Supporting information for

N-methyl-N-propyl Pyrrolidine Bromide (MPPBr) as A Bi-functional Redox Mediator for Rechargeable Li-O_2 Batteries

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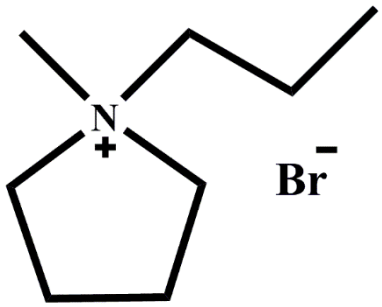

Scheme S1. Structurer of MPPBr

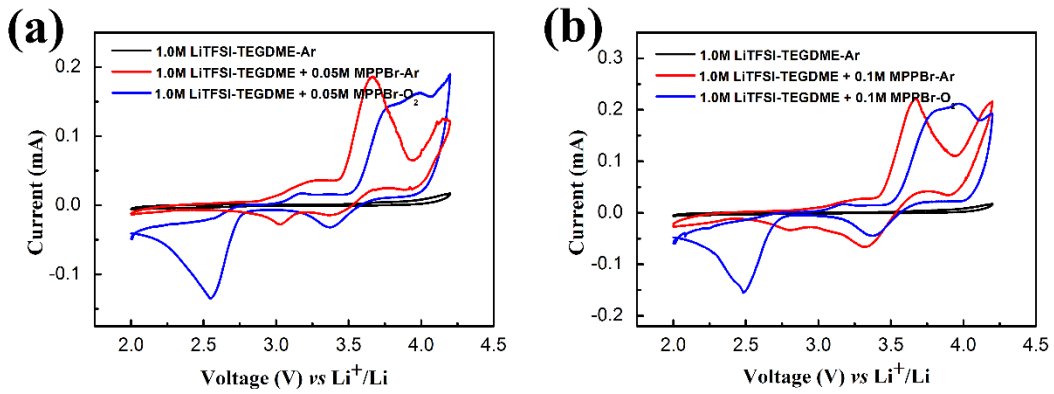

Fig. S1 Cyclic voltammetry (0.1 mV/s) of different concentrations MPPBr dissolved in 1.0 M LiTFSI-TEGDME under Ar or O_2 atmosphere. (a) 0.05 M MPPBr; (b) 0.1 M MPPBr. Black lines in both figure represent the primitive 1.0 M LiTFSI-TEGDME electrolyte under Ar atmosphere.

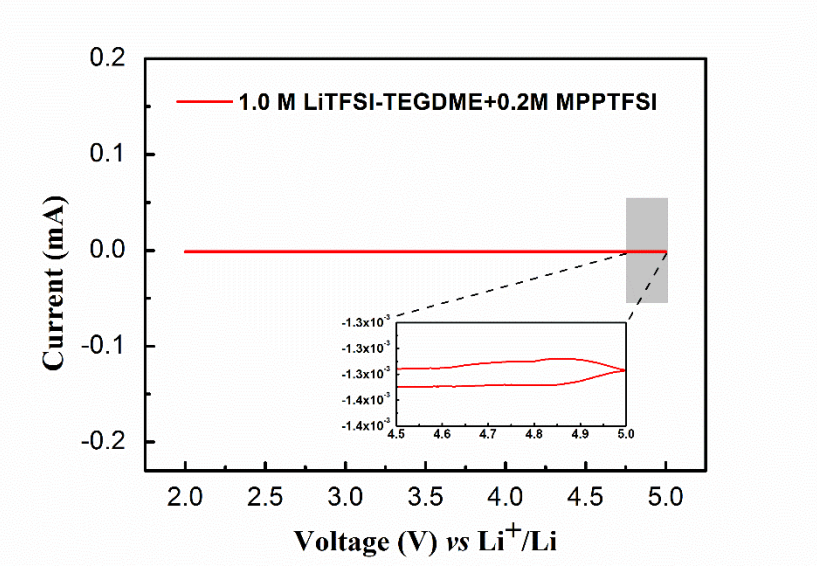

Fig. S2 Electrochemical windows of MPPTFSI at Super P as work electrode, Li foil acting as both anode and the reference electrode, sweeping rate was set at 0.1 mV/s.

