

## **Electronic Supporting Information (ESI)**

# **Single ion conducting separator and dual mediators-based electrolyte for high-performance lithium-oxygen battery with non-carbon cathode**

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## **Experimental section**

### **Cathode**

The commercial RuO<sub>2</sub> hydrate particles (Alfa Aesar) were calcined at 200 °C for 2 h to remove water and then used as cathode materials. The cathodes were prepared by coating the mixture of RuO<sub>2</sub> and lithiated Nafion polymer (LITHion™ Dispersion in an isopropyl alcohol solvent, 10%, Ion Power) with a weight ration 90 : 10 wt% in isopropyl alcohol onto Al foil. The mass loading is about 0.2 mg cm<sup>-2</sup>. The electrode discs with diameter of 7 mm were punched and drilled with a needle. Before using, cathodes were dried in a vacuum oven at 80 °C for 12 hrs.

### **Anode**

The Li foil (0.4 mm thickness) was used as the Li metal anode in coin cells. For the LiSICON-protected Li metal anode, the Li foil was independently sealed by using a lithium ion conductive glass ceramic (LiSICON, thickness 600 μm, Ohara Inc., Japan) membrane<sup>1</sup> to separate anode from the DMPZ crossover described in previous work.

### **Electrolyte**

Tetraglyme (G4, 99%, Sigma-Aldrich) was dried by 4Å molecular sieves for 1 week. LiTFSI was dried in a vacuum oven at 120 °C for 12 hrs. The concentration of LiTFSI (lithium bistrifluoromethanesulfonimide, TCI) in G4 is 1 M. After preparation, the electrolyte was stored in Ar-filled glove box. Its H<sub>2</sub>O content was measured to be about 11 ppm by Karl-Fischer titration. 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ, Sigma-Aldrich) was used as redox mediator for the oxygen reduction reaction. The DBBQ-containing electrolyte was prepared by adding DBBQ into the 1.0 M LiTFSI-G4 electrolyte. The molar concentration of DBBQ was 0.05 M. 5,10-dimethylphenazine (DMPZ, Sigma-Aldrich) was used as redox mediator for the oxygen evolution reaction. The DMPZ-containing electrolyte was prepared

by adding DBBQ into the 1.0 M LiTFSI-G4 electrolyte. The molar concentration of DBBQ was 0.05 M. The DBBQ and DMPZ-containing electrolyte was prepared by adding DBBQ and DMPZ into the 1.0 M LiTFSI-G4 electrolyte. The molar concentrations were 0.05 M (DBBQ) and 0.10 M (DMPZ), respectively.

### **Separator**

Glass fiber separator (GF/A, Whatman) was dried at 80 °C for 24 h and stored in glove box. For the preparation of Li<sup>+</sup>-Nafion membrane, Nafion 117 membranes (Sigma-Aldrich) were firstly boiled in water-ethanol (1:1) solution with 1.0 M LiOH for 12 h and then washed in pure water at 100 °C for 12 h. After being dried at 60 °C for 12 h in a vacuum box, they were immersing in 1.0 M LiTFSI-G4 electrolyte in a glove box.

### **Permeation experiment**

Permeation experiments were performed with a home-made V-shaped device, which consisted of two glass tubes and the glass fiber, Celgard or the Li<sup>+</sup>-Nafion separator. These three components were assembled together by organic-proof black instant adhesive and water-proof transparent instant adhesive. The DBBQ/DMPZ-containing electrolyte was slightly injected on the right side and the blank 1.0 M LiTFSI-G4 electrolyte was added on the left side. The changes of the solution on two side were monitored and recorded by a digital camera.

