

Supplementary Materials

Ethyl Bromofluoroacetate Redox Mediator Enables Robust LiF-Rich Solid Electrolyte Interphase for Advanced Lithium-Oxygen Batteries

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Experimental Section¹⁻³

MWCNT cathode

The weight ratio of MWCNT (XFNANO, 8-15nm), single layer graphene and polyvinylidene fluoride (PVDF) is 8:1:1, and then add appropriate N-methyl-2-pyrrolidone (NMP). The mixture is ultrasonicated for 30 minutes followed by magnetic stirring for over 12 hours. And then, the slurry is casted onto the round carbon paper whose diameter is 12 mm and thickness is 0.2 mm. Then the cathode is dried at 80 °C in vacuum for 24 hours. The loading weight of the cathode is ~0.1 mg.

Cu foil

Cu foil whose thickness is ~0.2mm is cut into a disc of 12 mm in diameter.

Li anode

The Li foil whose thickness is ~0.2 mm is cut into a disc of 15.6 mm in diameter.

Separator

A Waterman GF/C glass fiber separator is cut into a disc of 16 mm in diameter.

Assembling lithium-oxygen coin battery

Two-electrode batteries configuration using CR2032 coin-type batteries with holes for O₂ access are employed and assembled in an argon-filled glove box with O₂ and H₂O content below 0.1 ppm. The lithium-oxygen batteries are assembled with MWCNT cathode, Waterman GF/A glass fiber separators and lithium metal anodes. The amount of 1.0 M lithium bis (trifluoromethane sulfonyl) imide/Tetraethylene glycol dimethyl ether (LiTFSI/TEGDME) electrolyte in a coin battery is ~120 μL. 100 mM lithium bromide (LiBr, Adamas, 99.99%) or ethyl bromofluoroacetate (EBFA, TCI, 98%) is added as electrolyte additive. After assembly, the lithium-oxygen batteries are transferred into a glass test chamber inflated with 1.0m bar of high-purity O₂ and rest for 3h.

Assembling symmetrical Li|Li battery

Two-electrode batteries configuration using CR2032 coin-type batteries is employed and assembled in an argon-filled glove box with O₂ and H₂O content below 0.1 ppm. The Li foil is the working electrode. The amount of 1M lithium bis (trifluoromethane sulfonyl) imide/Tetraethylene glycol dimethyl ether (LiTFSI/TEGDME) electrolyte in a coin battery is ~60 μL. 50 mM lithium bromide (LiBr, Adamas, 99.99%) or ethyl bromofluoroacetate (EBFA, TCI, 98%) is added as electrolyte additive.

Assembling Li|Cu battery

Two-electrode batteries configuration using CR2025 coin-type batteries is employed and assembled in an argon-filled glove box with O₂ and H₂O content below 0.1 ppm. The Li foil and Cu foil are the working electrode. 2wt% Lithium nitrate/ 1,3-

Dioxolane/ 1,2-Dimethoxyethane (LiNO₃/DOL/DME) electrolyte in a coin battery is ~60 μL. 50 mM lithium bromide (LiBr, Adamas, 99.99%) or ethyl bromofluoroacetate (EBFA, TCI, 98%) is added as electrolyte additive.

Electrochemical pretreatment of lithium-oxygen batteries

The Li|MWCNT coin batteries are transferred into a glass test chamber with argon-filled atmosphere and rest for 3h. Then the coin batteries discharge from open-circuit voltage (OCV) for 2h, and then charge for 2h at a current density of 1000 mA/g on the LAND electrochemical testing system. The process repeats for 3 cycles. After pretreatment, the lithium-oxygen batteries are transferred into a glass test chamber inflated with 1.0m bar of high-purity O₂ and rest for 3h.

Electrochemical analysis

Galvanostatic discharging/ charging curve tests are using the LAND electrochemical testing system. Cyclic voltammetry (CV) measurement is tested using Bio-logic VSP in the voltage range of 2.0-4.2 V at a scan rate of 0.1 mV/s. Electrochemical Impedance Spectroscopy (EIS) is performed using Gamry Interface 5000 E with a voltage amplitude of 10 mV and a frequency range of 10⁶ to 10⁻¹.