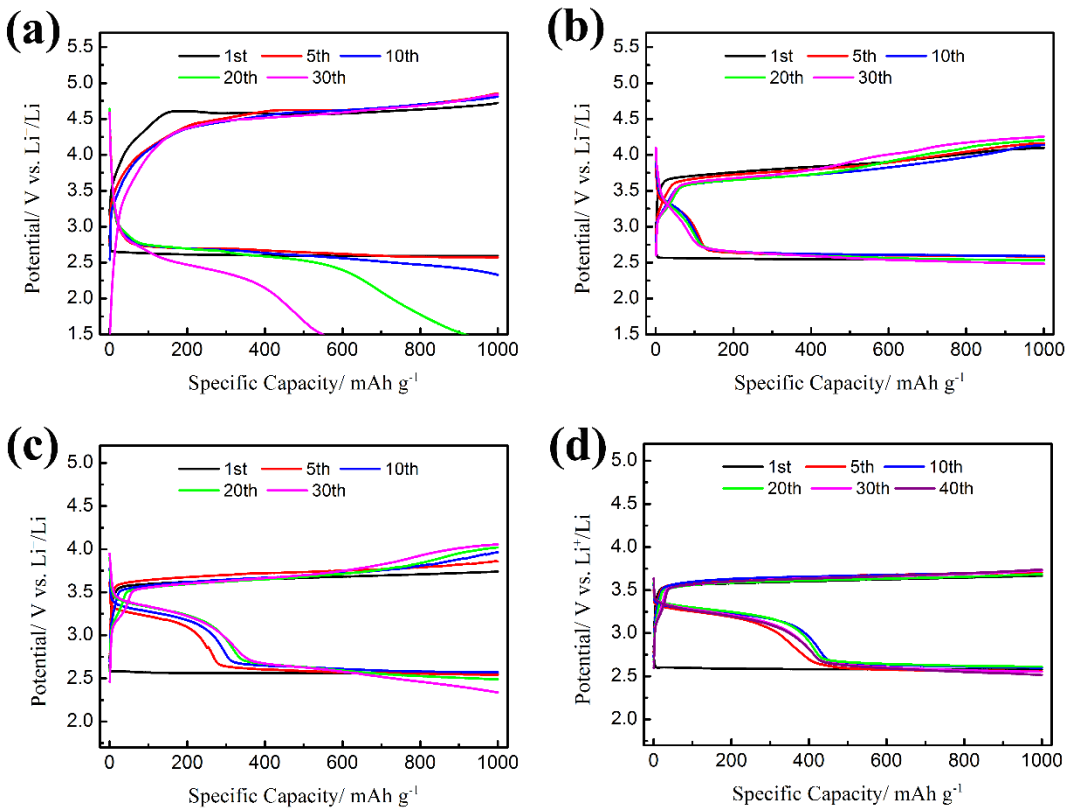

Fig. S3 Voltage profiles of Li-O_2 cells during prolonged cycling with diglyme solution: (a) 1.0 M LiTFSI; (b) 1.0 M LiTFSI + 0.05 M MPPBr; (c) 1.0 M LiTFSI + 0.1 M MPPBr; (d) 1.0 M LiTFSI + 0.2 M MPPBr. The current density is 500 mA g^{-1}.

