

Supplementary Materials

π -Conjugated Dual-Functional Redox Mediator Facilitate the Construction of Dendrites-Free Lithium-Oxygen Batteries

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Experimental Section¹⁻³

MWCNT cathode

MWCNT (XFNANO, 8-15nm), single layer graphene and polyvinylidene fluoride (PVDF) were mixed with weight ratio of 8:1:1 in N- methyl- 2- pyrrolidone (NMP). The mixture was ultrasonicated for 30 minutes followed by magnetic stirring for 24 hours. And then, the slurry was casted onto the round- shape carbon paper with a diameter of 11 mm and a thickness of ~0.2 mm and vacuum dried at 80 °C for 24 hours. The loading weight of the cathode was ~0.1mg. The loading area was ~0.25 cm².

Li anode

The Li foil of thickness 0.2 mm was cut into 15.6 mm diameter discs.

Cu foil

A 0.2 mm thick Cu foil was cut into a disc of 11.0 mm in diameter.

Assembling Li-O₂ coin cell

Two-electrode system cells were assembled using CR2032-type coin cells with hole for O₂ channel in an Ar-filled glove box (O₂ and H₂O < 0.5 ppm). The lithium-oxygen batteries were 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/ Methyl sulfoxide (LiTFSI/ DMSO) electrolyte in a coin cell is ~120 μL. 100 mM lithium bromide (LiBr, Adamas, 99.99%) or tert-Butylmethoxyphenylsilyl Bromide (TBMPSiBr, Sigma-Aldrich, 96%) is added as redox mediators. After assembly, the Li-O₂ batteries are transferred into a glass test chamber inflated with 1.0m bar of high-purity O₂ and rest for 3h.

Three-electrode system cells were using a silicon carbon rod as the working electrode, Au as the counter electrode and Ag as a reference electrode.

Assembling Li | Li symmetric batteries and Li | Cu batteries

Symmetric Li | Li metal batteries are assembled using CR2032-type coin cells using the Li foil as working electrodes, Waterman GF/C as separator. The amount of 1.0 M lithium hexafluorophosphate/ ethylene carbonate / dimethyl carbonate (LiPF₆/EC/DMC) electrolyte in a coin cell was ~70 μL.

Li | Cu batteries were assembled using CR2025-type coin cells. The amount of 1.0 M Lithium hexafluorophosphate/ ethylene carbonate / dimethyl carbonate (LiPF₆/EC/DMC) electrolyte in a coin cell was ~70 μ L. 100 mM lithium bromide (LiBr) or tert-Butylmethoxyphenylsilyl Bromide (TBMPSiBr) is added as redox mediators in both Li | Li symmetric batteries and Li | Cu batteries.

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. And in a three-electrode system, the voltage range is -0.8-1.8V at a scan rate of 50 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 10^6 to 10^{-1} .

Characterization

Lithium-oxygen batteries after cycling, are disassembled in the argon-filled glove box. Then, the anodes were washed in 1,2-Diethoxyethane (DME) for 30 min, and dried for 2 h. Field emission scanning electron microscopy (SEM, Apreo 2C) was used to observe the microstructure of the lithium anodes. Fourier transform infrared spectroscopy (FTIR) was

performed using a Bruker Scientific spectrometer (TENSOR II) from 4000 to 400 cm^{-1} . The X-ray photoelectron spectroscopy (XPS) results were obtained on a Thermo Fisher ESCALAB Xi+ spectrometer with a monochromatic Al $K\alpha$ X-ray source.

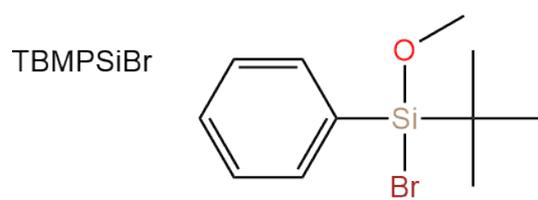


Fig S1. The structural formula of tert-Butylmethoxyphenylsilyl Bromide.

