Electronic Supplementary Information (ESI)

An Amide-Based Gel Polymer Electrolyte for Li-O_2 Batteries: Advancing Towards Practical Li-Air Batteries

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Experimental Section

Preparation of GPEs

N-phenylmethacrylamide (PMA, TCI, >98.0%) and LK-001 electrolyte (1 M LiTFSI/TEGDME, DodoChem) were mixed with mass ratios of 1:1, 1:2, 1:3, 1:4 and 1:5, and appropriate amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, TCI, >98.0%) were added to maintain the volume concentration of the electrolytes (1 M), and 0.2 wt% 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aladdin, 99%) was used as an initiator. The mixtures were absorbed by a glass fiber (GF/D, Whatman) separator and kept warm overnight at 60 ℃ to obtain a clear gel. The above operations were all completed in a glove box filled with Ar, with the water and oxygen contents controlled below 0.1 ppm. The as-prepared electrolytes were denoted as P1, P2, P3, P4 and P5, respectively.

Characterizations

Scanning electron microscope (SEM) images were taken by JSM-7800 and the attached energy-dispersive X-ray spectrometry (EDS) was utilized to obtain the elemental distribution information. Fourier transform-infrared (FT-IR) spectroscopy measurements were performed using a Brook ALPHA FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were taken by Thermo Scientific ESCALAB 250Xi. XRD patterns were obtained using a Rigaku D/Max-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 10° min^{-1}. XPS analysis was operated on Thermo Scientific ESCALAB 250Xi.

Electrochemical Measurements

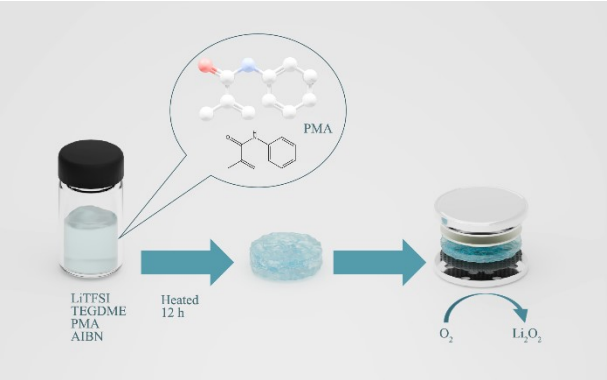
CR2032 coin-type cells were assembled in the above-mentioned glove box with or without holes on cathode shells according to whether oxygen was required in different tests. The cathode was prepared by coating a slurry composed of polyvinylidene fluoride (PVDF) and Ketjen black (KB) with a mass ratio of 1:9 onto a carbon paper (12 mm in diameter), and the active material mass loading was 0.25mg cm^{-2}.

A typical cell consisted of a lithium anode, a glassfiber separator with LEs or GPEs and a KB cathode. All cells were stabilized for 5 h before electrochemical measurements on LAND-CT2001A testers or LSV and CV measurements on a CHI760E electrochemical workstation.

All measurements were performed at room temperature.

Computational details related to DS-PAW

The binding energies of O_2 on the monomer of PMA and TEGDME were calculated using DS-PAW[1] software. Perdew-Burke-Ernzerhof (PBE) functional[2] within the generalized gradient approximation was used to describe the exchange-correlation interaction. A single gamma-centered Monkhorst–Pack scheme[3] was applied for structure relaxation due to the large cell (40 × 40 × 40 $Å^3$) used. 520 eV was used as the energy cutoff for the plane-wave basis set. Van der Waals (vdW) interactions were included using Grimme's DFT-D3 method with zero damping[4]. The convergence criteria for the electronic self-consistent field calculations and the ionic relaxation loop were set to 10^{-5}eV and 0.05 eV/Å, respectively.



Scheme 1 A schematic diagram regarding the synthesis of a PPMA GPE and the assembly of the Li-O_2/air battery.

