

## Supporting Information

### **Protecting Li-metal in O<sub>2</sub> atmosphere by sacrificial polymer additive for Li-O<sub>2</sub> Battery**

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## Experimental Section

*Synthesis of polymer PAMMA.:* In a 50 mL Schlenk flask, AM (4.12 g, 58.0 mmol), MA (0.88 g, 10.2 mmol), AIBN (0.005 g, 0.03 mmol) and DMF (15 mL) were mixed under stirring for 30 min. The flask was then sealed and purged with high-purity nitrogen for 30 min, and placed in an oil bath at 70 °C for 6 h. After concentrating the solution, the product was precipitated in ethyl alcohol for three times. The sample was dried in a vacuum oven at 60 °C for 24 h. The synthesized PAMMA determined by <sup>1</sup>H NMR consists of 86 mol% AM and 14 mol% MA, which is almost consistent with the initial feed ratio (85 mol% AM: 15 mol% MA).

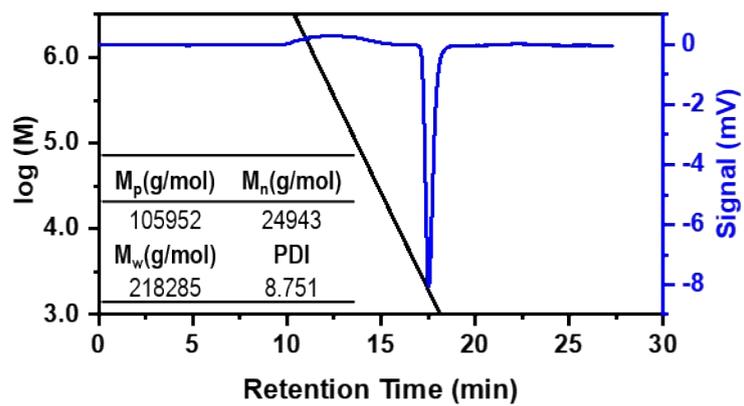
*Preparation of electrolytes:* Ether-based electrolyte, composed of LiTFSI salt and TEGDME solvent (1.0 M), was purchased from Dongguan Canrd experimental equipment Technology Co., Ltd., China. PAMMA additive with 0.03, 0.08, 0.15 wt% were directly dissolved in ether-based electrolyte. All electrolytes with/without PAMMA were stored in an Ar-filled glove box and used without further purification.

*Electrochemical measurements:* In this study, CR-2032 coin-type cells (top-holing) were assembled in glove box under inert Ar environment. Li-O<sub>2</sub> cell was assembled by Li foil (0.5 mm), glassfiber separator with 100 μL electrolyte, and carbon cloth as gas diffusion layer. PP/PE/PP separator with 75 μL electrolyte was utilized for Li-Li symmetric cell assembling. Both cyclic voltammetry (CV) and linear scan voltammetry (LSV) measurement were carried out on CHI660E electrochemical workstation (Chenhua, China). The galvanostatic cycling measurements of Li/Li symmetrical cells and Li-O<sub>2</sub> cells were conducted on Neware battery testing system (CT-4008T-5 V10 mA-164, Shenzhen, China) at room temperature. Before each charge/discharge measurement, the tested cells were kept on open circuit for 8~10 h.

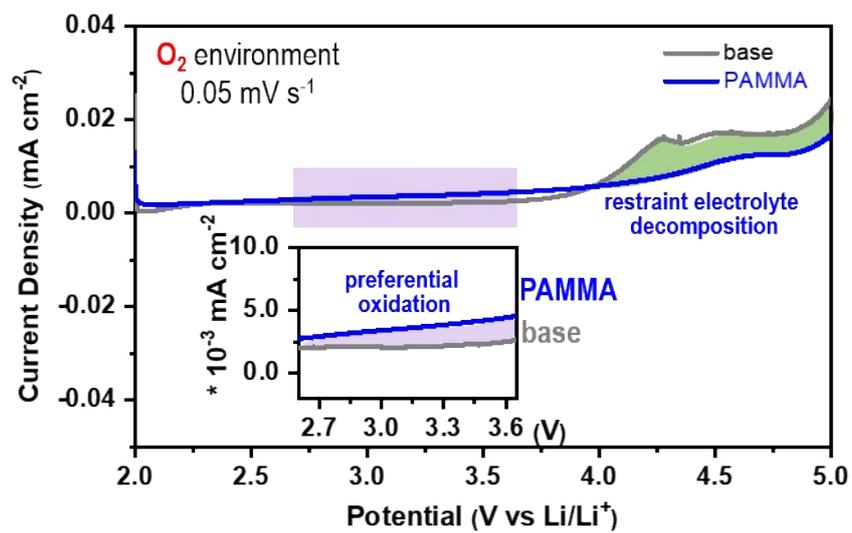
*Characterizations:* Scanning Electron Microscopy (SEM, Zeiss GeminiSEM 500) was conducted to characterize morphological differences of Li-metal anode with/without PAMMA