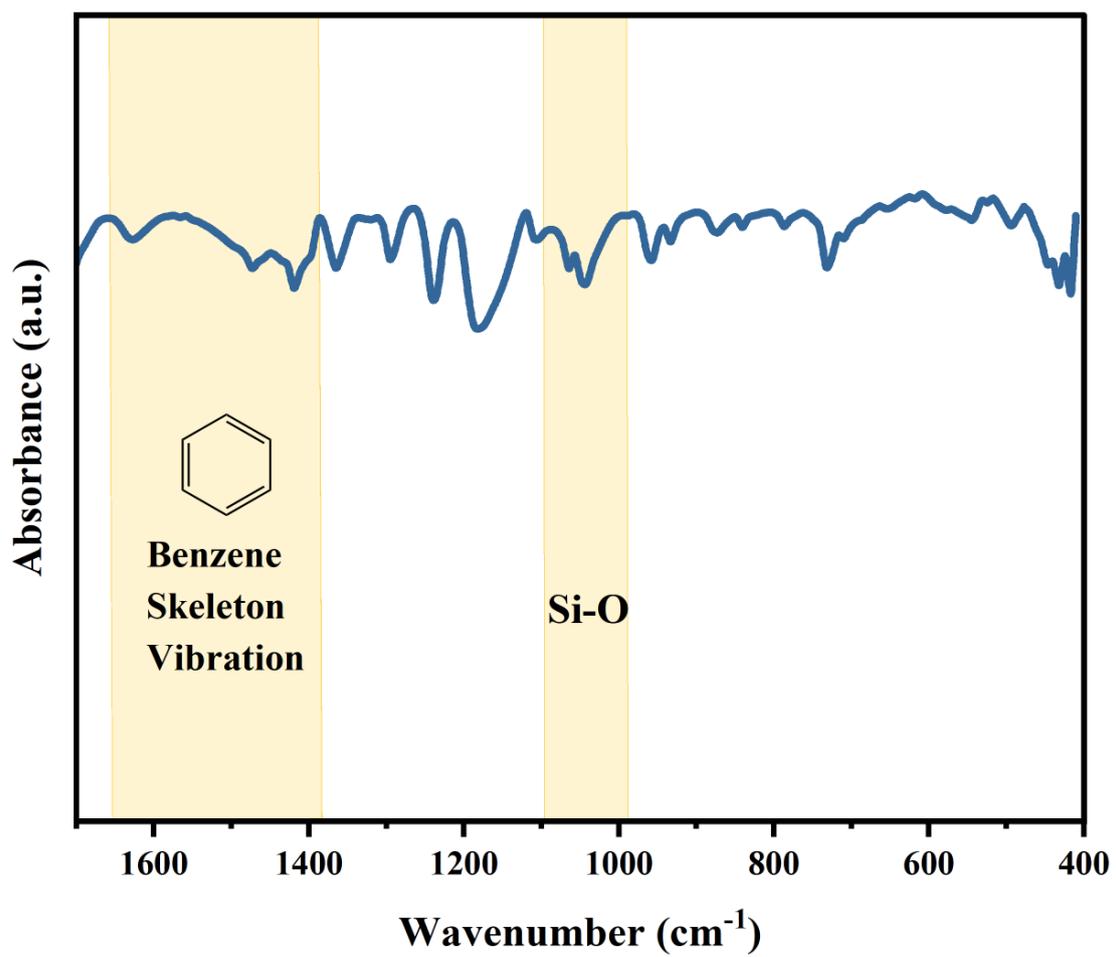


Fig S2. FTIR spectra of lithium metal tablet after dropping 20 μL TBMPsiBr | DMSO | LiTFSI electrolyte.

