Supporting Information

Trifunctional imidazolium bromide: a high-efficiency redox mediator for high-performance Li-O2 batteries

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Experimental section

Materials

For the components in the electrolytes, 1-Aminopropyl-3-methylimidazolium Bromide (APMImBr) was obtained from Lanzhou Greenchem ILs. Lithium bis(trifluoromethanesulfonic)imide (LiTFSI), lithium bromide (LiBr), and dimethyl sulfoxide (DMSO) were obtained from Sigma Aldrich. The salts were dried under vacuum at 120°C for 12 h, and solvents were dried by using activated 4 Å molecular sieves prior to use. The Super P carbon was milled in a planetary ball mill apparatus for 24 h at 500 rpm.

Characterizations

The electrodes from the disassembled batteries were washed with dimethyl ether and dried in argon first, and then sealed in the mould to exclude normal atmospheric air components before characterization. The morphology of electrodes was observed by field emission scanning electron microscope (FESEM, Hitachi SU8010). Raman spectroscopy measurements were carried out to acquire the components of electrodes during different processes. Raman spectra were recorded in the range of 400–1800 cm^{-1}. Powder X-ray diffraction (XRD) measurements were carried out to analyze the discharge products by employing a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ =0.154 nm) in the 2θ range of 20−70°. The states of surface elements on the anodes were characterized through XPS (Thermo Fisher Scientific Model K-Alpha spectrometer) equipped with Al Ka radiation (1486.6 *eV*) at a working voltage of 12 *kV* and a current of 10 mA. The nitroblue tetrazolium (NBT) reduction test was employed to evaluate the superoxide radical scavenging capability of the APMImBr[1-4]. KO_2 and 18-crown-6 were added into 0.2 M LiTFSI-DMSO solution to generate superoxide radicals. The superoxide radical concentration can be reflected by the color of the solution with NBT. The degree of NBT reduction can be measured by UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., P.R. China) absorbance at 560 nm.

Battery assembly and electrochemical measurements

The cathode was prepared by rolling the mixture of Super P carbon and PTFE binder (W: W=85: 15) into a film and pressing on a stainless steel mesh. The mass loading of the electrode was 0.2 ± 0.05 mg. They were dried for 12 h at 105 °C under vacuum to remove residual water. The electrolyte was prepared by dissolving APMImBr or LiBr in DMSO with 1 M LiTFSI, and the molar concentration was 0.1 M.

The Li-Li symmetrical batteries were assembled using coin-type cell. The lithium metals were pre-cut to 12 mm diameter. Glass fiber separators were used to absorb electrolytes. The current density was 0.1 mA cm^{-2}. The battery was alternatively discharged for 1 h and charged for 1 h in each cycle.

Cyclic voltammetry (CV) measurements were conducted on electrochemical workstation (CHI760E, Chenhua Co., Shanghai, P. R. China) and at 25°C. The scan rate was 0.5 mV s^{-1}. The cyclic voltammetry for two-electrode configuration was operated by using a lithium metal foil as anode, a glass fiber as separator soaking with electrolyte, and a Super P electrode as cathode. The electrochemical impedance spectroscopy tests were conducted with a frequency range from 1 MHz to 0.1 Hz and an amplitude of 5 mV. Galvanostatic tests were performed on LAND 2001A Battery Testing Systems (Wuhan LAND electronics Co., Ltd, P. R. China) under O_2 atmosphere.

In-situ DEMS measurements were performed by electrochemical reactions. After assembly, a mixture of O_2/Ar (V: V=9: 1) was purged continuously in the battery for 6 hours before discharge. The electrochemical reaction was conducted by a home-made Li–O_2 battery mold with two PEEK valves connected to a quadrupole mass spectrometer with a turbomolecular pump (Pfeiffer Vacuum). During the discharge process, the flux of the gas was 0.5 mL min^{-1}. With regard to the charge process, the battery was purged with pure Ar for 6 hours to replace the O_2 with a flux of 0.5 mL min^{-1}. The DEMS battery was also performed on LAND 2001A Battery Testing Systems.