additive in harsher O<sub>2</sub> environment during different electrochemical cycling condition. Fourier-transform infrared (FTIR) measurement with attenuation total reflection (ATR) mode was performed on Bruker Vertex 70V in the Tan Kah Kee Innovation Laboratory to investigate the functional groups of PAMMA polymer. X-ray Diffraction (XRD) measurements, which is fitted with Cu-K $\alpha$  X-rays ( $\lambda = 1.5406 \text{ \AA}$ ) at a scan rate of 2 °/min, were utilized to analyze the specific components of cycled Li-metal under O<sub>2</sub> condition. All X-ray photoelectron spectroscopy (XPS) data were collected from Thermo Fisher Escalab Xi+ XPS in the Tan Kah Kee Innovation Laboratory. Depth profiling were achieved by using Ar<sup>+</sup> sputtering. All XPS spectra were calibrated using the reference C-C peak at BE=284.5 eV.

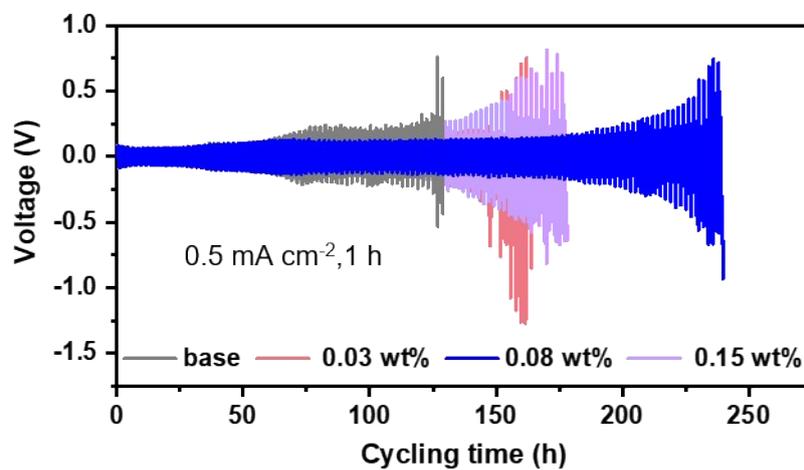
*Theoretical calculation:* electrostatic potential (ESP) calculation of PAMMA molecule was performed with the Gaussian09 package along with the basis set of B3LYP/6-31G(d, p) after structure relaxation.



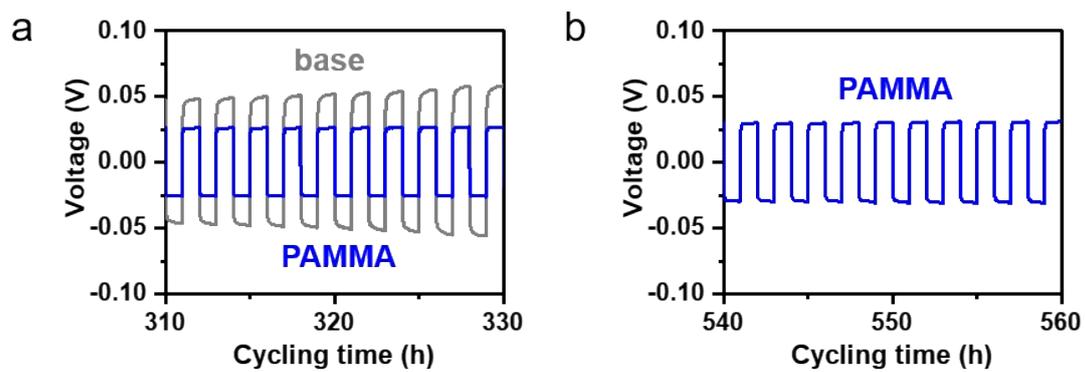
**Figure S1.** GPC characterization of PAMMA.