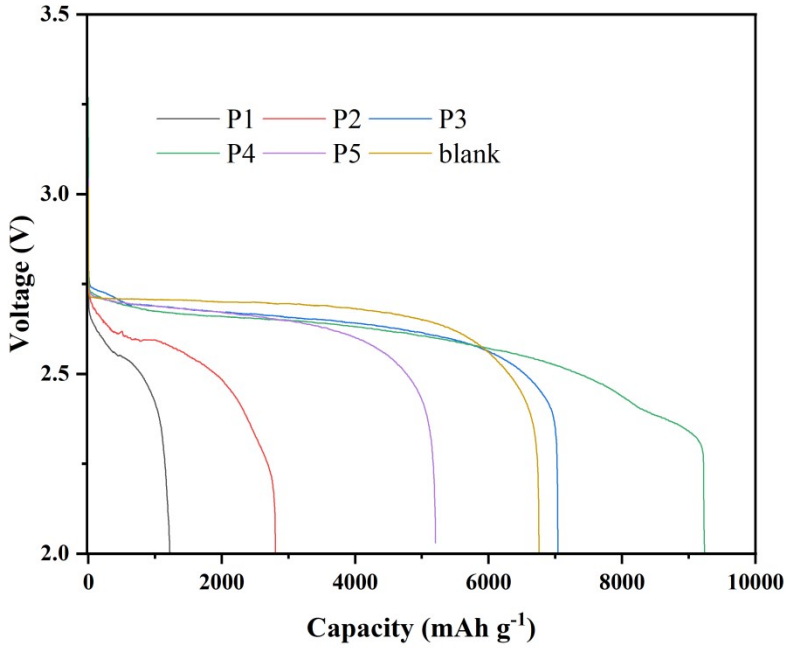


Fig. S1. Discharge curves of Li-O_2 batteries with different electrolytes at 200 mA g^{-1}.

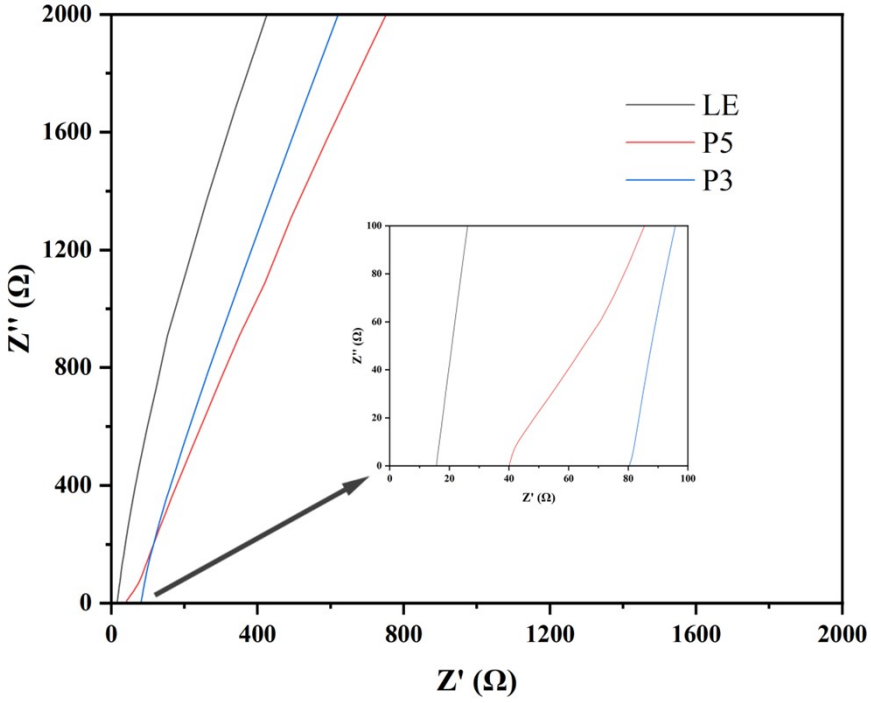


Fig. S2. Nyquist plots for EIS measurements of different electrolytes.