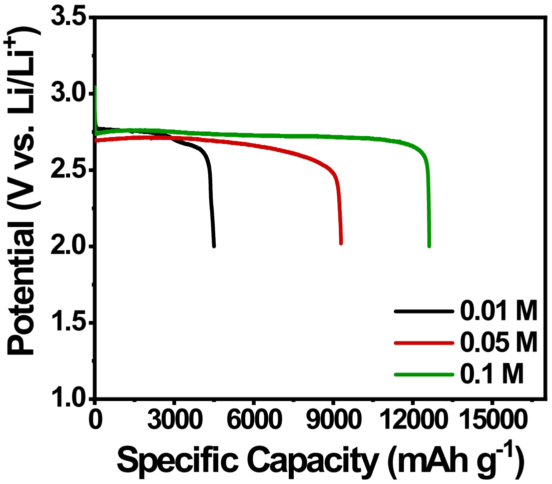

Fig. S1 Deep discharge profiles of Li–O_2 batteries containing different concentrations of APMImBr with DMSO based electrolyte. Current density was fixed at 100 mA g^{-1}.

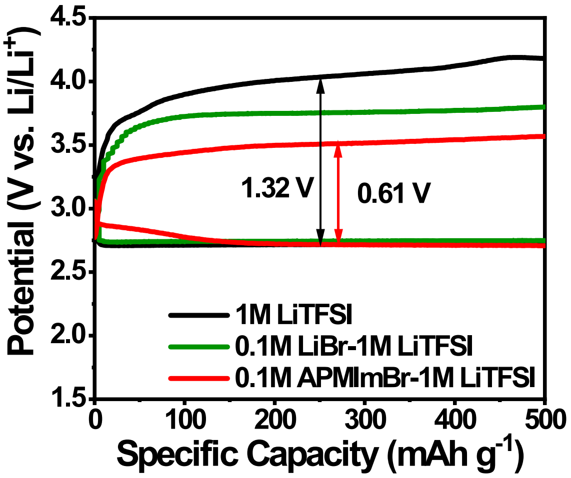

Fig. S2 Voltage profiles of Li–O_2 batteries with the DMSO electrolytes containing 1 M LiTFSI,1 M LiTFSI-0.1 M LiBr and 1 M LiTFSI-0.1 M APMImBr at current density of 100 mA g^{-1}.

$$Li^+ + O_2 + e^- \rightarrow LiO_2 \tag{1}$$

$$APMIm^+ + O_2 + e^- \rightarrow APMIm^+ \cdots O_2^{\cdot -} \tag{2}$$

$$Li^+ + APMIm^+ \cdots O_2^{\cdot -} \rightarrow APMIm^+ + LiO_2 \tag{3}$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \tag{4}$$

$$3Br^- \rightarrow Br_3^- + 2e^- \tag{5}$$

$$Br_3^- + Li_2O_2 \rightarrow 3Br^- + 2Li^+ + O_2 \tag{6}$$

Fig. S3 The related reactions of Li-O_2 batteries with APMImBr during the discharge/charge processes.

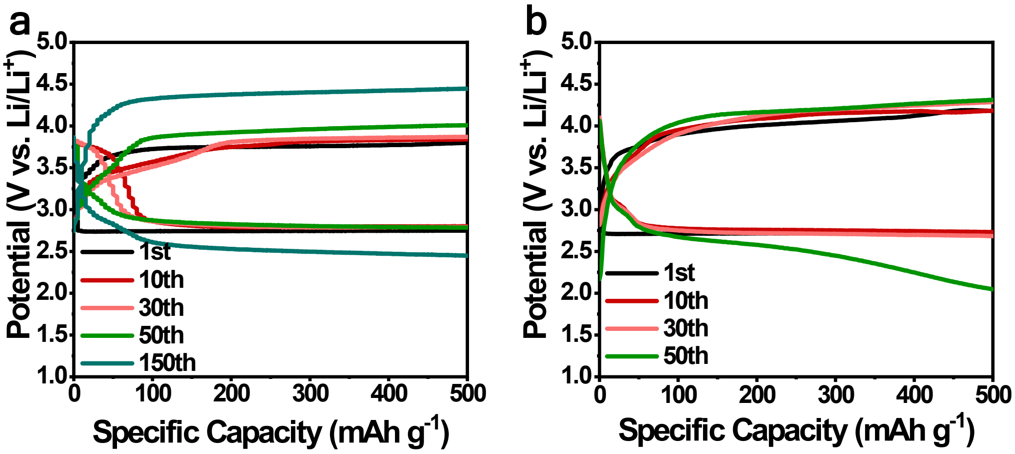

Fig. S4 Voltage profiles of the Li–O_2 batteries during prolonged galvanostatic cycling with the DMSO based electrolyte containing (a) 1 M LiTFSI-0.1 M LiBr and (b) 1 M LiTFSI. The current density is 500 mA g^{-1}.