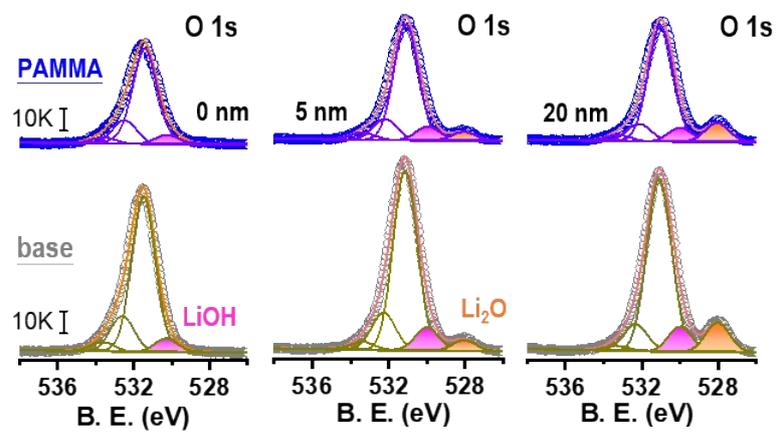
**Figure S2.** LSV profiles of ether-based electrolyte with/without PAMMA in the voltage range of 2.0 to 5.0 V under O<sub>2</sub> atmosphere. Scan rate: 0.05 mV s<sup>-1</sup>.



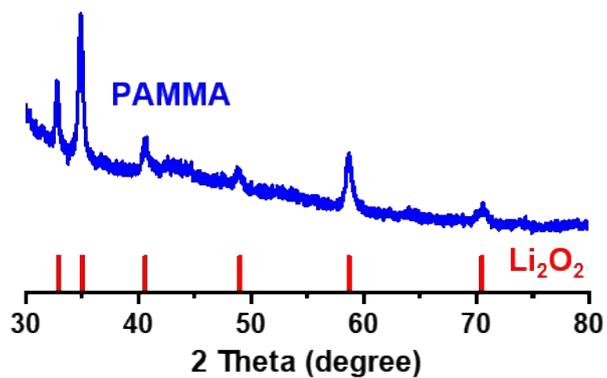
**Figure S3.** Optimization of PAMMA concentration in Li/Li symmetrical cells in inert Ar atmosphere ( $0.5 \text{ mA cm}^{-2}$ ,  $0.5 \text{ mAh cm}^{-2}$ ).



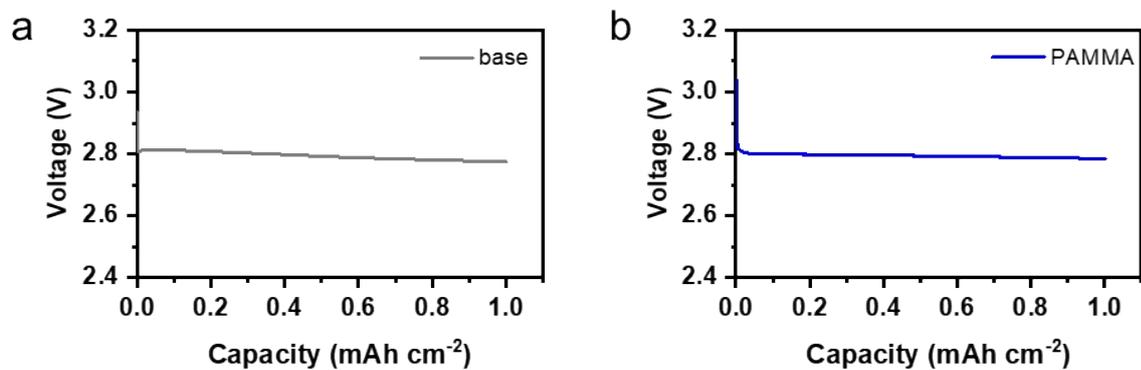
**Figure S4.** Magnified profiles of (a) 310-330 and (b) 540-560 cycling hours in Li/Li symmetrical cell without/with PAMMA under O<sub>2</sub> condition (0.2 mA cm<sup>-2</sup>, 1 h).