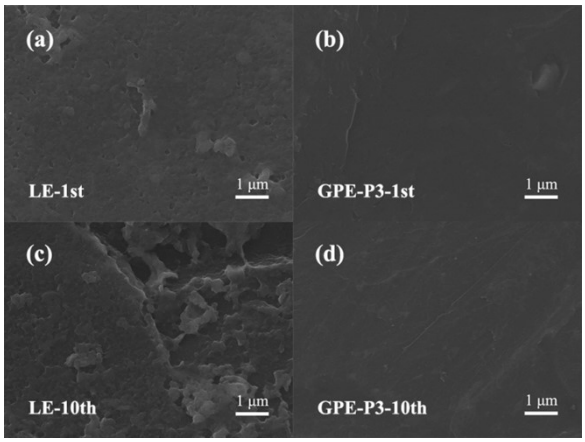


Fig. S3. SEM images of Li anodes after stripping and deposition in symmetric cells.

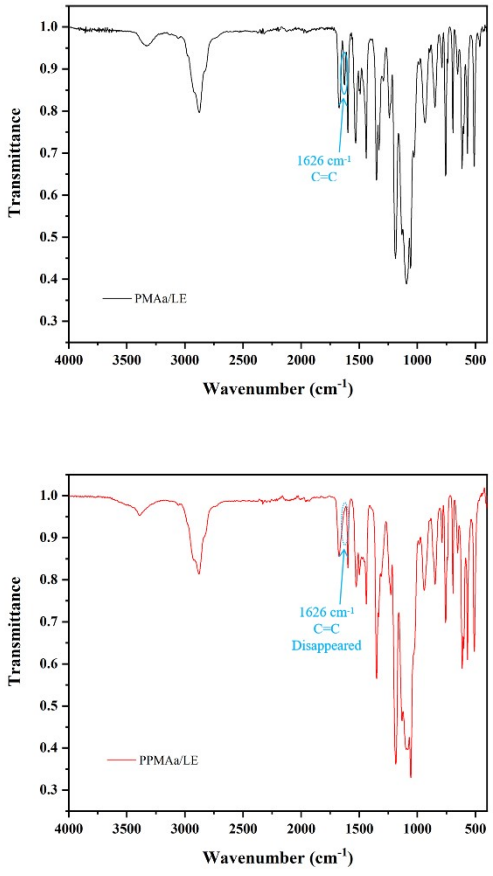


Fig. S4 FT-IR spectroscopy of GPE-P3 (a) before and (b) after polymerization.

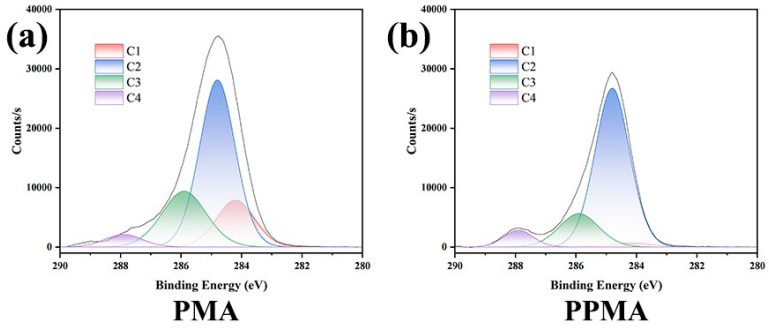


Fig. S5. XPS of PMA and PPMA (a) before and (b) after polymerization.