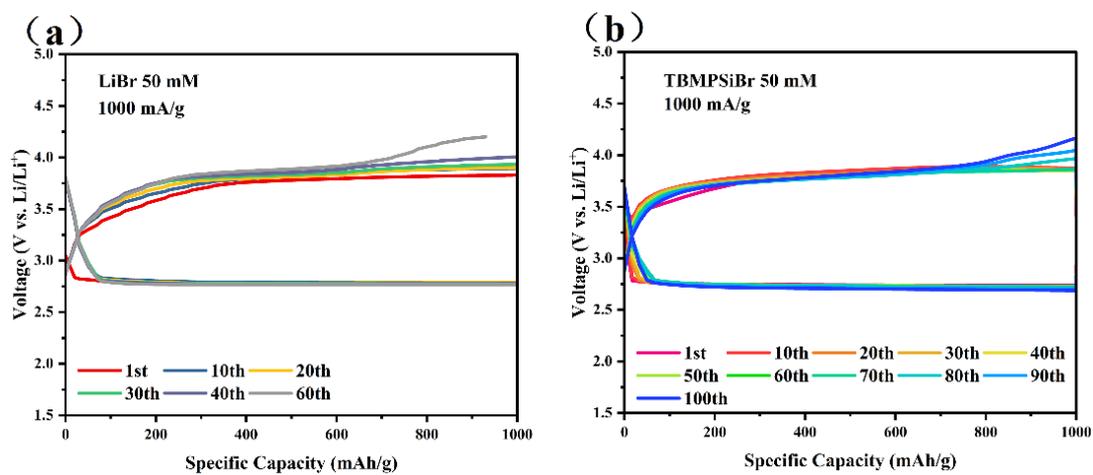


Fig S3. Cycling stability of the lithium-oxygen batteries with 50 mM (a) LiBr or (b) TBMPSiBr additives.

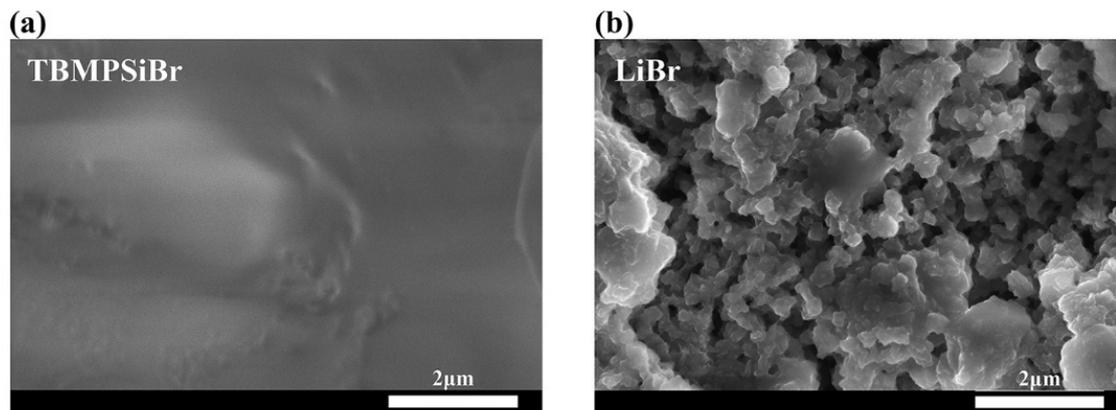


Fig S4. SEM images of the lithium anode in the 50 mM (a) TBMPSiBr-containing (b) LiBr-containing lithium-oxygen battery after 30 cycles.