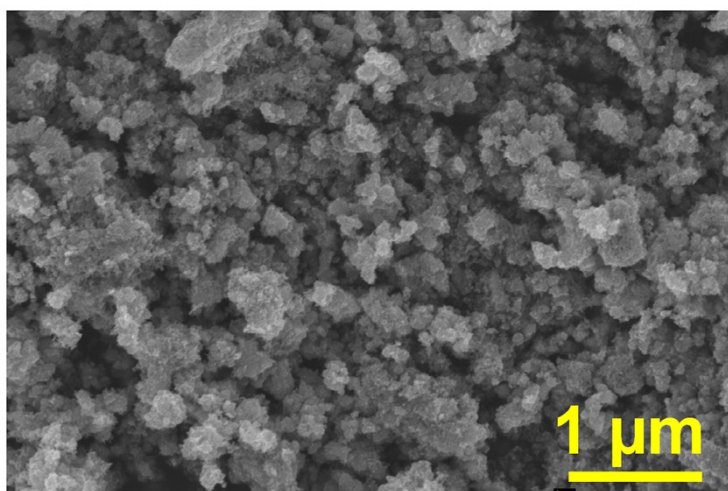
### **Reaction between Li and DBBQ**

The Li metal was immersed in the DBBQ-containing electrolyte in a glove box. For control experiment, the Li meal was also immersed in the 1.0 M LiTFSI-G4 electrolyte. The changes of the solution were monitored and recorded by a digital camera.

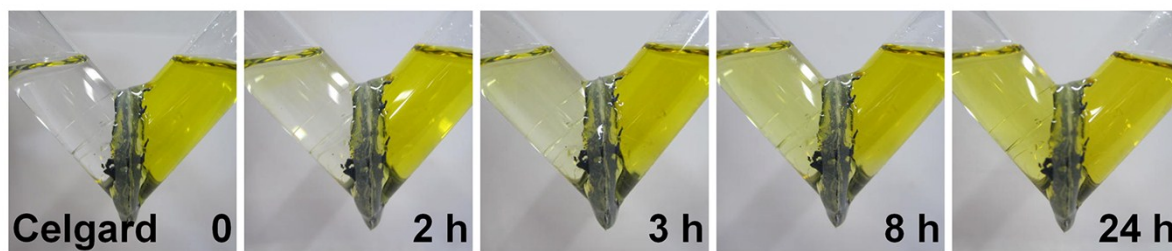
**Electrochemical characterization:**

The Li-O<sub>2</sub> battery with GF separator was fabricated by stacking Li metal anode, GF separator infiltrating 60 μL of electrolyte, cathode in a coin cell. The Li-O<sub>2</sub> batteries with Li<sup>+</sup>-Nafion separators were fabricated by stacking Li metal anode, GF infiltrating 30 μL of 1.0 M LiTFSI-G4 electrolyte, Li<sup>+</sup>-Nafion separator, GF infiltrating 30 μL of electrolyte, cathode in a coin cell. The LiSICON-protected Li-O<sub>2</sub> battery was fabricated by firstly covering a glassy fiber membrane (GF/A, Whatman) with diameter of 8 mm infiltrating 30 μL of electrolyte on LiSICON-sealed anode side. After that, the cathode and an Al mesh connector (100 mesh, Nilaco Co. Ltd.) were placed. The prepared cells were placed in the sealed chamber (650 mL). The chamber was fully purged with O<sub>2</sub> for 1 hrs. Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. The specific capacities and current densities were based on the mass of RuO<sub>2</sub> in cathode. For evaluating the cycling performance, the batteries were firstly discharged to 2.9 V to reduce the residual oxidized redox mediator. This ensured that the oxygen reduction reactions dominated the following discharge process. All of the electrochemical measurements were conducted at a constant room temperature (~25 °C).

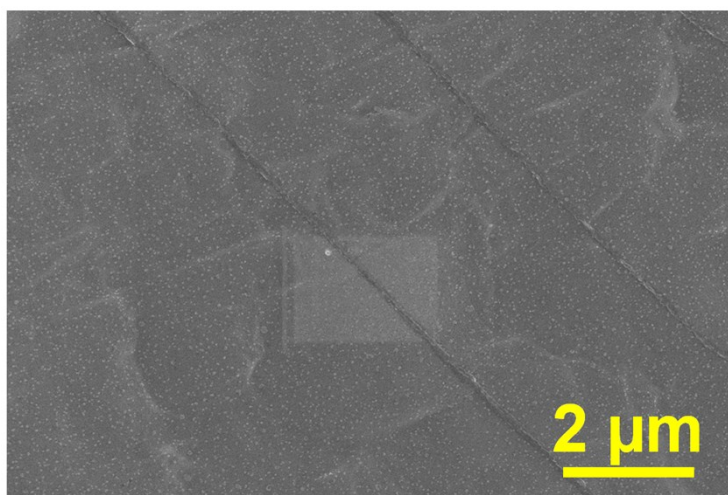
For scanning electron microscopy (SEM) measurement, and Raman spectra of the discharged/recharged cathodes and anodes, the cells were disassembled in an Ar-filled glove box and the cathodes and anodes were extracted. The cathodes and anodes were further thoroughly washed by dimethyl ether (DME) for 3 times to remove residual solvent and lithium salt and finally dried in a vacuum chamber connected to the glove box. SEM images were taken using a LEO Gemini Supra 35 system. The Raman spectra were recorded using a JASCO microscope spectrometer (NRS-1000DT). The samples were sealed into a gas-tight homemade Raman sample holder with a piece of quartz window (thickness 0.5 mm) optimized for the observations.