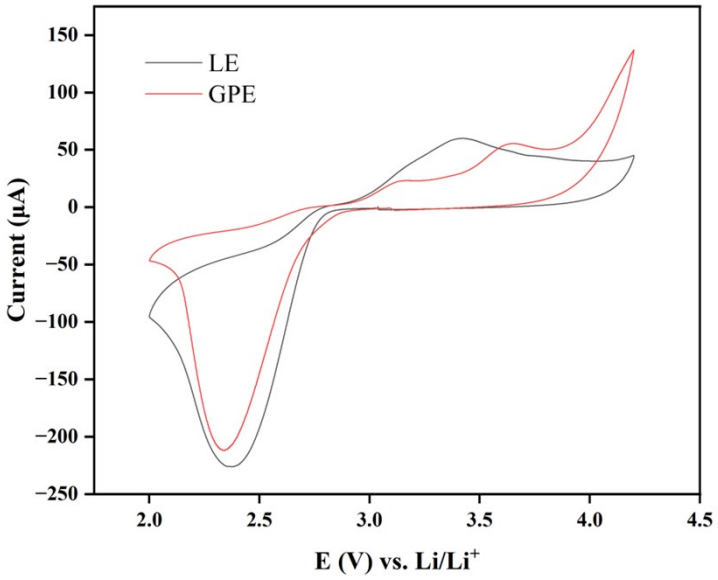


Fig. S6. CV curves of Li-O_2 batteries with LEs or GPE-P3.

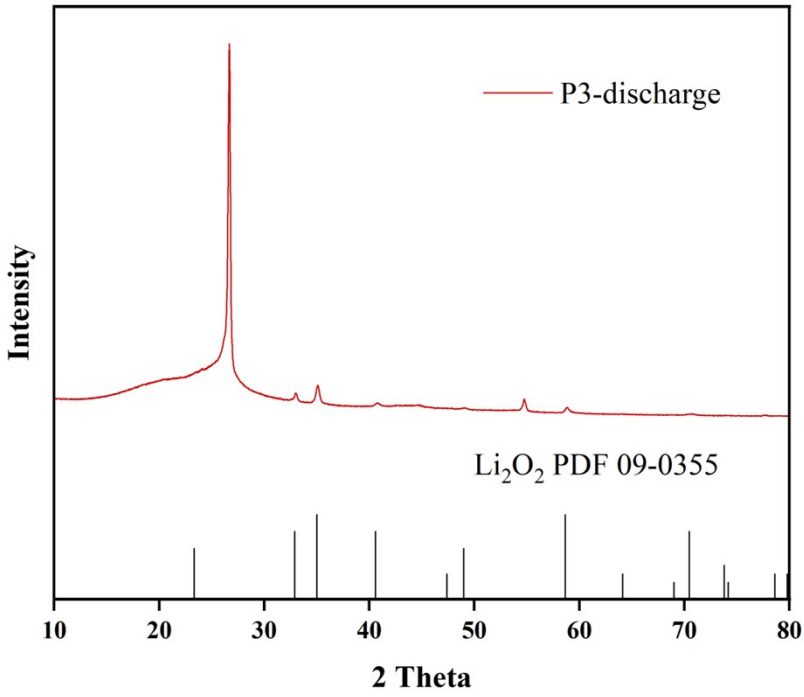


Fig. S7. XRD patterns of Li-O_2 batteries with GPE-P3 and standard PDF card of Li_2O_2.