Characterization

Li-O₂ batteries after cycling, are disassembled in the argon-filled glove box. Then, the anodes are washed in 1,2-Diethoxyethane (DME) for 30 min, and dry for 2 h. Field emission scanning electron microscopy (SEM, Apreo 2C) is used to observe the microstructure of the lithium anodes. Fourier transform infrared spectroscopy (FTIR) is performed using a Bruker Scientific spectrometer (TENSOR II) from 4000 to 400

cm⁻¹. The X-ray photoelectron spectroscopy (XPS) results are obtained on a Thermo Fisher ESCALAB Xi+ spectrometer with a monochromatic Al K α X-ray source.

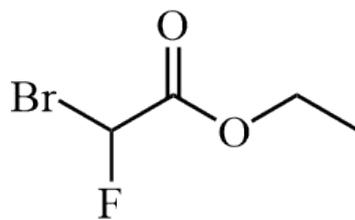


Figure S1. The structural formula of ethyl bromofluoroacetate (EBFA).

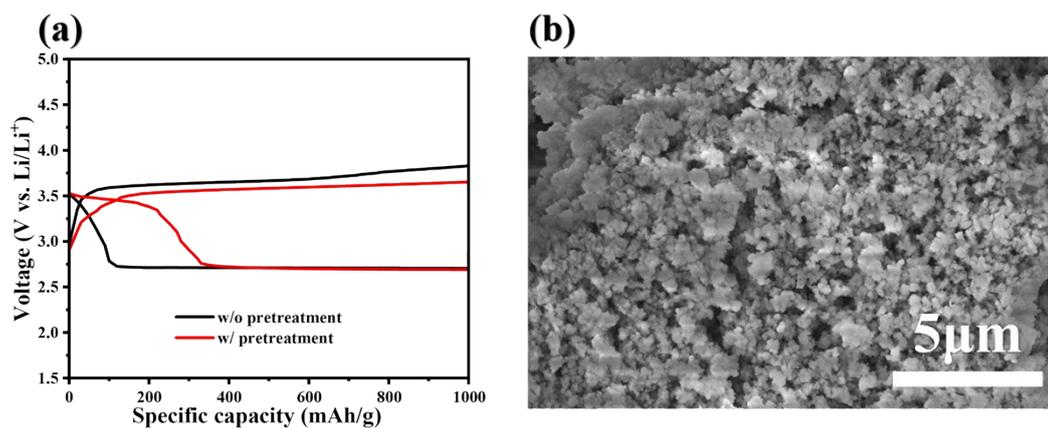


Figure S2. (a) Galvanostatic discharge/ charge curves of the EBFA-containing Li-O₂ batteries with or without pretreatment additive at 1000 mA/g of the first cycle. (b) SEM image of the lithium anode surface of the Li-O₂ battery without pretreatment after 20 cycles. Scale bar is 5 μm.

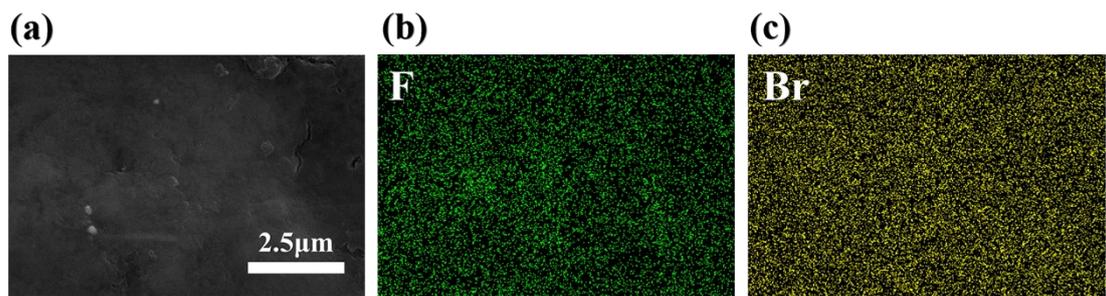


Figure S3. (a) SEM image of lithium-oxygen battery with EBFA after pretreatment. EDS spectra of F (b) and Br (c) for lithium anode surface of Li-O₂ battery with EBFA after pretreatment.