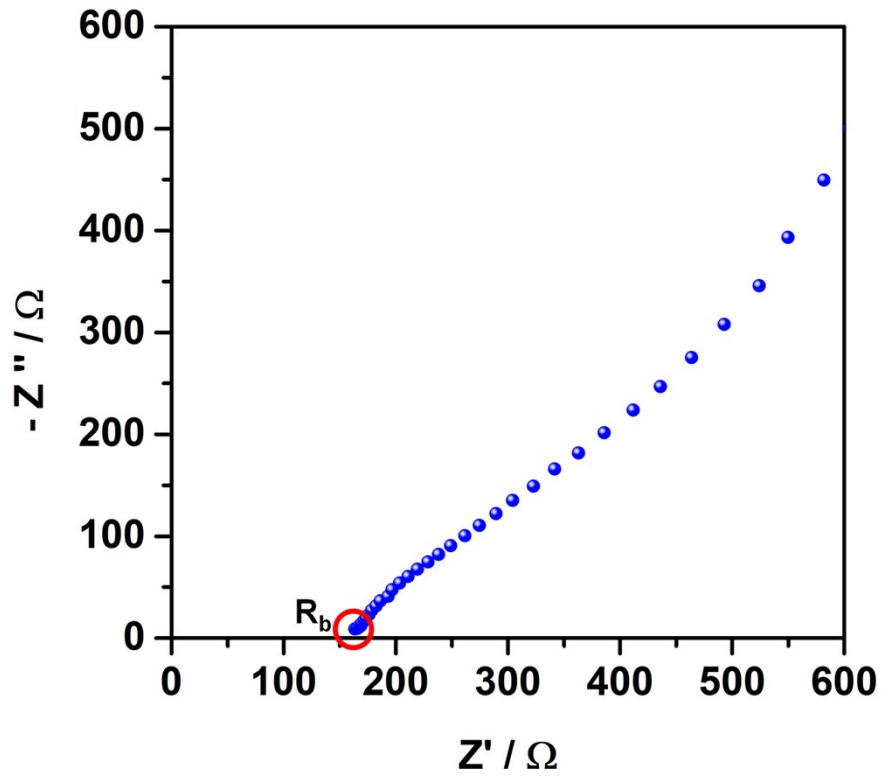
**Figure S1.** SEM image of the commercial pristine RuO<sub>2</sub> powder.