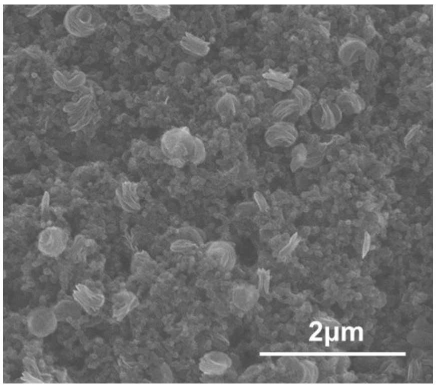

Fig. S5 SEM image of the Super P electrode extracted from the Li–O_2 batteries with 1 M LiTFSI-DMSO. Scale bar is 2 μm.

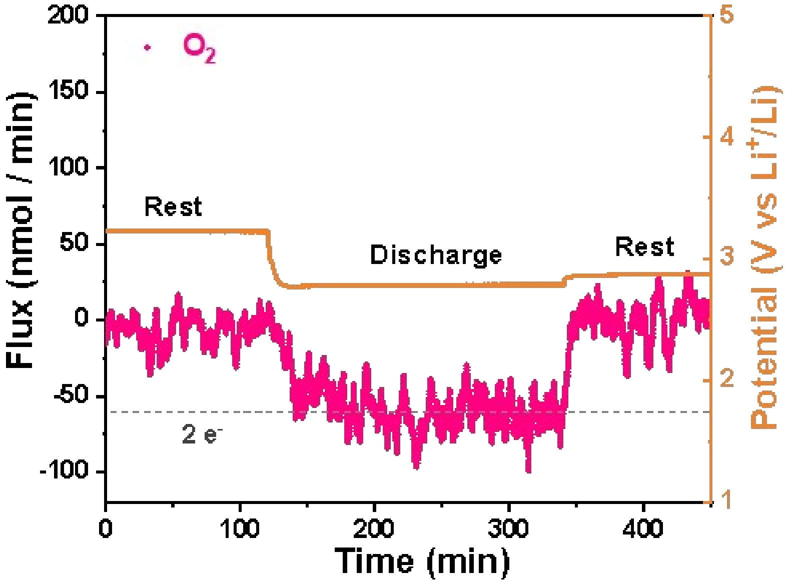

Fig. S6 In situ differential electrochemical mass spectrometry (DEMS) analysis of the gas consumption during Li–O_2 battery operation during discharge to 0.72 mAh at current density of 1000 mA g^{-1}.

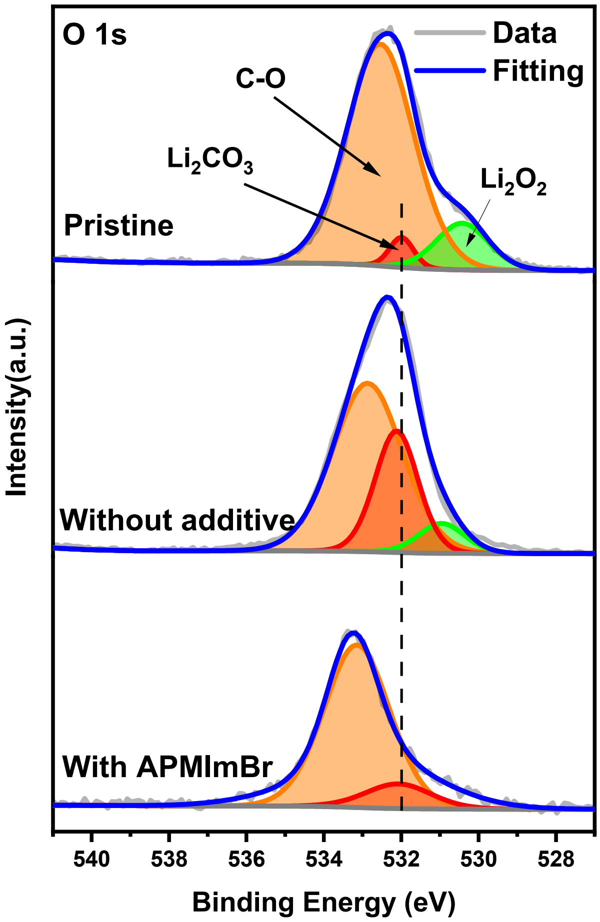

Fig. S7 O 1s XPS spectra of pristine electrode (Li_2O_2/Super P) and these after charged electrodes in DMSO-based electrolyte solution with or without APMImBr.