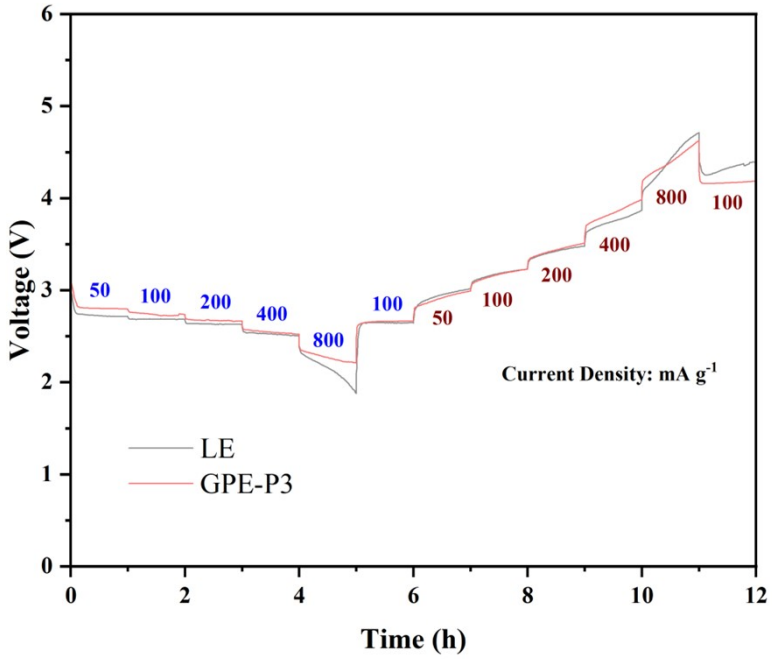


Fig. S8. Rate performance for Li-O_2 batteries with GPE-P3 or liquid electrolyte (LE).

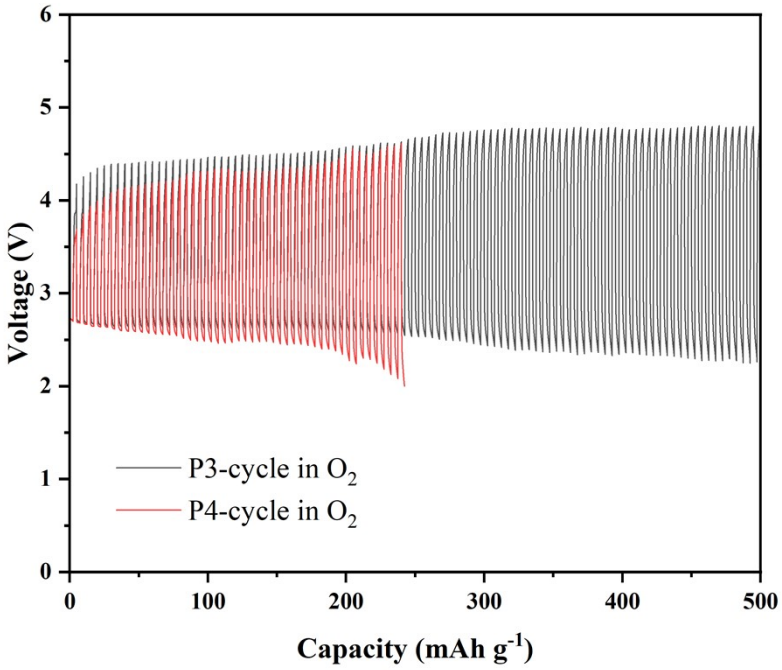


Fig. S9. Cycling curves of Li-O_2 batteries with GPE-P3 or P4 under 200 mA g^{-1}.