**Figure S2.** Permeation experiment to observe the block effect of Celgard separator towards DBBQ in electrolyte.

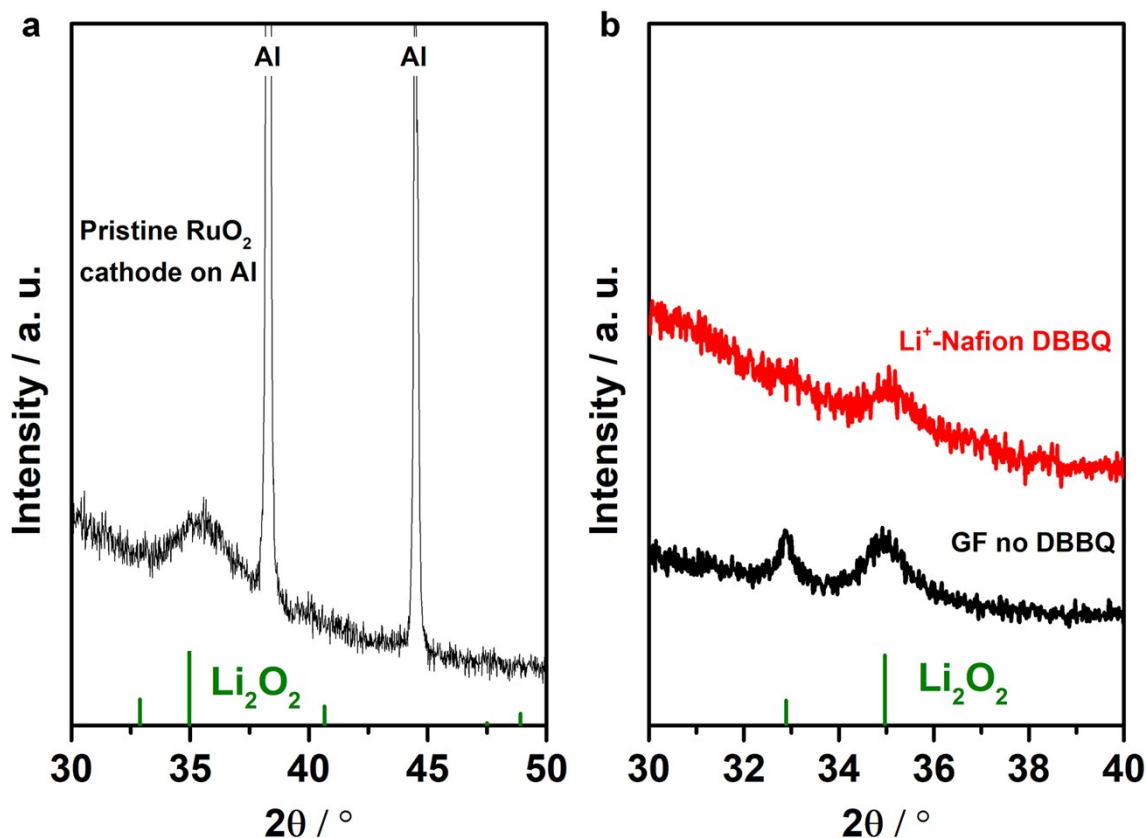


**Figure S3.** SEM image of pristine Li metal anode.



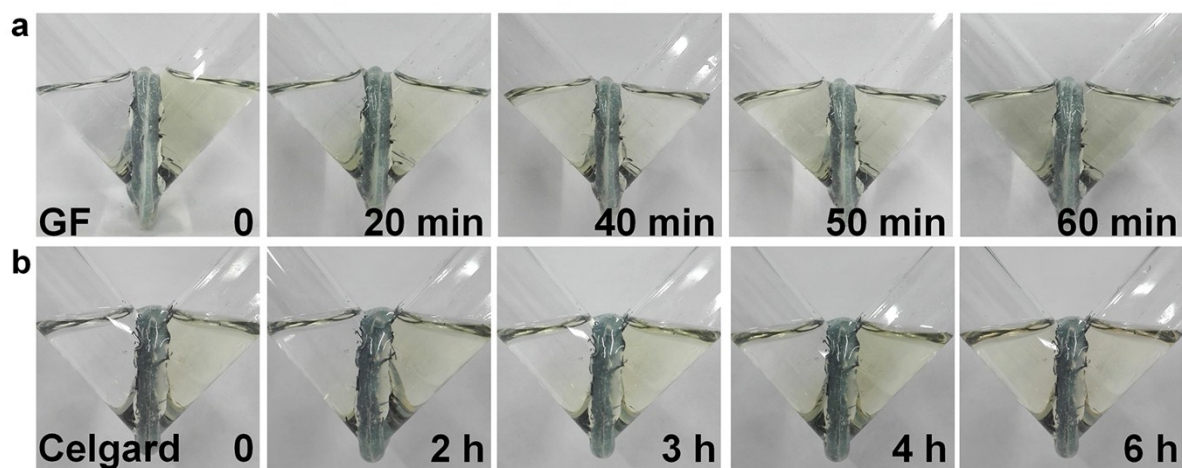
**Figure S4.** Ion conductivity measurement. Nyquist plots of the electrolyte with the cell structure of stainless steel (SS)/GF separator infiltrating electrolyte/Li<sup>+</sup>-Nafion/GF separator infiltrating electrolyte /SS. The ion conductivity was calculated via the formula  $\sigma=d/(R_bS)$ , where d is the thickness of GF and Li<sup>+</sup>-Nafion, S is the area of SS and  $R_b$  is obtained in EIS plot.