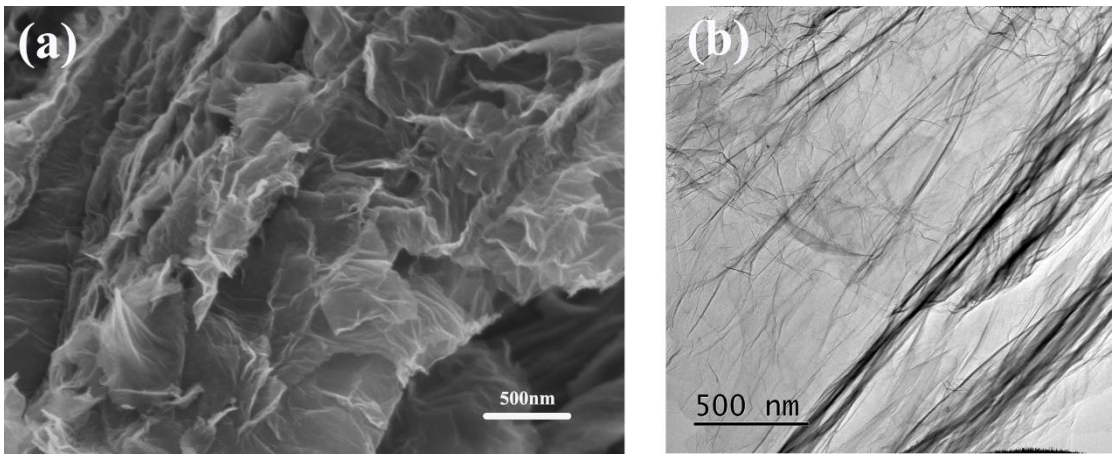

Fig. S4 SEM and TEM images of rGO.

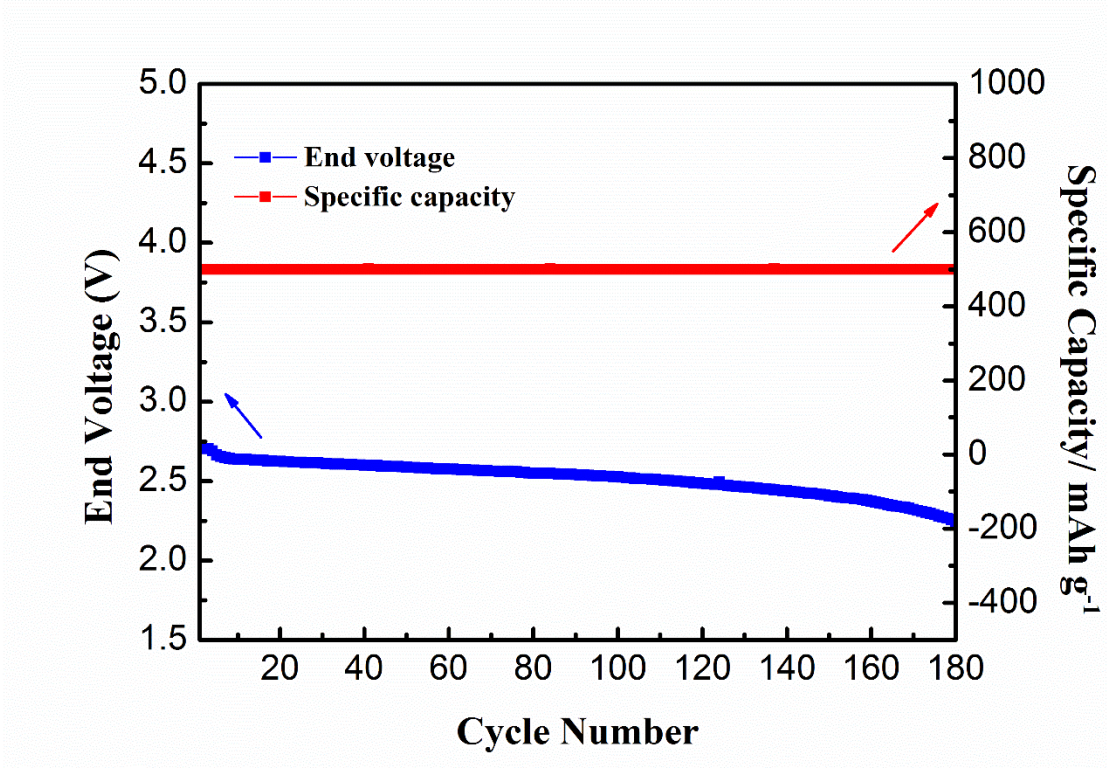

Fig.S5 The cycling performance of a Li-O_2 battery with 1.0 M LiTFSI-TEGDME + 0.2 M MPPBr with a rGO electrode. The current density is 500 mA g^{-1}.

