^-$ concentration at 6.0 mg/mL. The absorption spectra were taken at ambient temperature (ca. 20-25˚C).

5. Preparation of cathode samples.

The cathode sheets of the samples **I** and **II** were immersed in anhydrous DMSO for 24 h and washed with anhydrous chloroform for 3 times to remove electrolyte, and then dried in vacuo at room temperature for 3h. After the preparation, the samples were stored under argon atmosphere.

6. Estimation of Li_2O_2 in the cathode samples.

A typical experimental procedure is described below. 2.5 mg of the cathode samples were reacted with $TEMPO^+ClO_4^-$ and the absorption spectra of the solution were measured in the same way with lithium compounds described above. Quantity of Li_2O_2 in these parts of samples were estimated on the basis the ε_{475} ($M^{-1}cm^{-1}$) values of $TEMPO^+ClO_4^-$ solution. Quantity of Li_2O_2 in the whole cathode samples are estimated from these calculated values and weight of the samples.

7. References.

1) M. Shibuya, M. Tomizawa, Y. Iwabuchi, *J. Org. Chem.* **2008,** *73*, 4750.

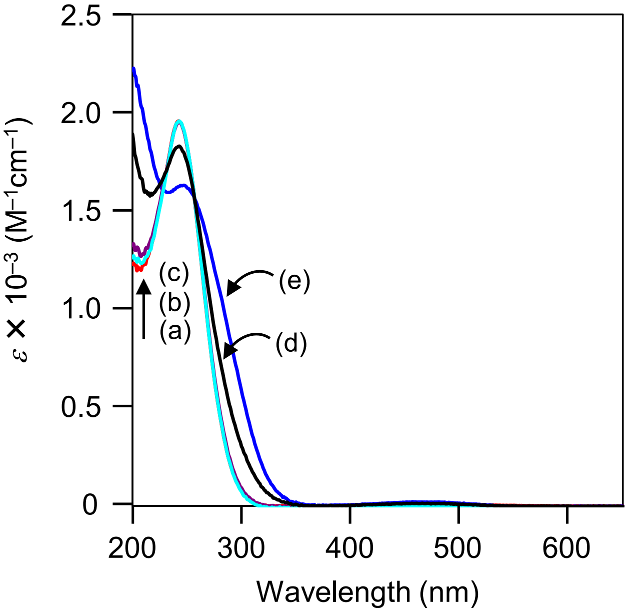

Fig. S1 Absorption spectra of (a) TEMPO, (b)-(d) reaction products of TEMPO$^+$ClO$_4^-$ with Li_2O_2 ([TEMPO$^+$ClO$_4^-$] / [Li_2O_2] = 1 (b), 2 (c), and 4 (d)), and (e) TEMPO$^+$ClO$_4^-$ in acetonitrile with a concentration of 1 mg/mL.

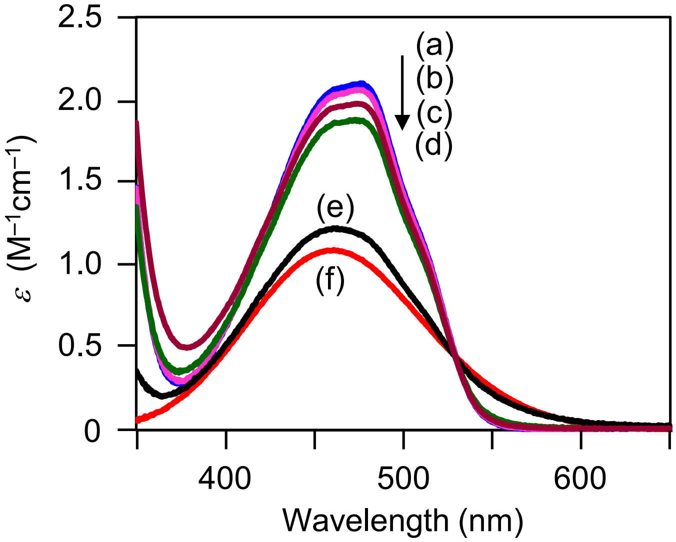

Fig. S2 Absorption spectra of (a) TEMPO, TEMPO$^+$ClO$_4^-$ (after reaction with (b) Li_2CO_3, (c) Li_2O, (d) LiOH, and (e) Li_2O_2), and (f) TEMPO$^+$ClO$_4^-$ in acetonitrile with a concentration of 6 mg/mL.

Table S1. Reaction yield and extent of reaction between TEMPO$^+$ClO$_4^-$ and Li compounds in acetonitrile

run	Li compound	molar ratio of Li compound to TEMPO$^+$ClO$_4^-$ [%][a]	reaction yield of TEMPO$^+$ClO$_4^-$ [%][b]	extent of reaction [%][c]
1	Li_2O_2	41	81	99
2	Li_2O	46	9.0	9.7
3	Li_2CO_3	35	3.9	5.6
4	LiOH	82	20	24

[a] Estimated from molar ratio of lithium compound to TEMPO$^+$ClO$_4^-$ in acetonitrile. [TEMPO$^+$ClO$_4^-$] = 6 mg/mL. [b] Estimated from the value of ε_{461} (M^{-1}cm^{-1}) of TEMPO$^+$ClO$_4^-$ solution. The samples had been allowed to stand at 25°C for 20 h. The absorption spectra were measured after filtration of lithium compounds. [c] Calculated from the ratio of the reaction yield to the values of [Li$^+$]/[TEMPO$^+$].