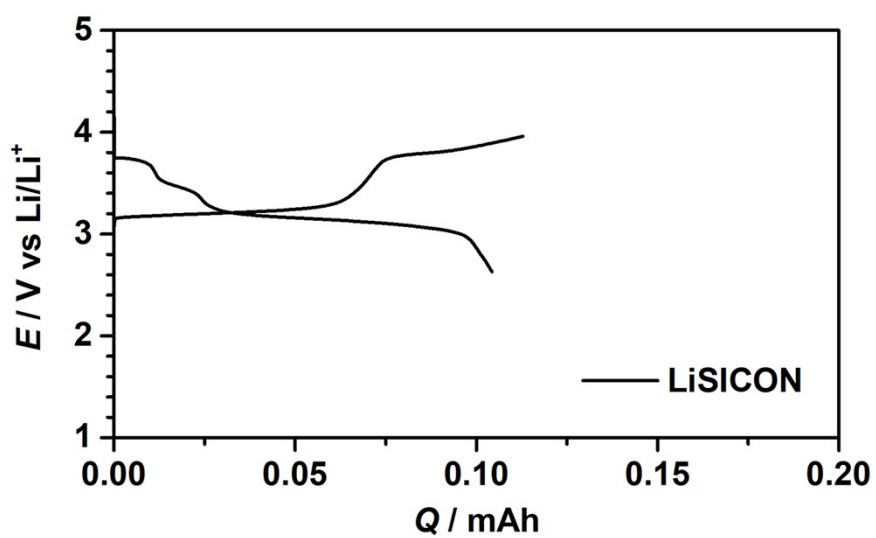


**Figure S5.** X-ray diffraction (XRD) patterns of (a) the pristine  $\text{RuO}_2$  cathode and (b) the discharged carbon cathodes with DBBQ and  $\text{Li}^+$ -Nafion separator and without DBBQ, respectively.

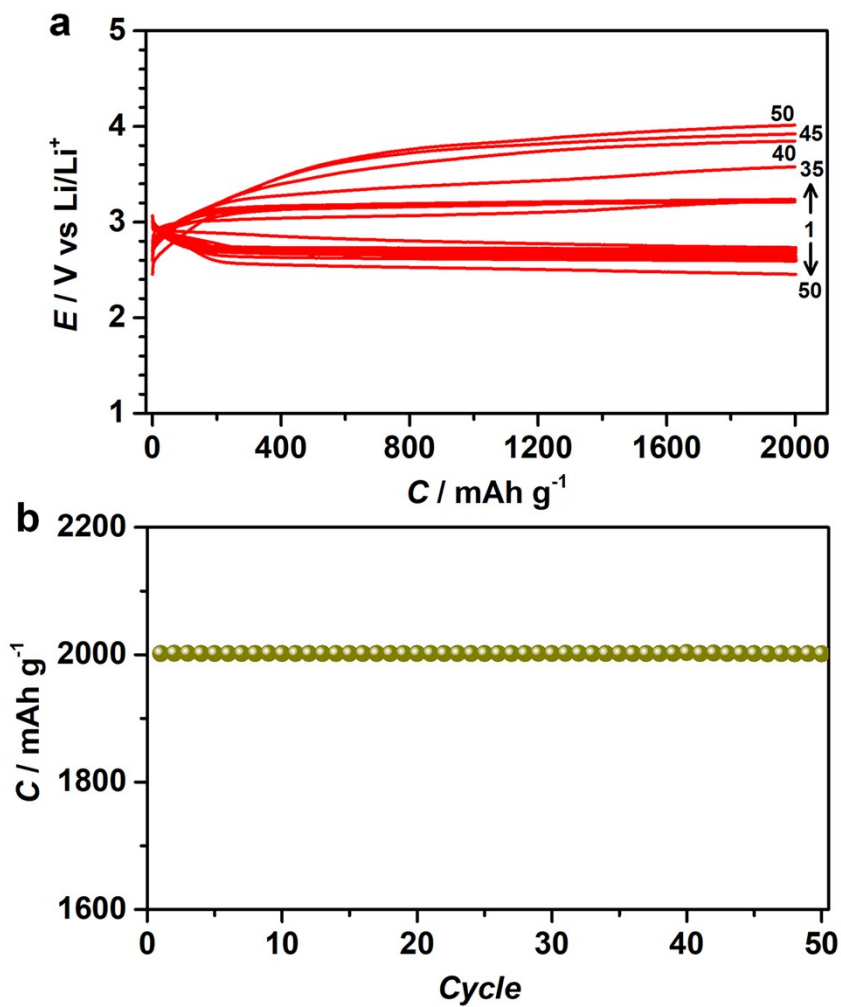
Figure S5a shows the XRD pattern of the pristine  $\text{RuO}_2$  cathode. Because their peaks overlap the main peaks of  $\text{Li}_2\text{O}_2$  at  $\sim 33^\circ$  and  $35^\circ$ , we used the carbon cathodes to examine the crystallization of the produced  $\text{Li}_2\text{O}_2$  in the presence of DBBQ (Figure S5b). Without DBBQ in the electrolyte, the XRD pattern shows two obvious peaks of  $\text{Li}_2\text{O}_2$  at  $\sim 33^\circ$  and  $35^\circ$ . While, in the presence of DBBQ, the intensities of  $\text{Li}_2\text{O}_2$  peaks at  $\sim 33^\circ$  and  $35^\circ$  are much weaker. As the discharged capacities were the same (1.5 mAh), this result indicates the crystallization of the  $\text{Li}_2\text{O}_2$  products in the presence of DBBQ is poor.