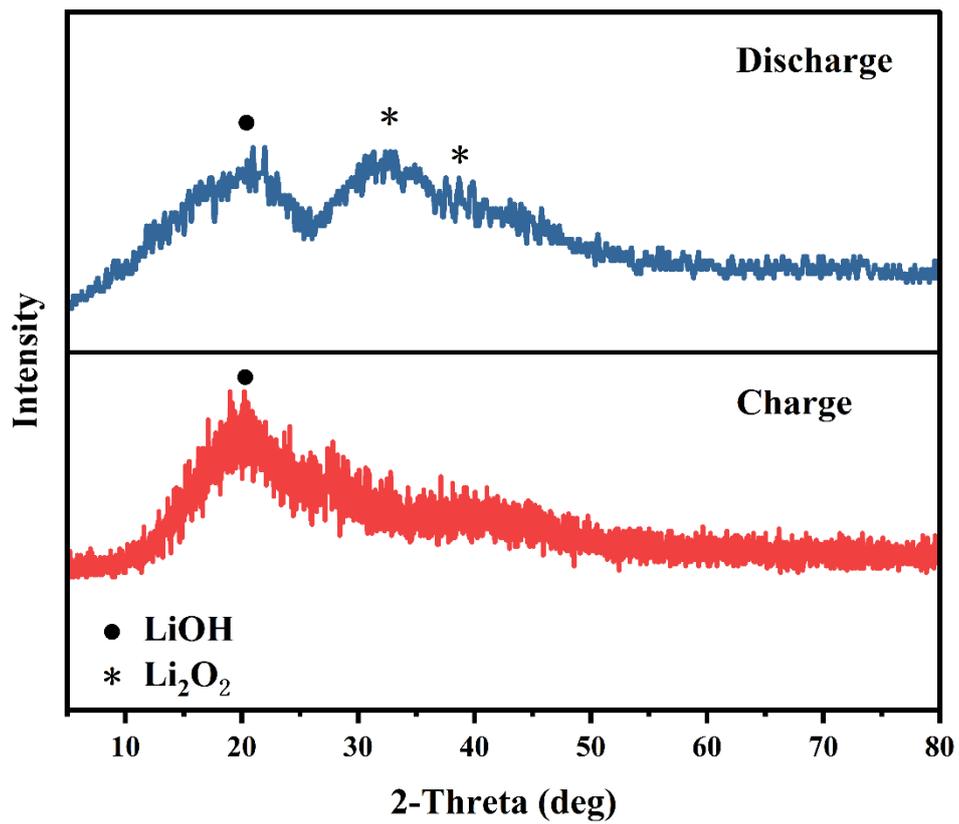


Fig S5. XRD patterns of the cathode at the end of discharge and the cathode at the end of charge.

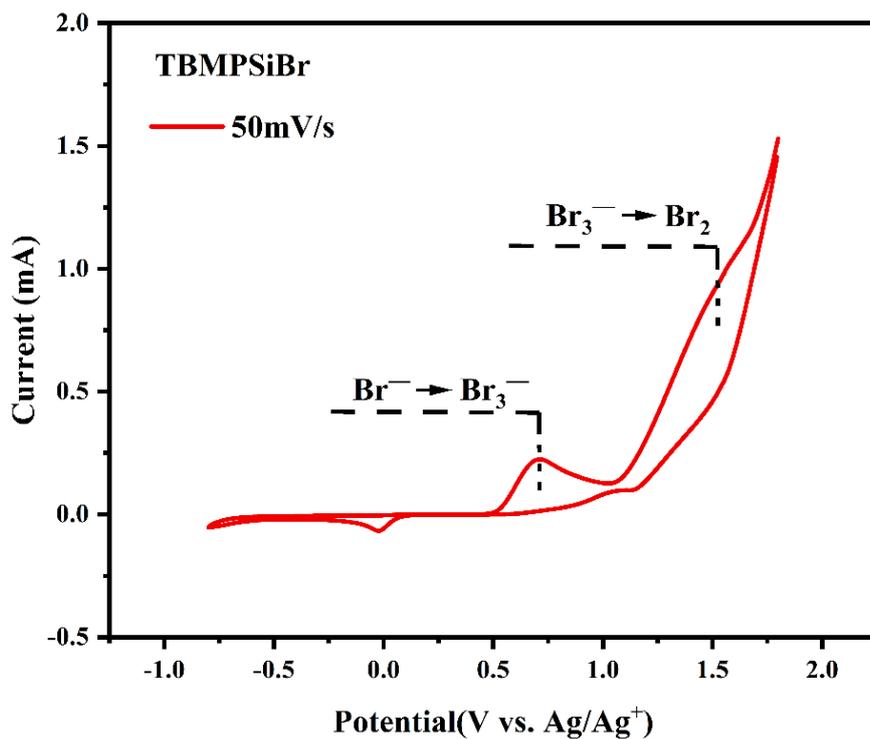


Fig S6. Cyclic voltammogram (CV) curves for a three-electrode system.

The scan rate is 50 mV/s.