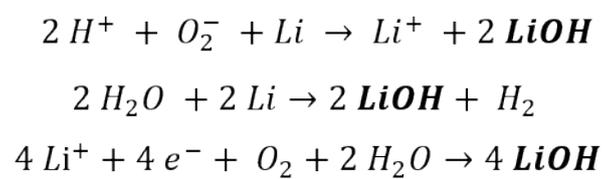
**Figure S5.** SEI characterization in Li/Li symmetrical cell after 50 cycles under O<sub>2</sub> atmosphere (current density: 0.2 mA cm<sup>-2</sup>, capacity: 0.2 mAh cm<sup>-2</sup>).



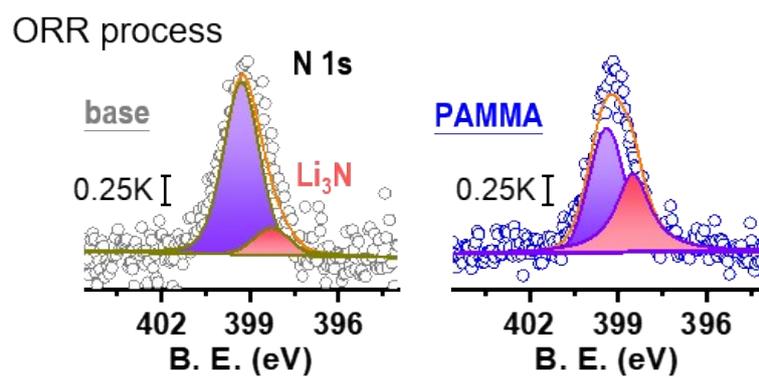
**Figure S6.** XRD characterization in Li-O<sub>2</sub> cell with PAMMA after full discharge (cut-off discharge: 2.0 V). Standard card for Li<sub>2</sub>O<sub>2</sub> (PDF 09-0355) marked as red trace is exhibited for comparison.



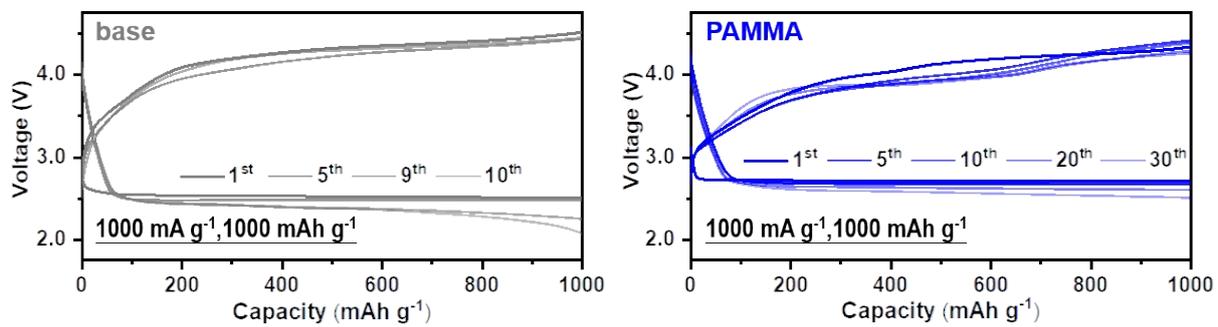
**Figure S7.** Voltage profiles of Li-O<sub>2</sub> cell during discharge process at a fixed capacity of 1.0 mAh cm<sup>-2</sup> (a) without and (b) with PAMMA additive (0.05 mA cm<sup>-2</sup>).



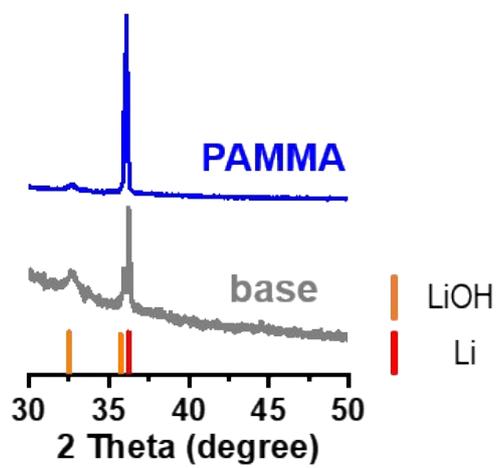
**Figure S8.** Proposed mechanism of LiOH formation of Li-metal anode in Li-O<sub>2</sub> cell.