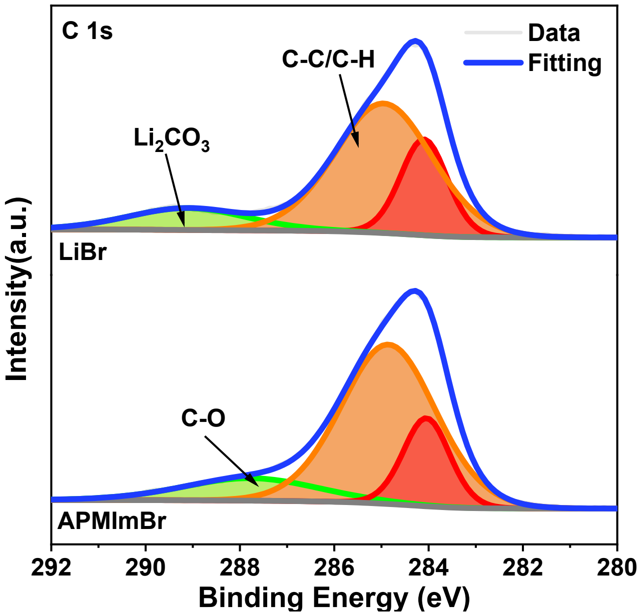

Fig. S8 C 1s XPS spectra on the surface of Li anodes. Two samples from the Li-Li symmetric cells with LiBr and APMImBr additives after 50 cycles were measured.

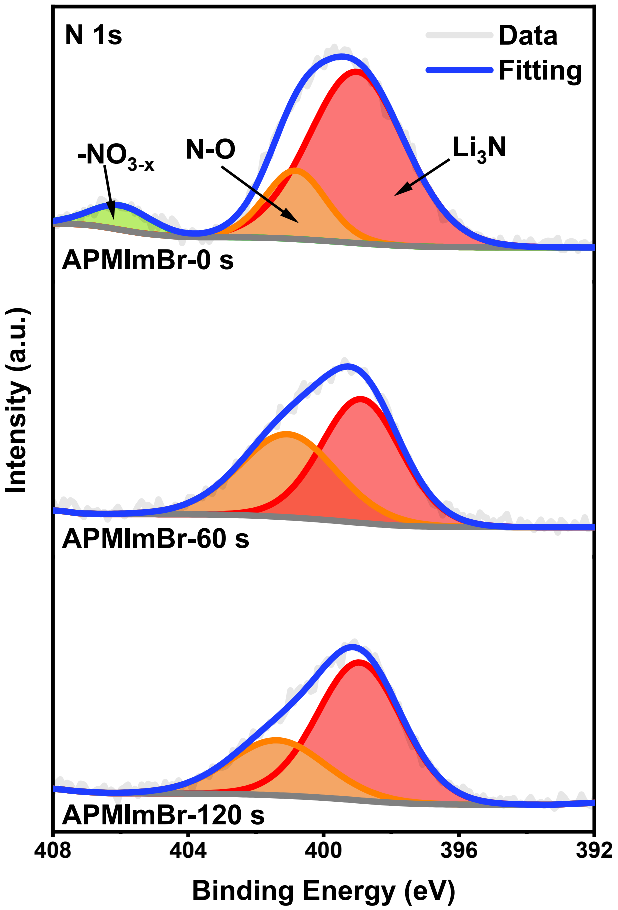

Fig. S9 N 1s XPS spectra for the lithium anode in the APMImBr-containing Li–O_2 battery after 50 cycles.

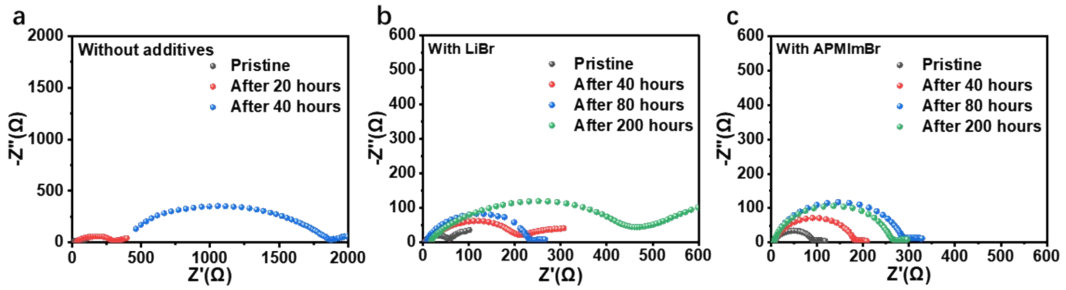

Fig. S10 Nyquist plots of the Li-Li symmetric battery after cycles with DMSO-based electrolytes: (a) without additives, (b) with 0.1 M LiBr and (c) with 0.1 M APMImBr.