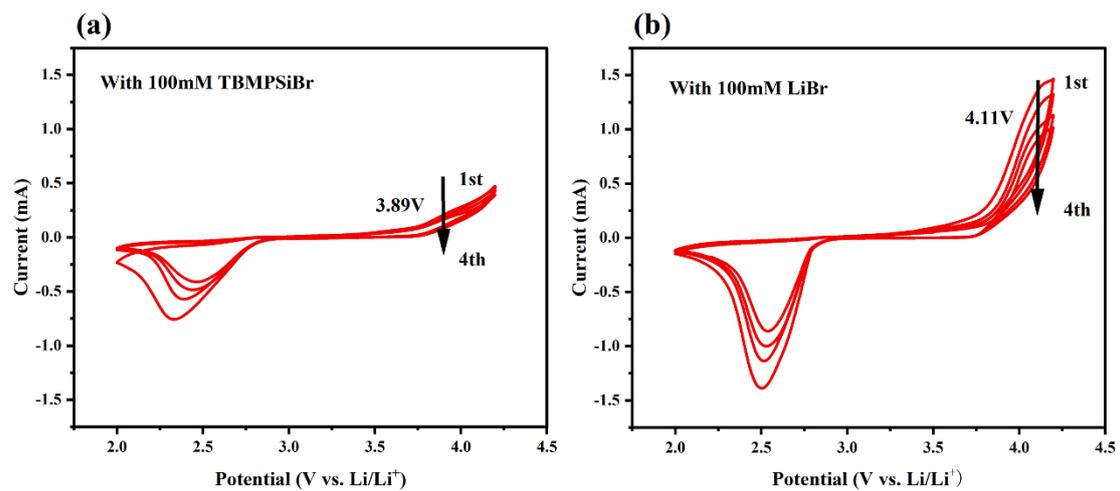


Fig S7. Cyclic voltammograms of lithium-oxygen batteries with (a) 100 mM TBMPsiBr and (b) 100 mM LiBr. The scan rate is 0.1 mV/s

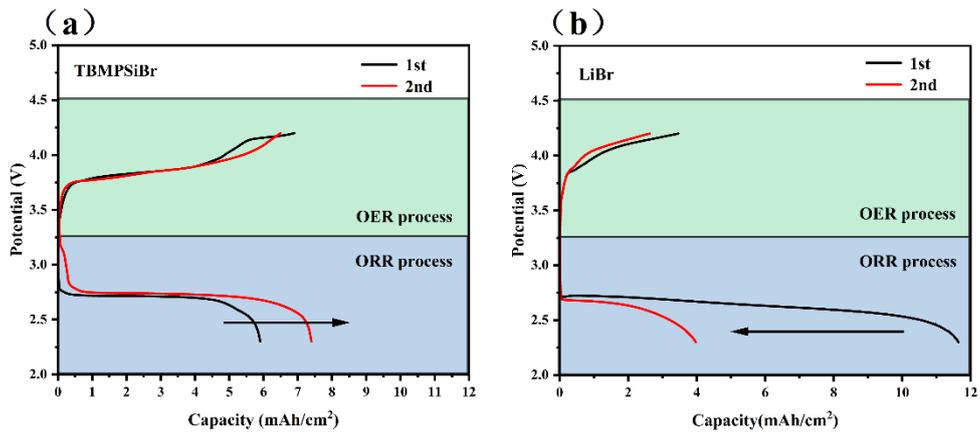


Fig S8. Voltage profiles of the first and second cycles of lithium-oxygen batteries. (a) TBMPsiBr (b) LiBr.