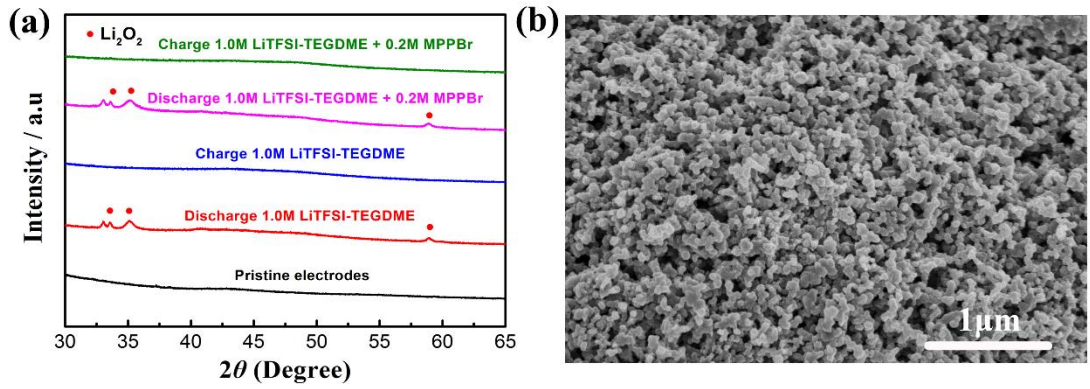

Fig. S6 (a) XRD patterns of the pristine cathode, discharged and charged cathodes cycled with and without the presence of 0.2 M MPPBr. (b) SEM image of the Super P cathode before discharge.

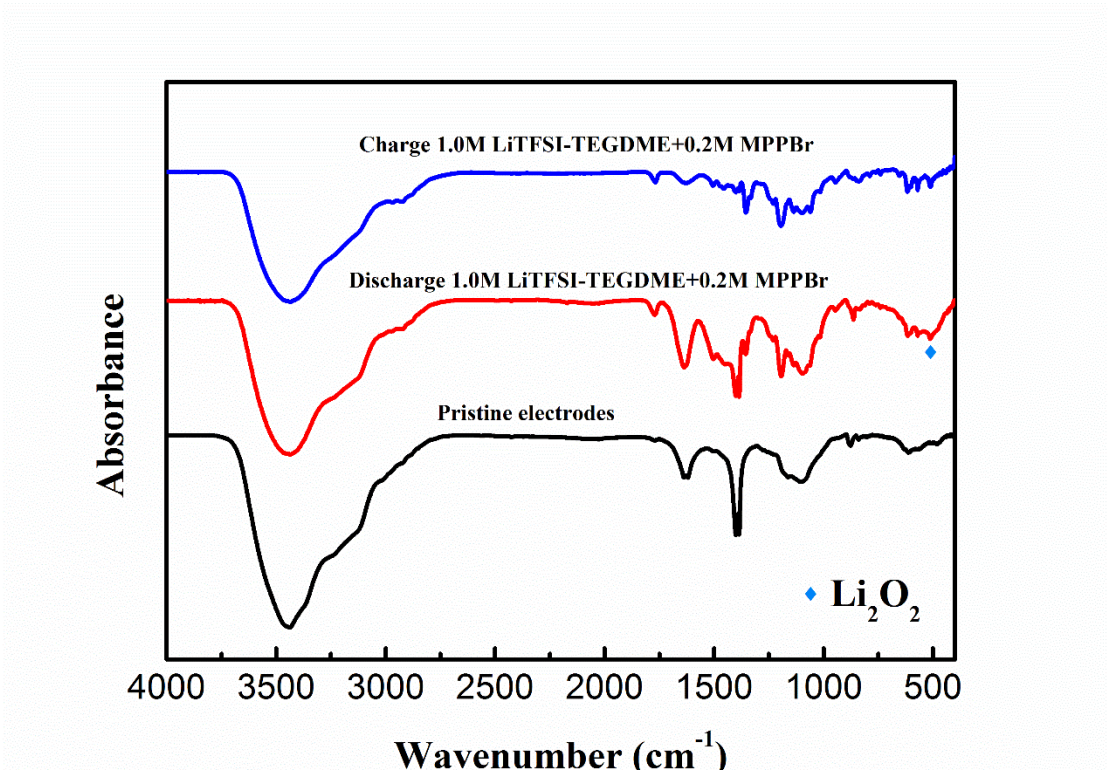

Fig. S7 FTIR spectra of cycled carbon cathodes of Li-O_2 batteries with 1.0 M LiTFSI-TEGDME + 0.2 M MPPBr.

