

Supporting Information

Bifunctional electrolyte additive MgI₂ for improved cycle life in high-efficiency redox-mediated Li-O₂ battery

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Experimental section

Materials and chemicals

The electrolyte components of magnesium iodide (MgI_2 , 99.9%), lithium iodide (LiI , 99.9%), lithium bis(trifluoromethanesulfonic)imide (LiTFSI , 99.9%), and dimethyl sulfoxide (DMSO , 99.9%) are purchased from Sigma Aldrich. The salts are dried in a vacuum drying oven at 100°C for 24 h, and solvents are dehydrated with activated molecular sieves (4 Å) before use. The Super P carbon is milled at 500 rpm in a planetary ball mill for 24 h. After processing, these materials need to be stored in the Ar-filled glovebox ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$).

Characterizations

The electrodes from the disassembled batteries are washed with dimethyl ether three times, dried in an Ar-filled glovebox, and then sealed in the homemade mould to isolate external atmosphere before characterization. The field emission scanning electron microscope (FESEM, Hitachi SU8010) is used to observe the morphology of electrodes in different states. Raman spectroscopy is conducted to obtain the components of electrodes in different states on a Renishaw in Via confocal microscope with an air-cooled He-Ne laser at 633 nm excitation ($600\text{-}1800 \text{ cm}^{-1}$). X-ray diffraction (XRD) spectroscopy is performed to analyze the components of electrodes in different states by using a Bruker D8 advanced X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). X-ray photoelectron spectroscopy is carried to analysis the chemical valence state of element through Thermo Fisher Scientific Model K-Alpha spectrometer equipped with $\text{Al K}\alpha$ radiation (1486.6 eV) at a working voltage of 12 kV and a current of 10 mA . Differential electrochemical mass spectrometry (DEMS) is conducted to monitor gas composition and volume through a quadrupole mass spectrometer (PrismaPro QMG 250 M2) with a turbomolecular pump (Pfeiffer Vacuum).

Preparation of electrode material

These cathodes are prepared by rolling the mixture of Super P carbon and polytetrafluoroethylene aqueous solution (12 wt%) into a film (Φ 12 mm) at a mass

ratio of 85:15 and pressing it onto a carbon paper. The mass loading of all cathodes is about 1.0 ± 0.1 mg. These cathodes are then dried in a vacuum oven at 105°C for 12 h and stored in an argon glove box.

Preparation of electrolyte

The electrolytes are prepared by dissolving MgI_2 (0.01 M) or LiI (0.01 M) with 1 M LiTFSI in DMSO.

Battery assembly

Electrochemical tests are performed in homemade battery mould containing a lithium metal anode, a pre-obtained cathode (Φ 12 mm), a glassy fiber separator (Whatman, Φ 14 mm) and electrolyte (80 ml, 1 M LiTFSI in DMSO or 1 M LiTFSI with 0.01M LiI in DMSO or 1 M LiTFSI with 0.01M MgI_2 in DMSO). All assembly procedures of homemade battery mould are carried out in an argon glove box with 1atm pressure and negligible O_2 and H_2O concentrations (< 0.1 ppm). All homemade battery moulds should be aerated with oxygen for 15 minutes and then allowed to rest for 6 hours before testing.

Electrochemical measurements

The cyclic voltammetry (CV) experiments are conducted on an electrochemical workstation (CHI760E, Chenhua Co., Ltd) at a rate of 0.1 mV s^{-1} from 2 to 4.5 V by using the assembled battery mould. The galvanostatic tests are performed on the Neware Battery Testing Systems (CT/CTE-4000, Shenzhen Neware electronics Co., Ltd) using the homemade battery mould. The electrochemical impedance spectroscopy (EIS) tests are carried out at an electrochemical station (CHI760E, Chenhua Co., Ltd) with a frequency range of 100 kHz to 0.1 Hz. The Li-Li symmetrical batteries are assembled using homemade battery mould. The current density is 0.1 mA cm^{-2} . Each cycle takes 2 h for Li stripping and plating. In-situ DEMS tests are also performed on the Neware Battery Testing System using our homemade battery mould, connecting two PEEK valves to a quadrupole mass spectrometer with a turbomolecular pump

(Pfeiffer Vacuum). During the discharging and charging process, the gas flow rate is 0.5 mL min^{-1} . Prior to discharge, the O_2/Ar (V: V= 9:1) mixture is continuously purged into the homemade battery mould for 8 hours to clear the baseline. Similarly, the homemade battery mould is purged with pure Ar for 8 hours to eliminate O_2 before recharging.