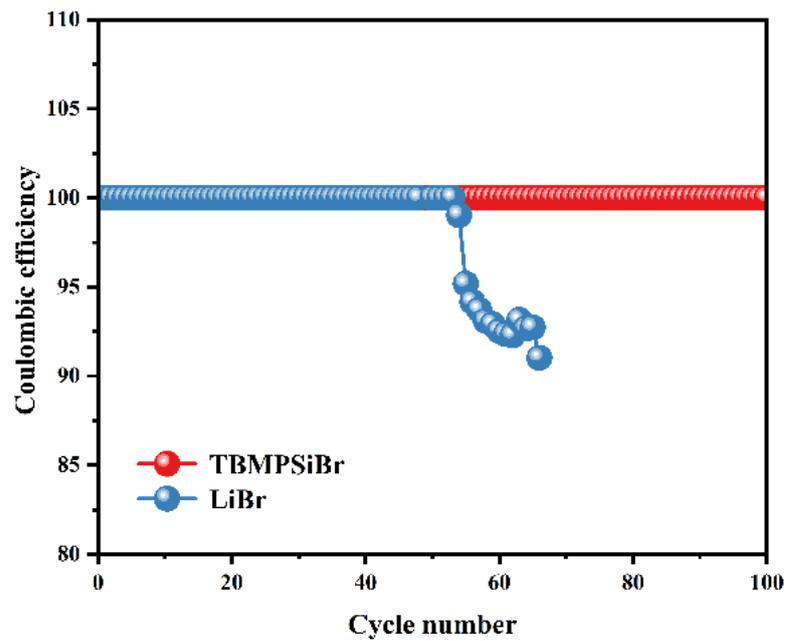


Fig S9. The comparison of coulombic efficiency of 50 mM TBMPSiBr or LiBr-containing lithium-oxygen batteries

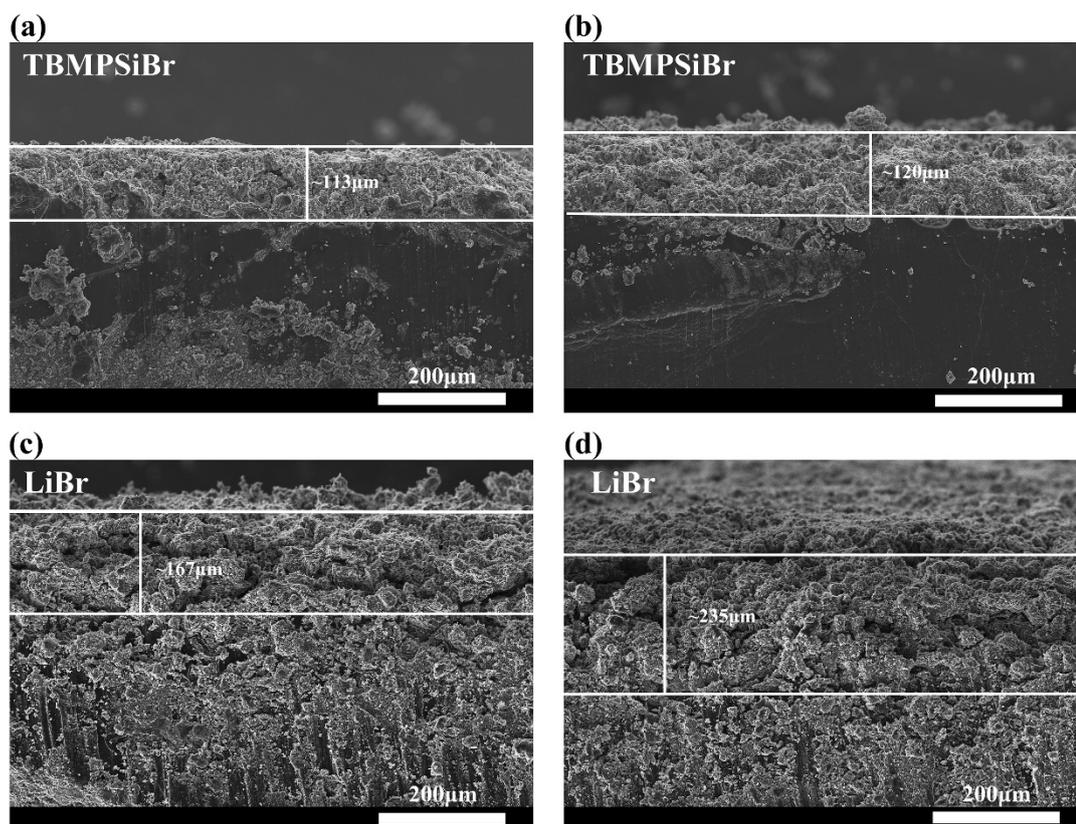


Fig. S10 Cross-section SEM images of lithium metal anodes after (a) 30 cycles and (b) 50 cycles of TBMPSiBr-containing lithium metal anodes, (c) 30 cycles and (d) 50 cycles of LiBr-containing lithium metal anodes tested under a current density of 1000 mAh/g and a current at 1000 mA/g.