Figure S7 shows the results of Fourier transform infrared spectroscopy (FTIR) of the pristine electrode and cycled electrodes. The spectra show that Li_2O_2 (sharp peak at ≈ 500 cm^{-1}) is formed during the discharge process, and there is no clear band of LiOH (sharp peak at ≈ 3670 cm^{-1}). All of these spectra of cycled electrodes have the pronounced ethers peaks around 1500 - 1000 cm^{-1}, which could be attributable to the residual electrolytes on the electrode surface species (TEGDME, MPPBr). The band at 1732 cm^{-1} can be attributed to the C=O stretching vibrations of Li_2CO_3. The surface of Li_2CO_3 compounds detected by these measurements were formed only because of CO_2 contamination, probably in the ambient environment.

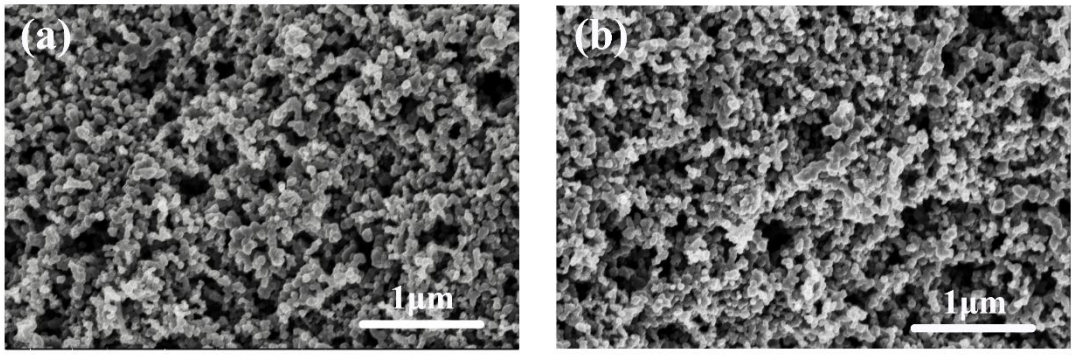

Fig. S8 SEM images of Super P cathodes after charge without 0.2 M MPPBr (a) and with 0.2 M MPPBr (b) dissolved in the 1.0 M LiTFSI-TEGDME electrolyte.