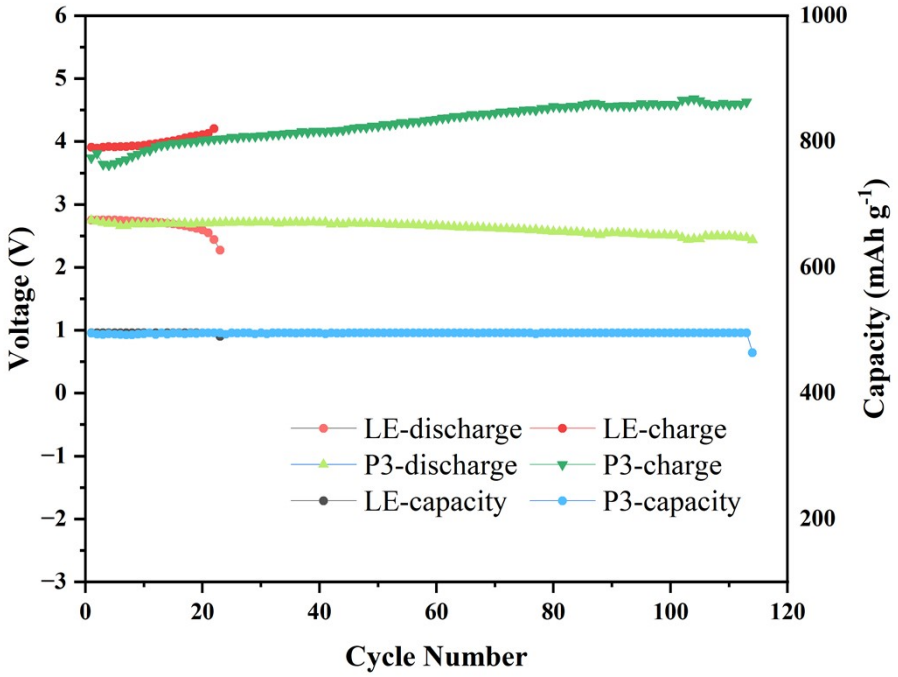


Fig. S10. Cycling performance of Li-O_2 batteries with LE or GPE-P3 under current

density of 100 mA g^{-1} with cut-off capacity of 500 mAh g^{-1}.

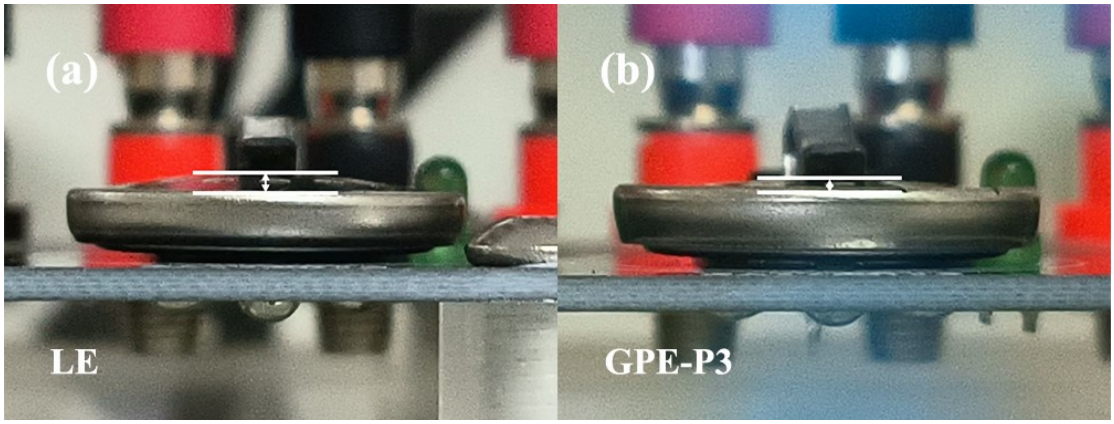


Fig. S11. Comparison of volume expansion of Li-O_2 batteries with LEs or GPE-P3 after 20 cycles of discharge and recharge.