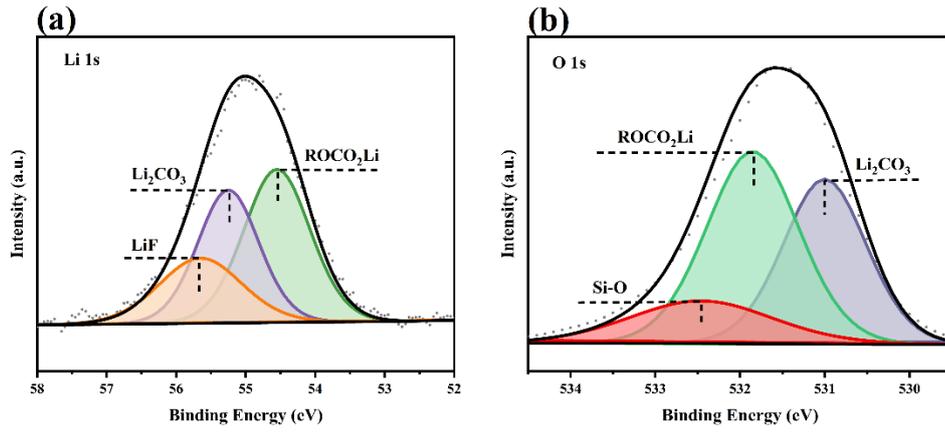


Fig. 11 XPS spectra for the lithium anode in the TBMPSiBr-containing lithium-oxygen battery after 30 cycles. (a) Li 1s. (b) O 1s.

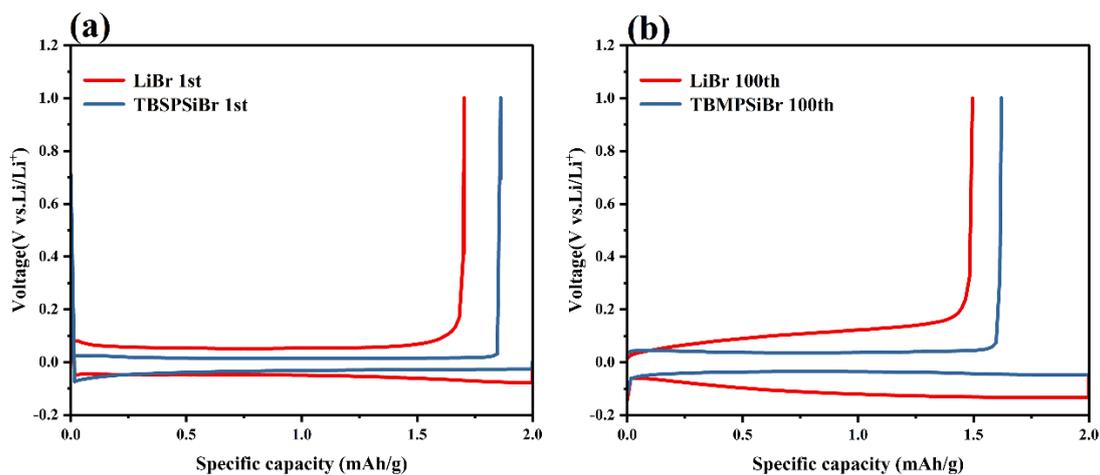


Fig. S12 Electrochemical performance of Li | Cu batteries. The electrodes are stripped/plated at a current density of 1 mA cm^{-2} with a fixed capacity of 2 mA h cm^{-2} . Galvanostatic discharge/charge profiles with 100 mM TBMPSiBr or LiBr additive at 1st cycle (a) 100th cycle (b).