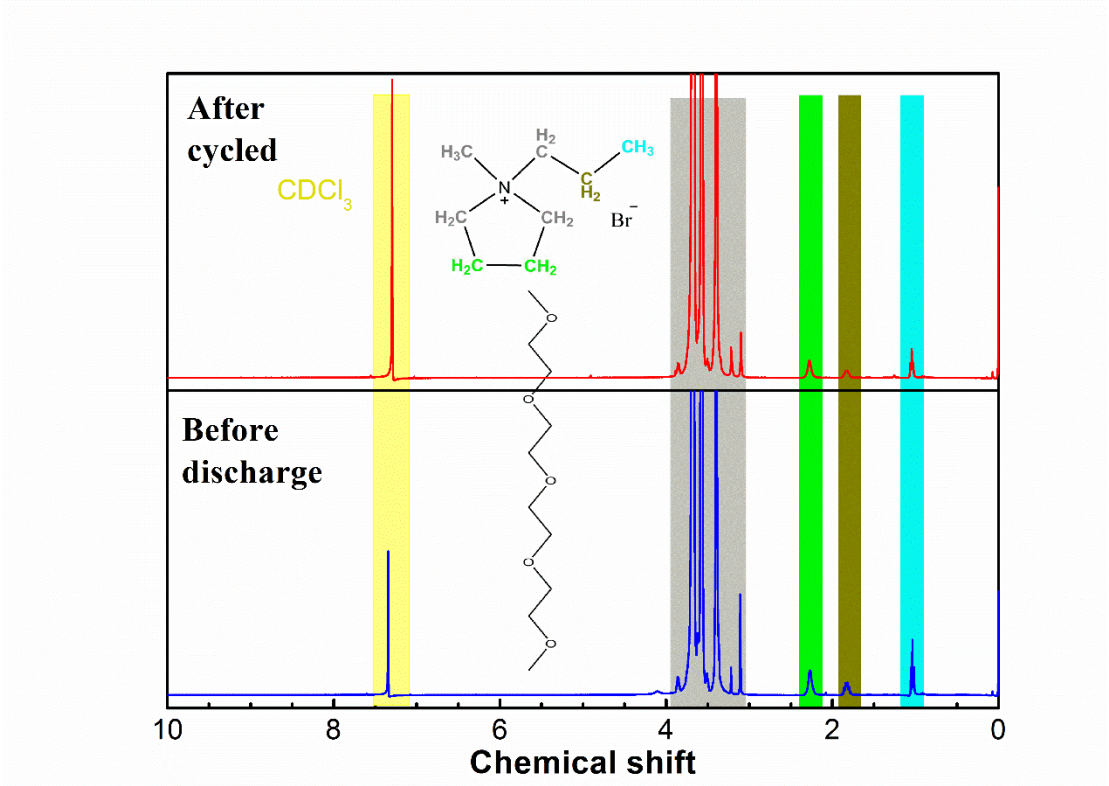

Fig. S9 ^{1}H NMR spectra of the 1.0 M LiTFSI-TEGDME + 0.2 M MPPBr electrolyte before electrochemical cycling and after 30 cycles of Li-O_2 cells at a current density of 500 mA/g for 1000 mAh/g of capacity.