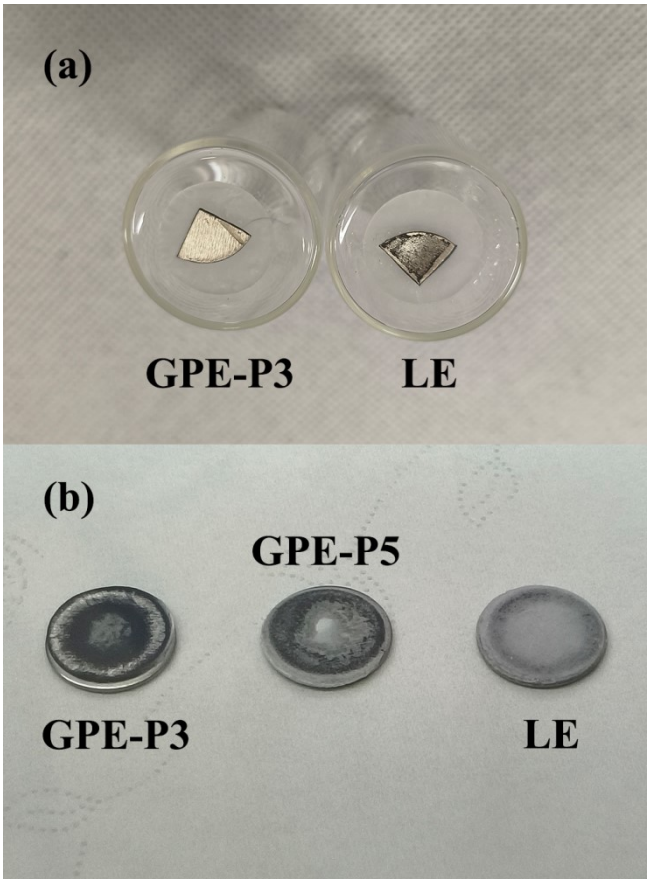


Fig. S12. Photos of Li anodes: (a) covered with different electrolytes and exposed to air for several hours, and (b) after cycling in O_2.

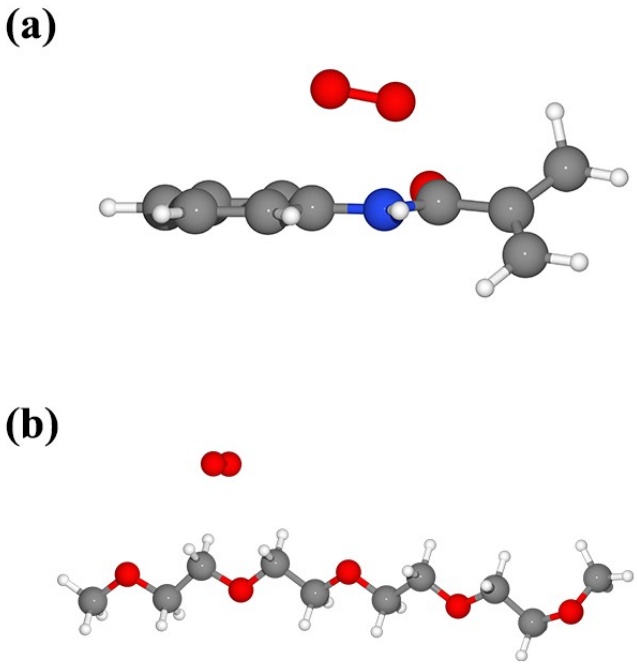


Fig. S13. Optimized atomic structures of O_2 on the monomer of (a) PMA and (b) TEGDME.

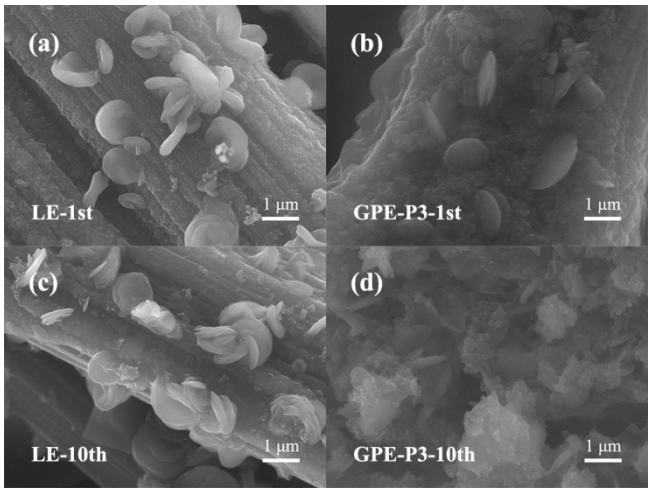


Fig. S14. SEM images of discharge products in Li-O_2 batteries after 1 cycle and 10 cycles.