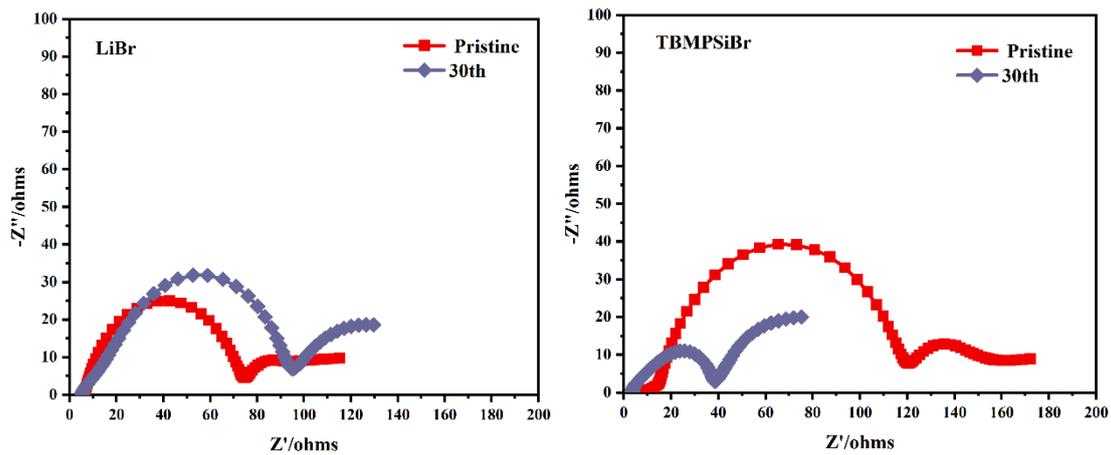


Fig.S13 EIS spectra for (a) TBMPSiBr (b) LiBr.

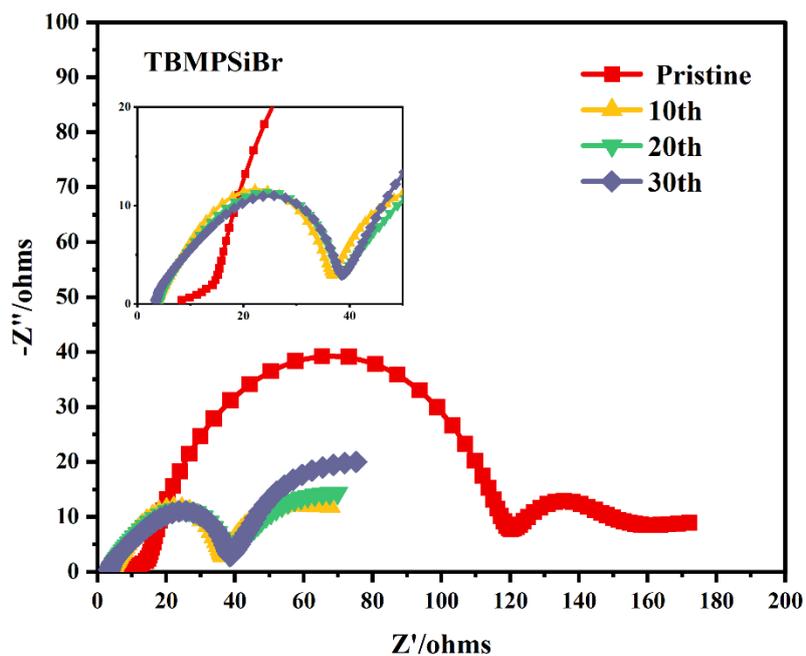


Fig. S14 The change of impedance for Li | Li symmetric batteries with TBMPSiBr.

1. T. Zhang, K. Liao, P. He and H. Zhou, *Energy & Environmental Science*, 2016, **9**, 1024-1030.
2. Y. N. Li, F. L. Jiang, Z. Sun, O. Yamamoto, N. Imanishi and T. Zhang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 16437-16444.
3. X. P. Zhang, Y. Y. Sun, Z. Sun, C. S. Yang and T. Zhang, *Nat Commun*, 2019, **10**, 3543.