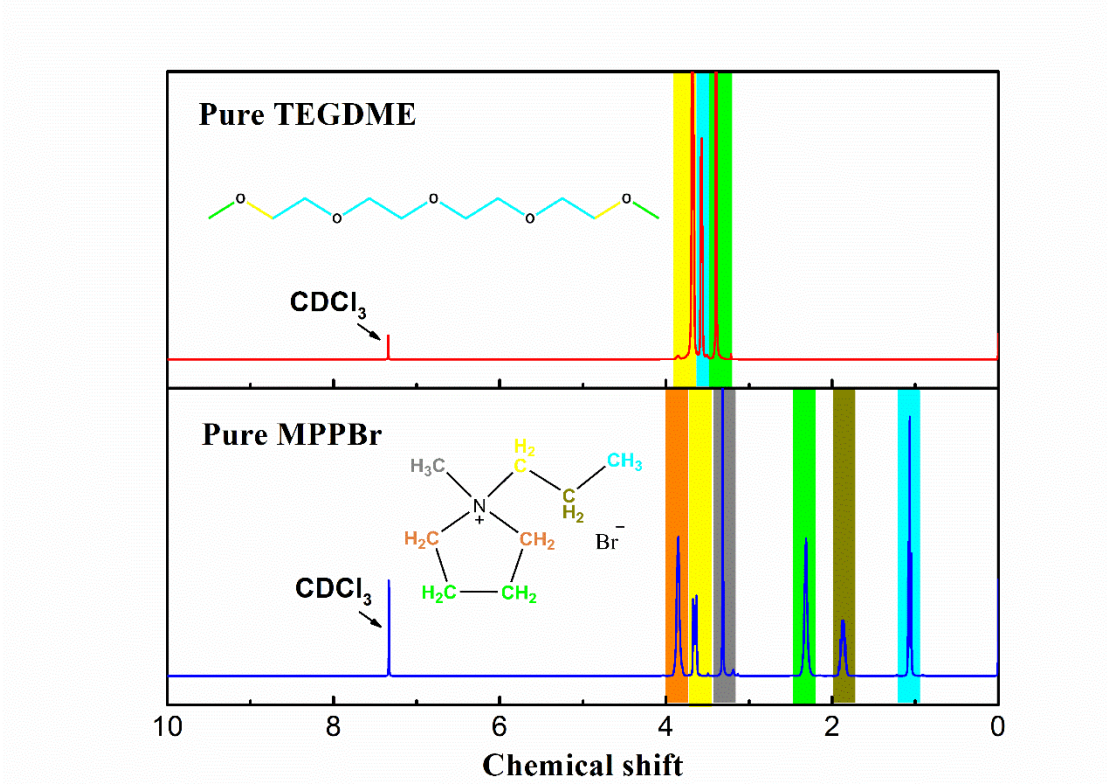

Fig. S10 ^{1}H NMR spectras of the pure TEGDME and pure MPPBr.

A summary of ^{1}H NMR spectra of the pure compounds

Tetraethylene glycol dimethyl ether (TEGDME)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 3.67 (d, J = 9.6 Hz, 12H), 3.57 (dd, J = 5.5, 3.6 Hz, 4H), 3.40 (s, 6H);

N-methyl-N-propyl pyrrolidine bromide (MPPBr)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 4H), 3.69 – 3.60 (m, 2H), 3.32 (s, 3H), 2.31 (s, 4H), 1.94 – 1.80 (m, 2H), 1.07 (t, J = 7.3 Hz, 3H).

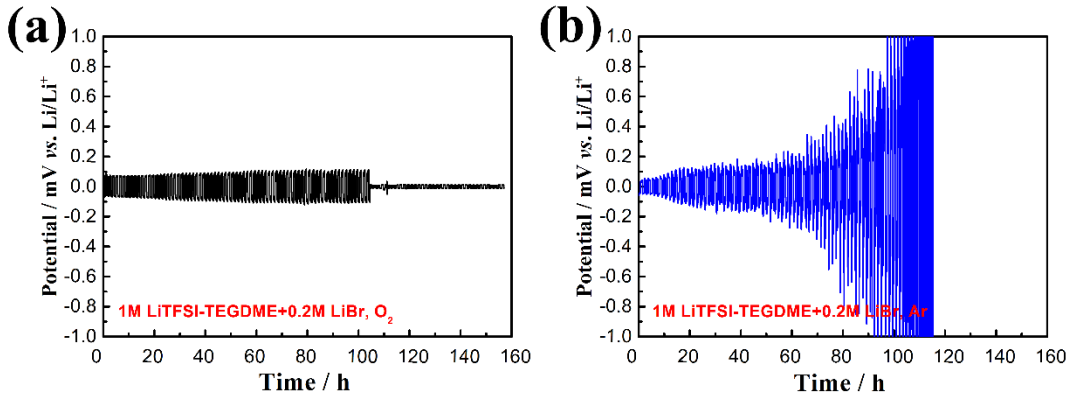

Fig. S11 Electrochemical performance of Li|Li symmetric cells containing 1.0 M LiTFSI-TEGDME + 0.2 M LiBr under O_2 (a) and Ar (b) atmosphere, respectively. The current density was fixed at 0.5 mA cm^{-2} with a stripping/plating capacity of 1.0 mAh cm^{-2}.