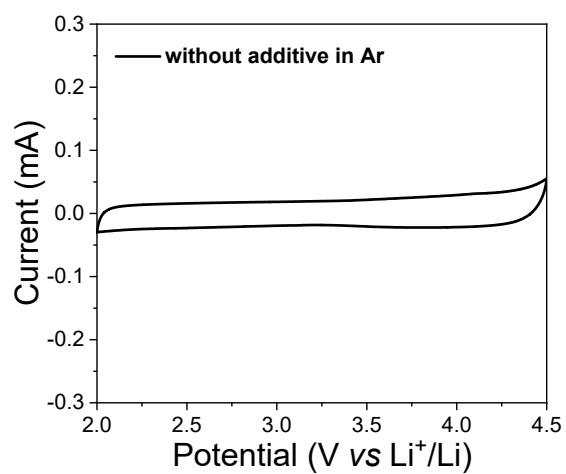


Fig. S1 Cyclic voltammetry of without additive under Ar atmosphere.

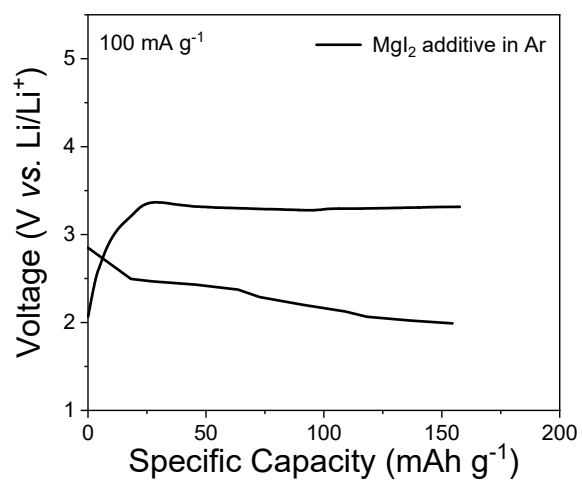


Fig. S2 The full discharge-charge performance of MgI₂ additive under Ar atmosphere.

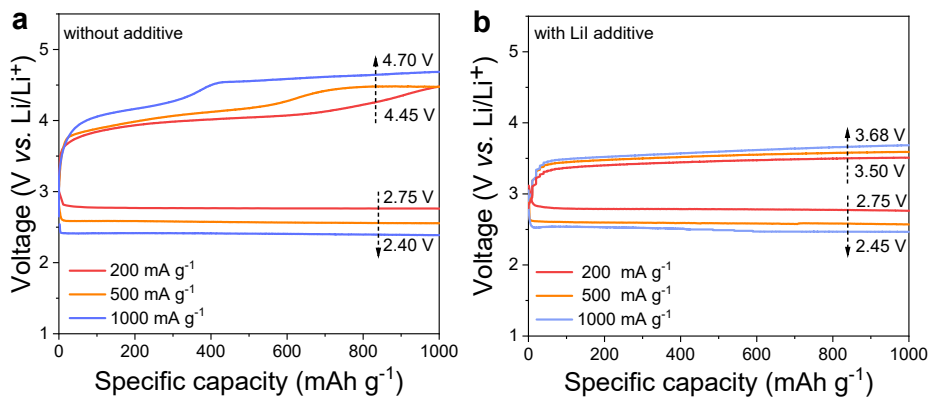


Fig. S3 The rate capability of Li-O₂ battery containing with or without LiI additive.

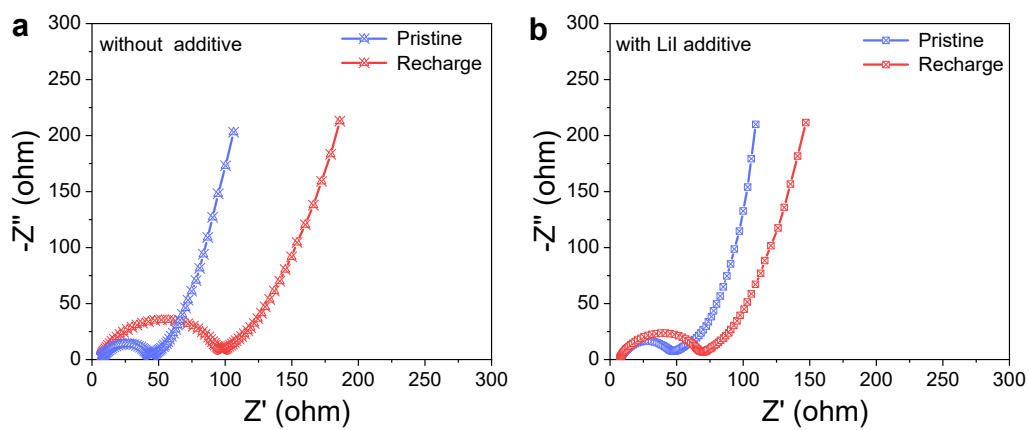


Fig. S4 The electrochemical impedance spectroscopy (EIS) before and after cycling experiments without additive or with LiI additive.