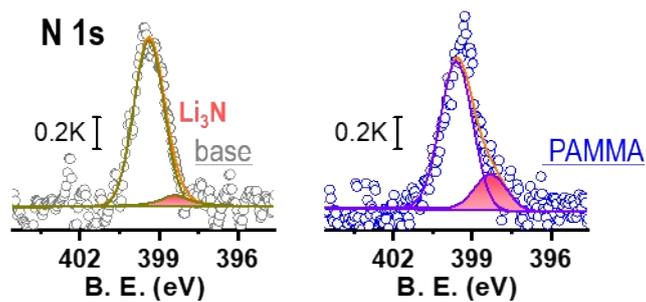
**Figure S9.** N 1s XPS spectrum of discharged Li-metal in Li-O<sub>2</sub> cell during ORR process (ORR capacity: 1.0 mAh cm<sup>-2</sup>).



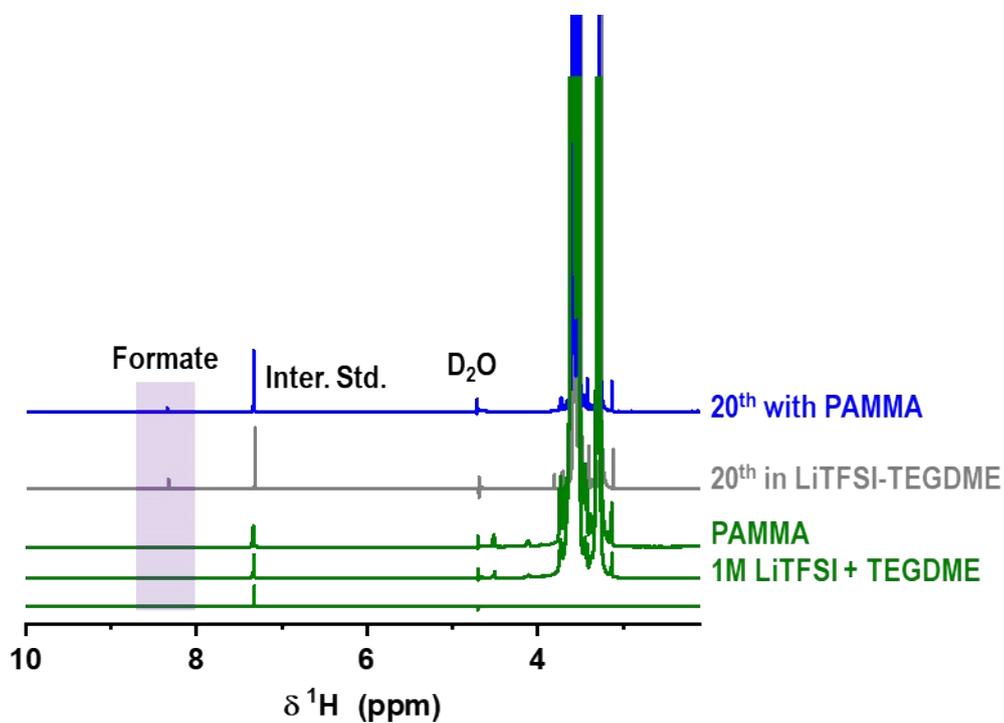
**Figure S10.** Typical charge-discharge curves of Li-O<sub>2</sub> cell without/with PAMMA.