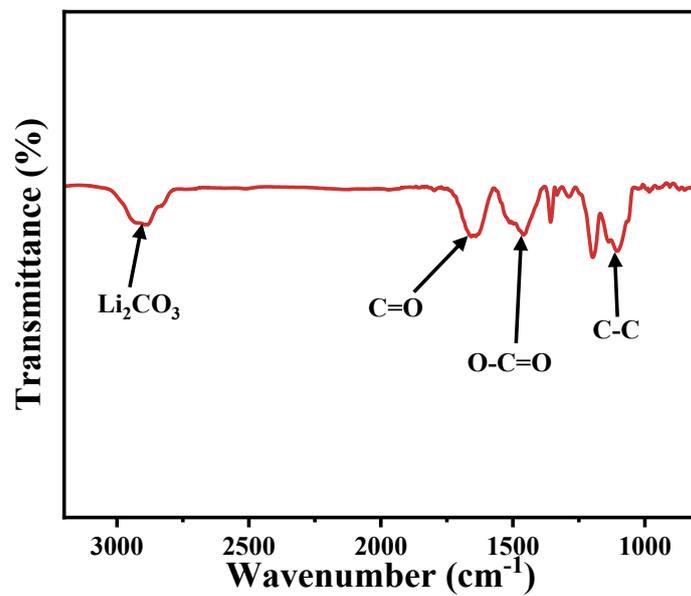


Figure S4. FTIR spectrum of the lithium anode of the Li-O₂ battery with EBFA after pretreatment.

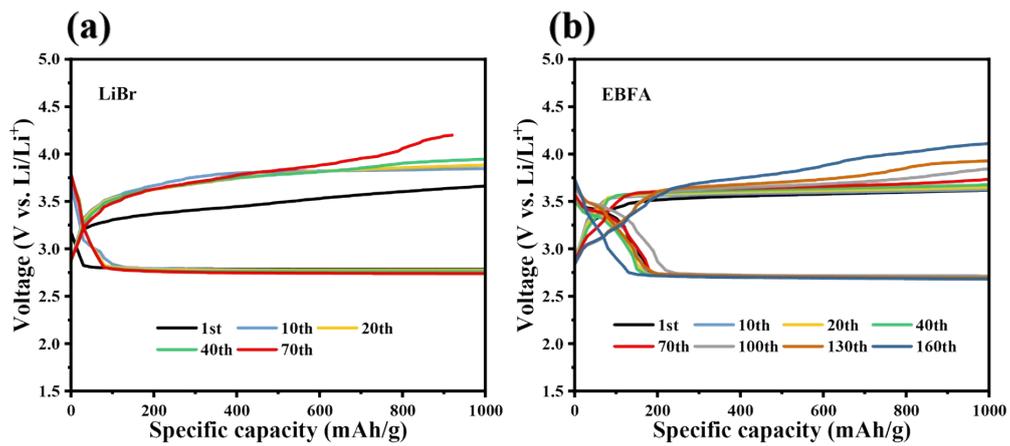


Figure S5. Long-term galvanostatic discharge/charge curves at 1000 mA g⁻¹ of the batteries with 50 mM LiBr (a) or EBFA (b).