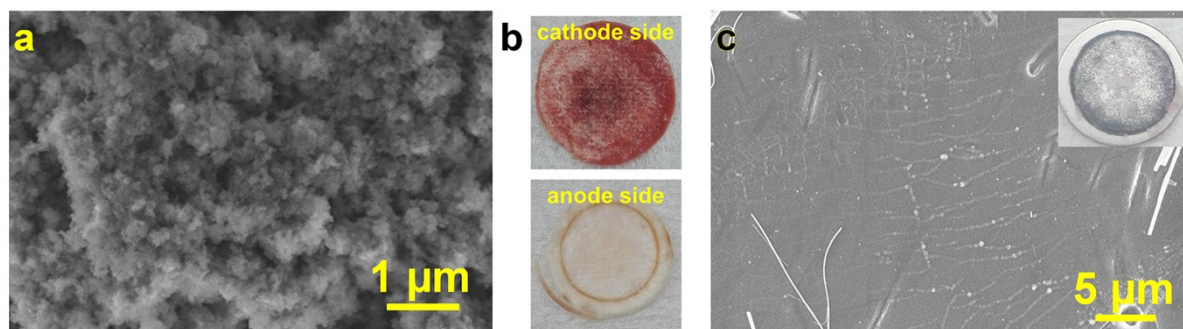
**Figure S6.** Permeation experiment of (a) GF and (b) Celgard toward DMPZ penetration, respectively.



**Figure S7.** Charge-discharge profile of Li-ion battery in Ar gas (RuO<sub>2</sub> cathode/ separator infiltrating DMPZ-containing electrolyte/LiSICON-protected Li anode).



**Figure S8.** Long-term cycling stability of non-carbon RuO<sub>2</sub>-based Li-O<sub>2</sub> battery with DBBQ and DMPZ in electrolyte and Li<sup>+</sup>-Nafion separator. (a) Selected discharge-charge profiles at 500 mA g<sup>-1</sup>. (b) Evolution of discharge capacities during cycling.



**Figure S9.** Characterizations of the cathode, separator and Li metal anode after cycling. (a) SEM image of the RuO<sub>2</sub> cathode. (b) Photos of GF separators on the cathode side and anode side. (c) SEM image and photo (inset) of the Li metal anode.

No toroid Li<sub>2</sub>O<sub>2</sub> particles accumulated on the RuO<sub>2</sub> cathode, indicating that DMPZ remained on the cathode side and could mediate the oxidation of Li<sub>2</sub>O<sub>2</sub> during charge. The color of the GF separator on the cathode side was dark red, corresponding to the reduced state of DMPZ. In contrast, the GF separator on the anode side hold nearly white color. The light-yellow color may be due to that a little DMPZ and DBBQ-containing electrolyte on the cathode side leaked from the unsealed space on the edges of Li<sup>+</sup>-Nafion and Li metal anode in a coin cell configuration. In addition, most of the Li anode surface kept the pristine light-yellow color except the edges and no Li<sub>2</sub>O<sub>2</sub> particles depositing on the surface of Li metal anode like the inset SEM image in Figure 1b were observed. These results confirmed the block effect of Li<sup>+</sup>-Nafion separator toward DMPZ in the actual environment inside the cell.

1 S. Wu, Y. Qiao, S. Yang, M. Ishida, P. He, H. Zhou, *Nat. Commun.* 2017, **8**, 15607.