Supporting information

Limited effect of redox mediator in lithium-oxygen batteries:

Indecomposable by-products

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Figure S1. Corresponding charge profiles for Figure 3, 4, and 5. Charge profiles of cells without RM for Figure 3 (A), 4 (B), and 5 (C). (D) Charge profile of cells with TEMPO for figure 3, 4, and 5.



Figure S2. Characterization of Li_2CO_3 pre-loaded electrode before and after charging. FTIR spectra of the CNT electrode without Li_2CO_3 , Li_2CO_3 pre-loaded electrode and retrieved electrode after charging without RM and with TEMPO in the $Li-O_2$ cell.



Figure S3. Characterization of pulverized Li₂CO₃ pre-loaded electrodes before and after charging. SEM images of (A) pulverized Li₂CO₃ pre-loaded electrode and (B) retrieved electrode after charging with TEMPO. (C) XRD results of pulverized Li₂CO₃ pre-loaded electrode before charging and after charging with TEMPO in the Li-O₂ cell.



Figure S4. Characterization of LiF pre-loaded electrode before and after charging. SEM image of (A) LiF pre-loaded electrode and retrieved electrode after charging the pre-loaded electrode (B) without RM and (C) with TEMPO in the Li-O₂ cell. (D) XRD data for LiF pre-loaded electrode and electrode retrieved after charging without RM and charging with TEMPO in the Li-O₂ cell.



Figure S5. Characterization of HCOOLi and CH₃COOLi pre-loaded electrode. XRD data for HCOOLi and CH₃COOLi pre-loaded. Shaded part indicates the carbon electrode on which by-product (HCOOLi, CH₃COOLi) is loaded.



Figure S6. Characterization of (A, B, C) HCOOLi, (D, E, F) CH₃COOLi pre-loaded electrode before and after charging. SEM image of (A) HCOOLi, (D) CH₃COOLi pre-loaded electrode and electrode retrieved after charging (B, E) without RM and (C, F) with TEMPO in the Li-O₂ cell.



Figure S7. Characterization of (A) HCOOLi and (B) CH₃COOLi pre-loaded electrode before and after charging. FTIR spectra of the 39BC electrode without by-product, (A) HCOOLi and (B) CH₃COOLi pre-loaded electrode and each of the retrieved electrodes after charging without RM and with TEMPO in the Li-O₂ cell.



Figure S8. Characterization of (A) HCOOLi and (B) CH₃**COOLi pre-loaded electrode before and after charging.** NMR spectra of (A) HCOOLi and (B) CH₃COOLi pre-loaded electrode and each of the retrieved electrode after charging without RM and with TEMPO in the Li-O₂ cell.



Figure S9. XRD results of electrodes after charging with DMPZ. Electrodes were prepared by pre-loading of the (A) Li_2CO_3 , (B) LiF, (C) LiOH on electrodes and charging test in the Li-O₂ cell.



Figure S10. Analyzing the amount of the Li₂O₂ of the electrodes in Li-O₂ cell after cycling. (A) UV-Vis results obtained from the retrieved electrodes from discharged Li-O₂ cell (as reference) and the cycled (5, 15, and 30 cycles) Li-O₂ cells in the 1M LiTFSI in TEGDME electrolyte with TEMPO and HCG4/TTE (1:1) electrolyte with TEMPO. In the UV-Vis results, Peak intensity at 406 nm can be converted into the amount of the Li₂O₂ and method is described in the experimental section. For convenience, 1M LiTFSI in TEGDME with TEMPO electrolyte is

expressed as A and HCG4/TTE (1:1) electrolyte with TEMPO is expressed as B.



Figure S11. Characterization of Li_2CO_3 pre-loaded electrode after charging in the cell using HCG4/TTE electrolyte with TEMPO. (A) SEM, (B) XRD results of Li_2CO_3 pre-loaded electrode after charging with HCG4/TTE electrolyte with TEMPO in the $Li-O_2$ cell.