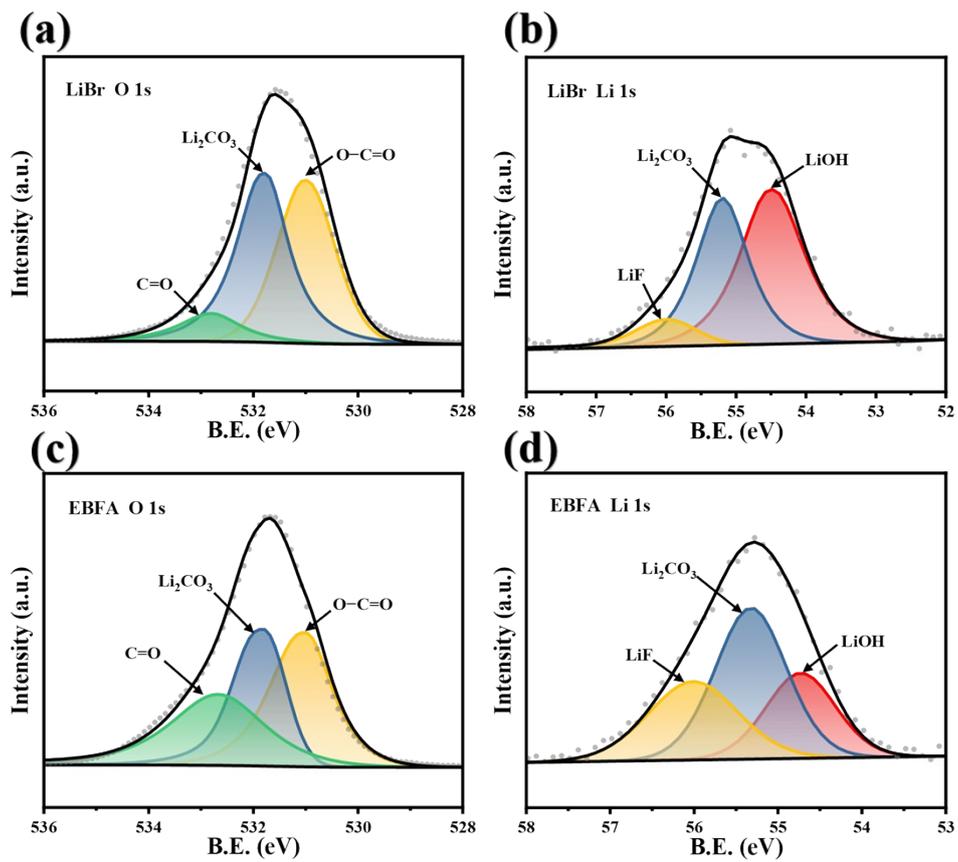


Figure S6. XPS spectra for lithium anode in Li-O₂ batteries after pretreatment. (a) O 1s with LiBr. (b) Li 1s with LiBr. (c) O 1s with EBFA. (d) Li 1s with EBFA.