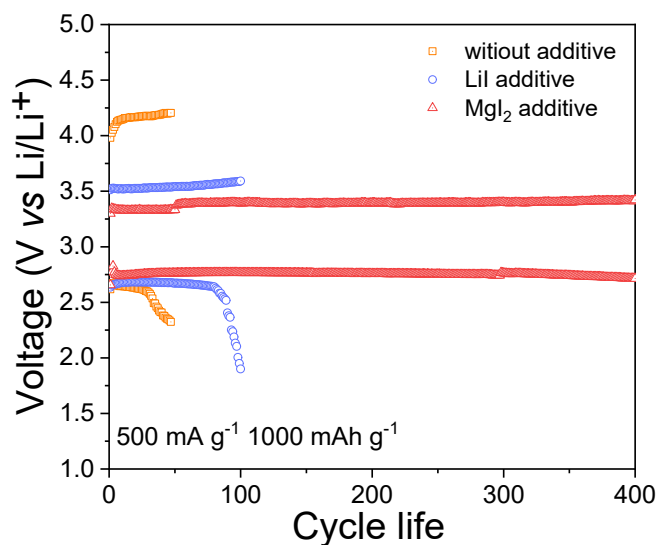


Fig. S5 Cycling behavior of Li-O₂ battery at a current of 500 mA g⁻¹ and curtailing capacity of 1000 mAh g⁻¹ with three electrolyte solution (without additive or LiI additive or MgI₂ additive).

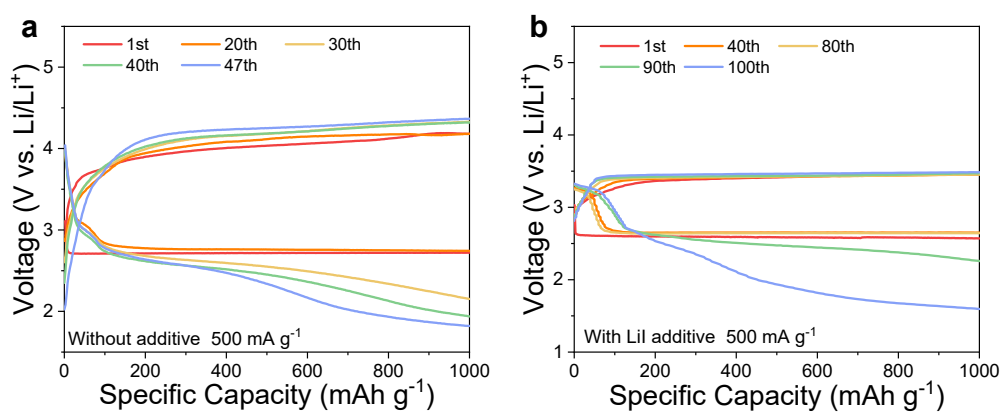


Fig. S6 Cycling behavior of Li-O₂ battery for the selected cycles at a current of 500 mA g⁻¹ and curtailing capacity of 1000 mAh g⁻¹ (without additive or LiI additive).

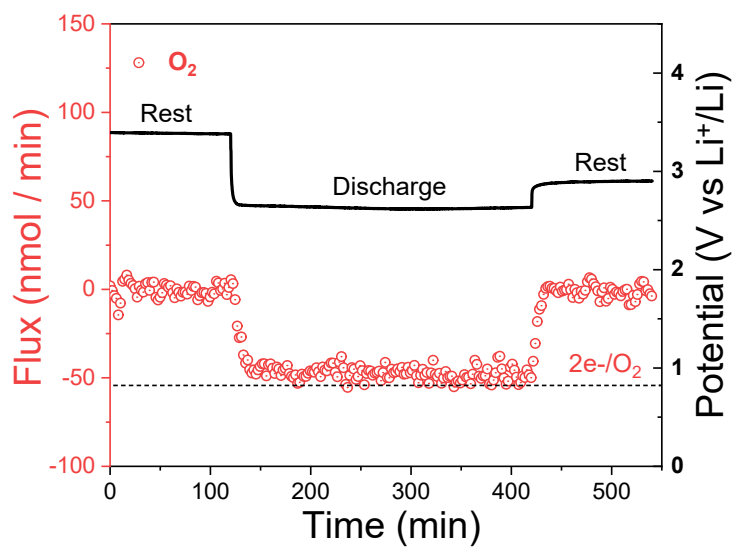


Fig. S7 In situ differential electrochemical mass spectrometry (DEMS) analysis of the gas consumption during Li-O₂ battery operation.