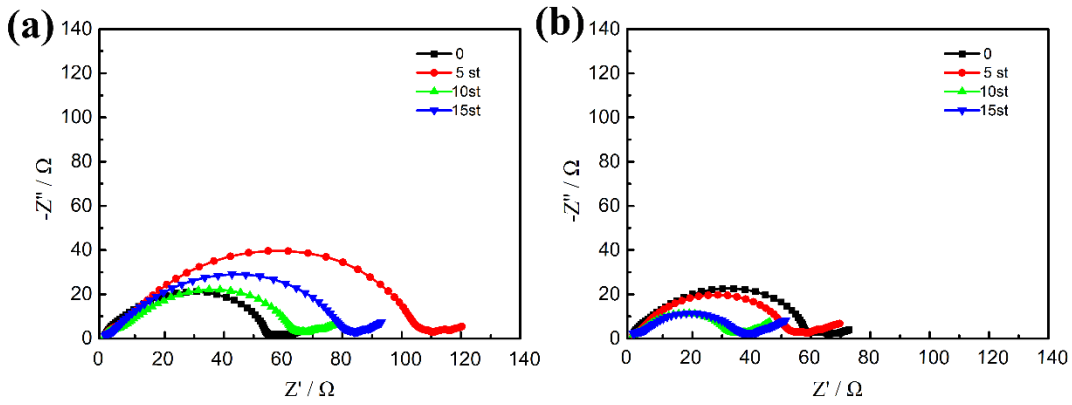

Fig. S12 Electrochemical impedance spectra of the Li|Li symmetric cells measured at the end of various cycle number with (a) 1.0 M LiTFSI-TEGDME and (b) 1.0 M LiTFSI-TEGDME + 0.2 M MPPBr, respectively.

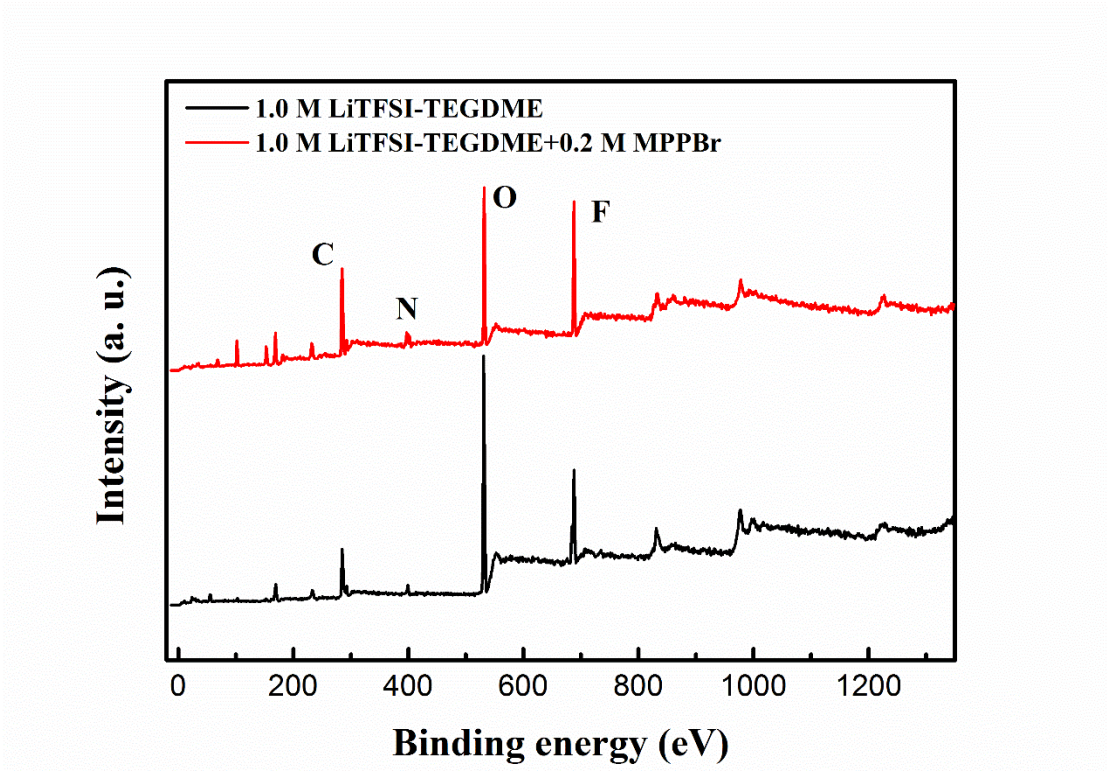

Fig. S13 XPS survey spectra of the Li metal on Li|Li symmetric cells with different electrolytes.

Table S1 XPS characterization of atomic ratio of elements on the Li metal anode on Li|Li sysmmetric cells after 50 cycles under O_2 atmosphere with 1.0 M LiTFSI-TEGDME and 1.0 M LiTFSI-TEGDME + 0.2 M MPPBr, respectively.

	Li	C	O	N	F
Without MPPBr	31.83%	22.31%	32.04%	2.27%	11.55%
With MPPBr	14.63%	44.63%	20.75%	6.27%	13.72%