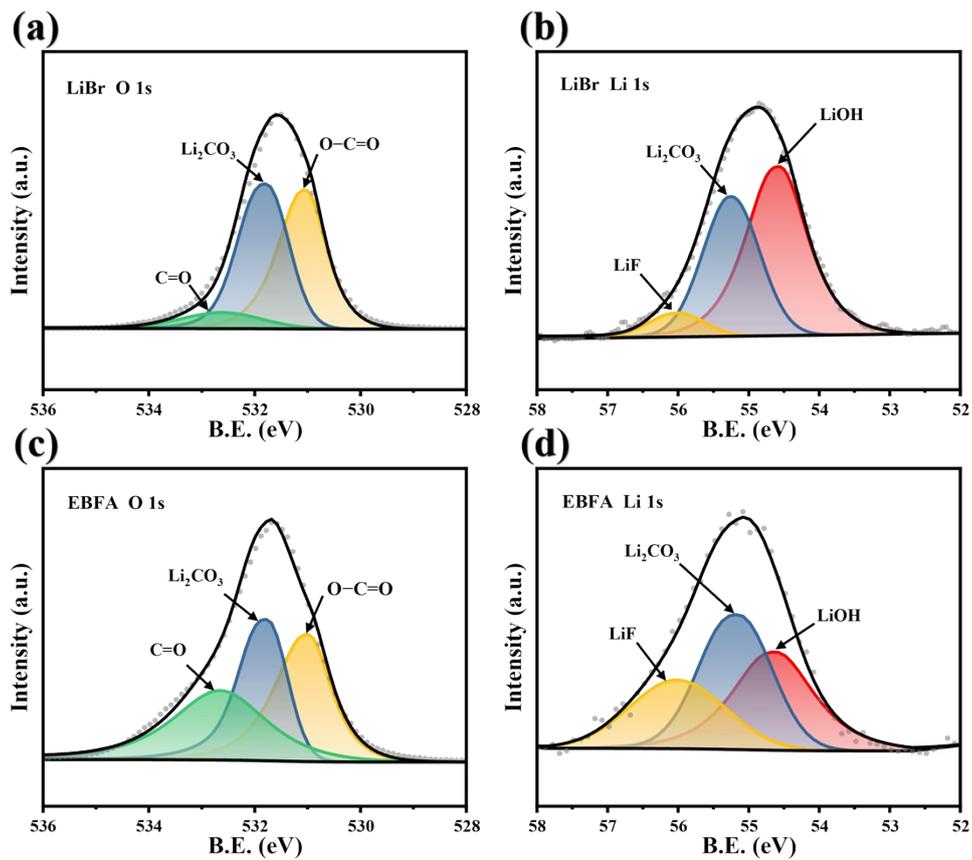


Figure S7. XPS spectra for lithium anode in Li-O₂ batteries with after 20 cycles. (a) O 1s with LiBr. (b) Li 1s with LiBr. (c) O 1s with EBFA. (d) Li 1s with EBFA.

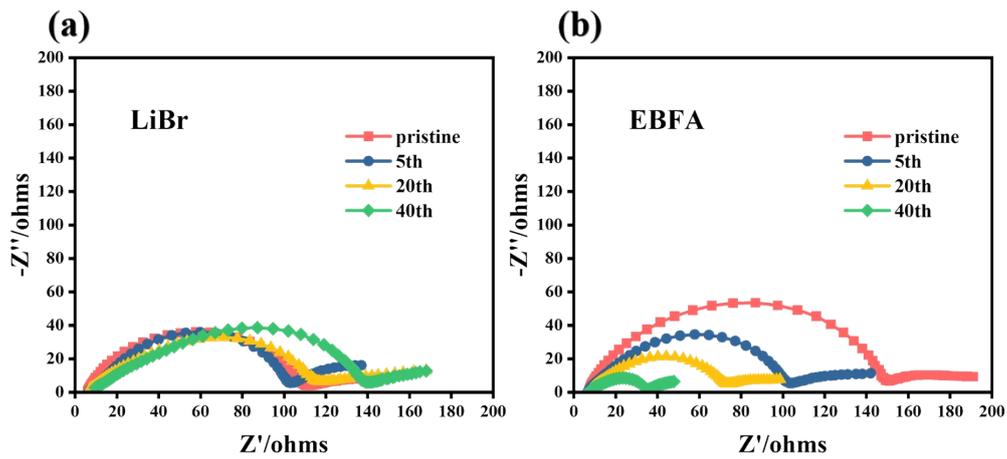


Figure S8. The Nyquist plots of impedance's evolution for the symmetrical Li | Li battery with LiBr (a) and EBFA (b).