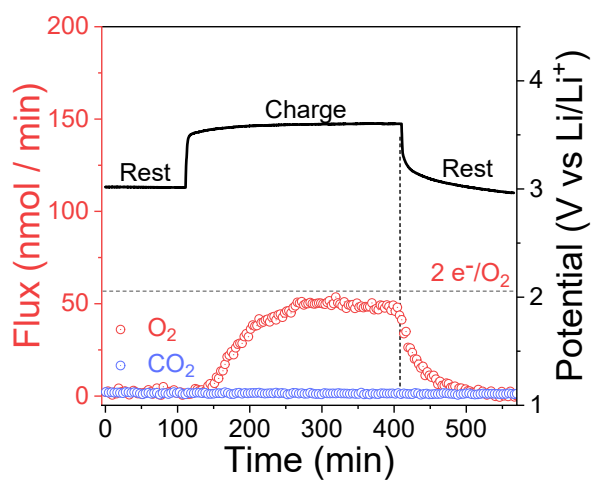


Fig. S8 DEMS experiment during charging of Li-O₂ battery using LiI additive.

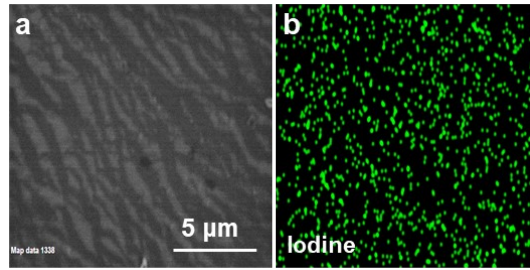


Fig. S9 Surface-sectional SEM images of the cycled Li anode retrieved from the Li|Li symmetric batteries containing 10 mM LiI additive (a), with a corresponding EDX mapping images of the SEI layer of (b) Iodine element.

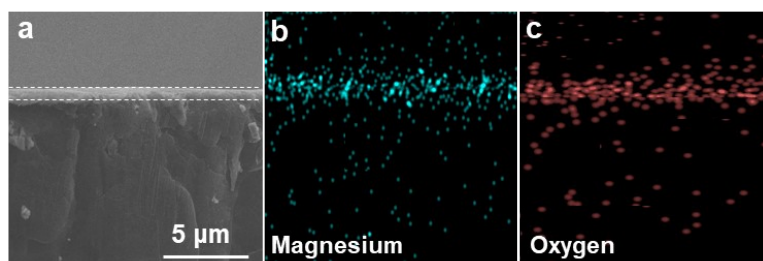


Fig. S10 Cross-sectional SEM images of the cycled Li anode retrieved from the Li|Li symmetric batteries containing 10 mM MgI_2 additive (a), with a corresponding EDX mapping images of the SEI layer of (b) Magnesium element, (c) Oxygen element.

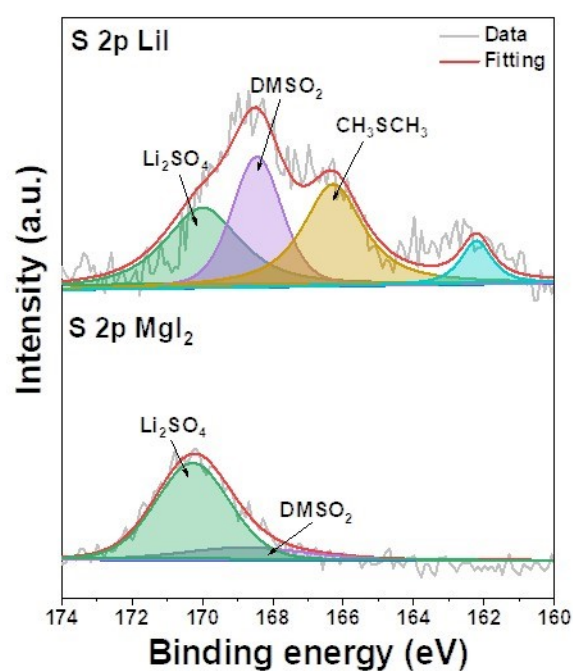


Fig. S11 The XPS of S 2p spectra on the surface of Li anodes extracted from Li-Li symmetric batteries with LiI or MgI_2 additive after 10 cycles.