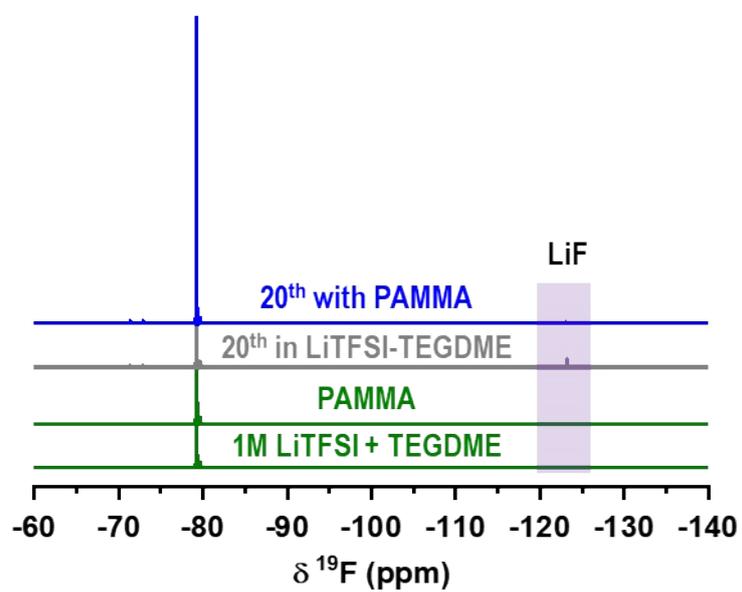
**Figure S11.** XRD pattern of Li-metal in Li-O<sub>2</sub> cell after cycling for 20 times. Standard card for LiOH (PDF 32-0564) and Li (PDF 15-0401) marked as orange and red traces are conducted for comparison, respectively.



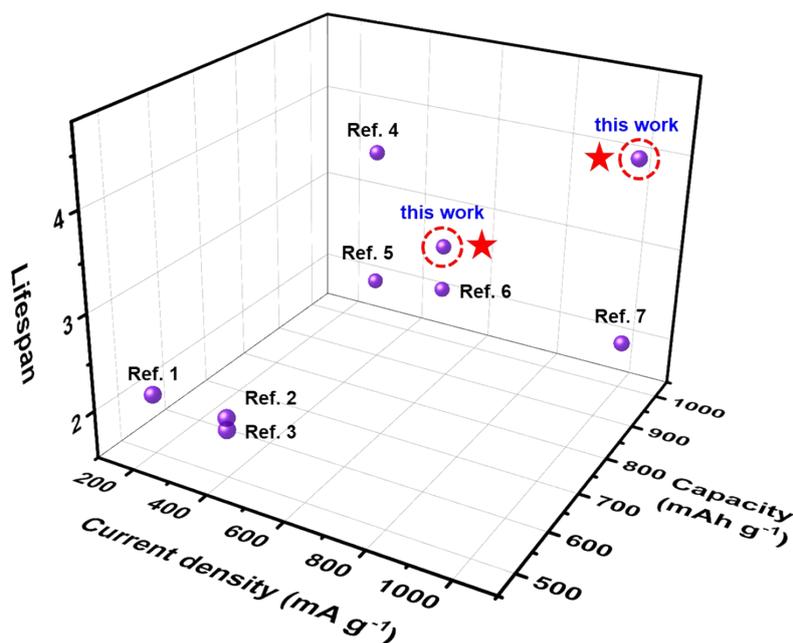
**Figure S12.** N 1s XPS spectrum of Li-metal in Li-O<sub>2</sub> cell after cycling for 20 times (base: gray trace; PAMMA: blue trace).



**Figure S13.** D<sub>2</sub>O-extracted  $^1\text{H}$  NMR spectra from cycled cathode plate and separator at a fixed capacity of  $0.5 \text{ mAh cm}^{-2}$  ( $0.25 \text{ mA cm}^{-2}$ ).



**Figure S14.** D<sub>2</sub>O-extracted  $^{19}\text{F}$  NMR spectra from cycled cathode plate and separator at a fixed capacity of 0.5 mAh cm<sup>-2</sup> (0.25 mA cm<sup>-2</sup>).



**Figure S15.** The multiple of the increase in cycle life before and after improvement of Li-O<sub>2</sub> cell concentrated on Li-metal protection between this work and other refs.

In relative refs. on the topic of Li-metal anode protection of Li-O<sub>2</sub> cell, there may be great differences in experimental details, such as cathode catalyst type and loading, amount of electrolyte, diameter of electrode, discharge/charge cut-off potential, etc. Herein, to make a reasonable comparison as much as possible between this work and other relative refs., we take the multiple of the cycle life before and after improvement of Li-O<sub>2</sub> cell concentrated on Li-metal protection as the comparison index. Compared with other relative ref., the introduction of PAMMA additive has a more prominent improvement effect on Li-O<sub>2</sub> cell at high current density (Figure S12).

Reference:

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