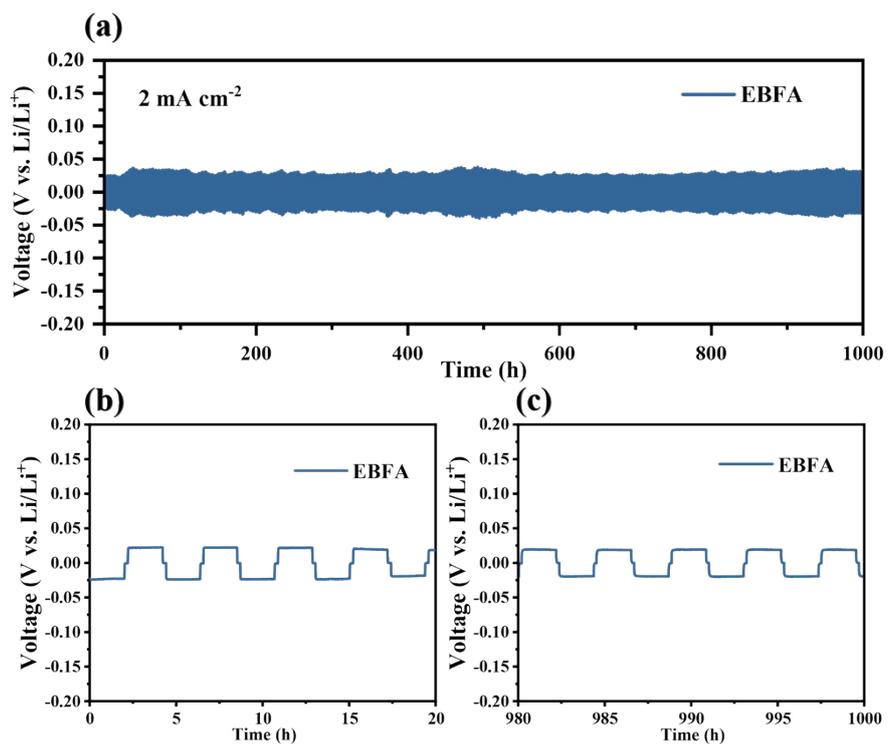


Figure S9. (a) The cycling performance of symmetrical Li | Li battery with EBFA at the current density of 2 mA cm⁻². (b) and (c) The magnified charge/discharge curves for particular selected period.

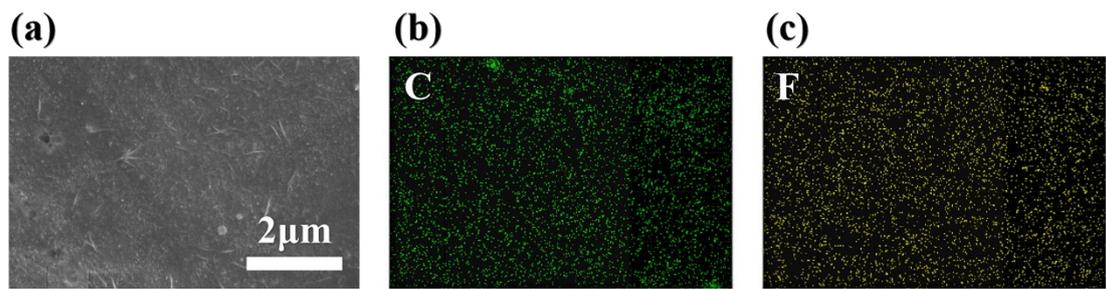


Figure S10. (a) SEM image of Li | Cu battery with EBFA after pretreatment. EDS spectra of C (b) and F (c) for lithium anode surface of Li | Cu battery with EBFA after pretreatment.

Table 1. Some electrolyte additives for Li–O₂ batteries and their effects.

Additive	Effect on cathode	Effect on anode	Cycling performance for Li metal batteries
LiI ⁴	The redox couples I ₃ ⁻ / I ⁻ catalyze the oxidation of Li ₂ O ₂ . But high concentration of LiI tend to promote a side reaction which produces LiOH as one of the major products.	The shuttle effect causes the lithium metal cathode to be consumed.	The LiTFSI/ TEGDME based Li–O ₂ battery with 50 mM LiI can cycle to ~50 cycles at 1000 mA g ⁻¹ .
LiBr ⁵	LiBr produces the redox couples Br ₃ ⁻ / Br ⁻ which catalyze the oxidation of Li ₂ O ₂ .	The shuttle effect causes the lithium metal cathode to be consumed.	The LiTFSI/ TEGDME based Li–O ₂ battery with 50 mM LiBr can cycle to ~65 cycles at 1000 mA g ⁻¹ .
Fluoroethylene carbonate(FEC) ⁶	No description.	It produces an FEC-induced SEI film. This artificial SEI film has high content of LiF and make the lithium deposition.	The Li NMC battery obtains a high initial capacity of 154 mA h g ⁻¹ (1.9 mA h cm ⁻²) at 180.0 mA g ⁻¹ .
Ethyl bromofluoroacetate (EBFA) (This work)	EBFA produces the redox couples Br ₃ ⁻ / Br ⁻ which catalyze the oxidation of Li ₂ O ₂ .	EBFA promotes the formation of a LiF-Rich SEI film on Li anode.	The LiTFSI/ TEGDME based Li–O ₂ battery with 50 mM LiBr can cycle to 170 cycles at 1000 mA g ⁻¹ .

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