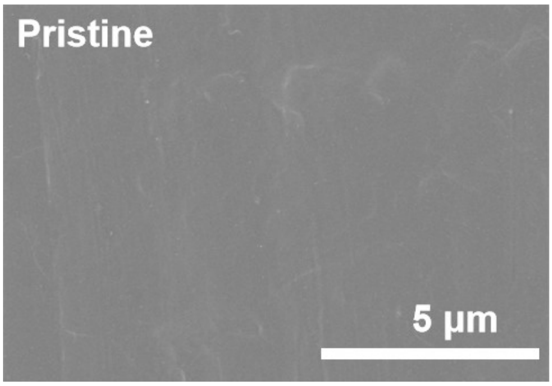

Fig. S11 Scanning electron microscope (SEM) images of fresh lithium metal. Scale bar is 5 μm.

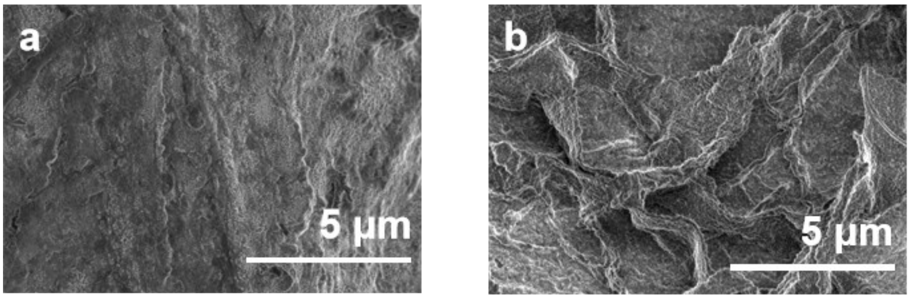

Fig. S12 (a) SEM images of the Li anode extracted from the Li-Li symmetric batteries after 50 cycles at a current density of 0.1 mA cm^{-2} with a limited capacity of 0.1 mAh cm^{-2} in DMSO-based electrolyte with 0.1 M LiBr. (b) SEM images of the Li anode extracted from the Li–O_2 batteries after 50 cycles in DMSO-based electrolyte with 0.1 M LiBr.

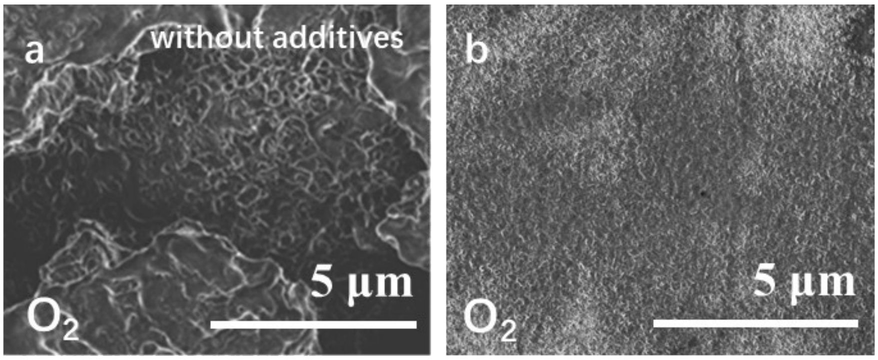

Fig. S13 SEM images of the Li anode extracted from the Li–O_2 batteries after 50 cycles in DMSO-based electrolyte (a) without additives and (b) with 0.1 M APMImBr. The constant current density was 500 mA g^{-1} with a limited capacity of 500 mAh g^{-1}.

References:

1. Z. Wang, S. Tian, B. Shao, S. Li, L. Li and J. Yang, *Journal of Power Sources*, 2019, **414**, 327-332.
2. R. N. Samajdar, S. M. George and A. J. Bhattacharyya, *The Journal of Physical Chemistry C*, 2019, **123**, 23433-23438.
3. S. E. Jerng, T. Y. Kim, S. Bae, J. Shin, J. Park, J. Yi and J. W. Choi, *Energy Storage Materials*, 2019, **19**, 16-23.
4. B. G. Kim, S. Kim, H. Lee and J. W. Choi, *Chemistry of Materials*, 2014, **26**, 4757-4764.