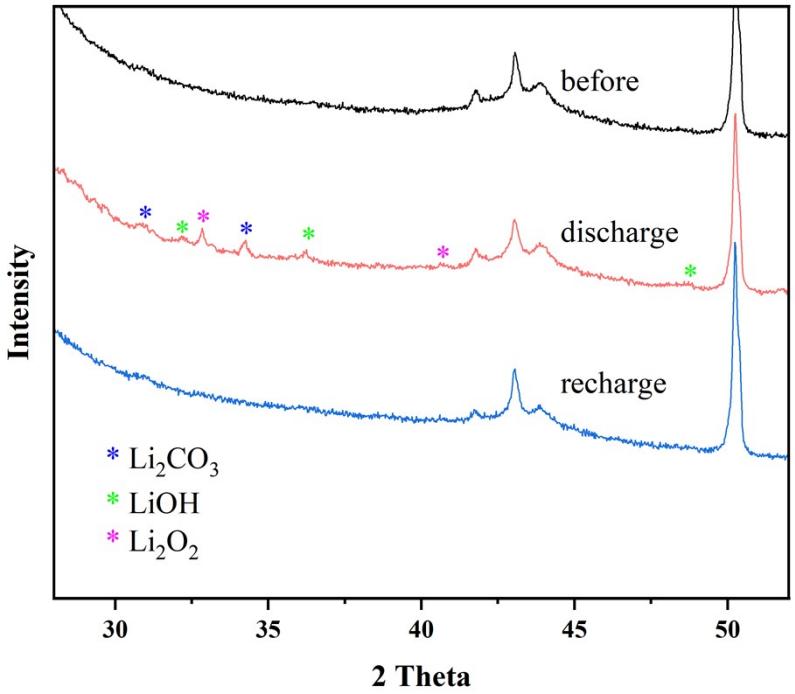


Fig. S15. XRD patterns of Li-air battery cathodes with GPE-P3 before discharge, after discharge and after recharge.

Table S1. Ionic conductivities of different electrolytes calculated based on EIS data.

	Bulk Resistance (Ω)	Ionic Conductivity (S cm^{-1})
LE	15.72	4.13×10^{-3}
GPE-P5	40.10	1.62×10^{-3}
GPE-P3	80.29	8.10×10^{-4}

Table S2. Assignment of various peaks for XPS in Fig. R2.

Peak	Assignment	Binding Energy (eV)
C1	C=C	284.2
C2	C-C	284.8
C3	C-N	285.9
C4	C=O	287.9

Table S3. DFT-calculated energies of O_2 on monomers of PMA and TEGDME.

	Total energy / eV
monomer of PMA	-2451.351
TEGDME	-4111.154
O_2 on monomer of PMA	-3325.072
O_2 on TEGDME	-4984.660
O_2	-873.459

Table S4. Performance comparison with previous reports.

	Atmosphere	Current Density & Cut-off Capacity	Cycles	Operating Time (h)
This Work	O_2	200 mA g^{-1} 500 mAh g^{-1}	127	635
5	O_2	312.5 mA g^{-1} 1250 mAh g^{-1}	194	1552
6	O_2	0.1 mA cm^{-2} 1 mAh cm^{-2}	34	680
7	O_2	200 mA g^{-1} 500 mAh g^{-1}	70	350
8	O_2	0.05 mA cm^{-2} 0.25 mAh cm^{-2}	117	1170
9	O_2	0.1 mA cm^{-2} 0.4 mAh cm^{-2}	39	312
10	O_2	500 mA g^{-1} 1000 mAh g^{-1}	250	1000
11	O_2	250 mA g^{-1} 500 mAh g^{-1}	55	220
This Work	Air	200 mA g^{-1} 500 mAh g^{-1}	120	600
12	Air	500 mA g^{-1} 500 mAh g^{-1}	100	200
13	Air	200 mA g^{-1} 500 mAh g^{-1}	235	1175
14	Air	500 mA g^{-1} 1000 mAh g^{-1}	241	964
15	Air	500 mA g^{-1} 1000 mAh g^{-1}	98	196

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