Supporting Information

Dendrite- and Oxygen-Proof Protective Layer for Lithium Metal in Lithium-Oxygen Batteries

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Supplementary Figures

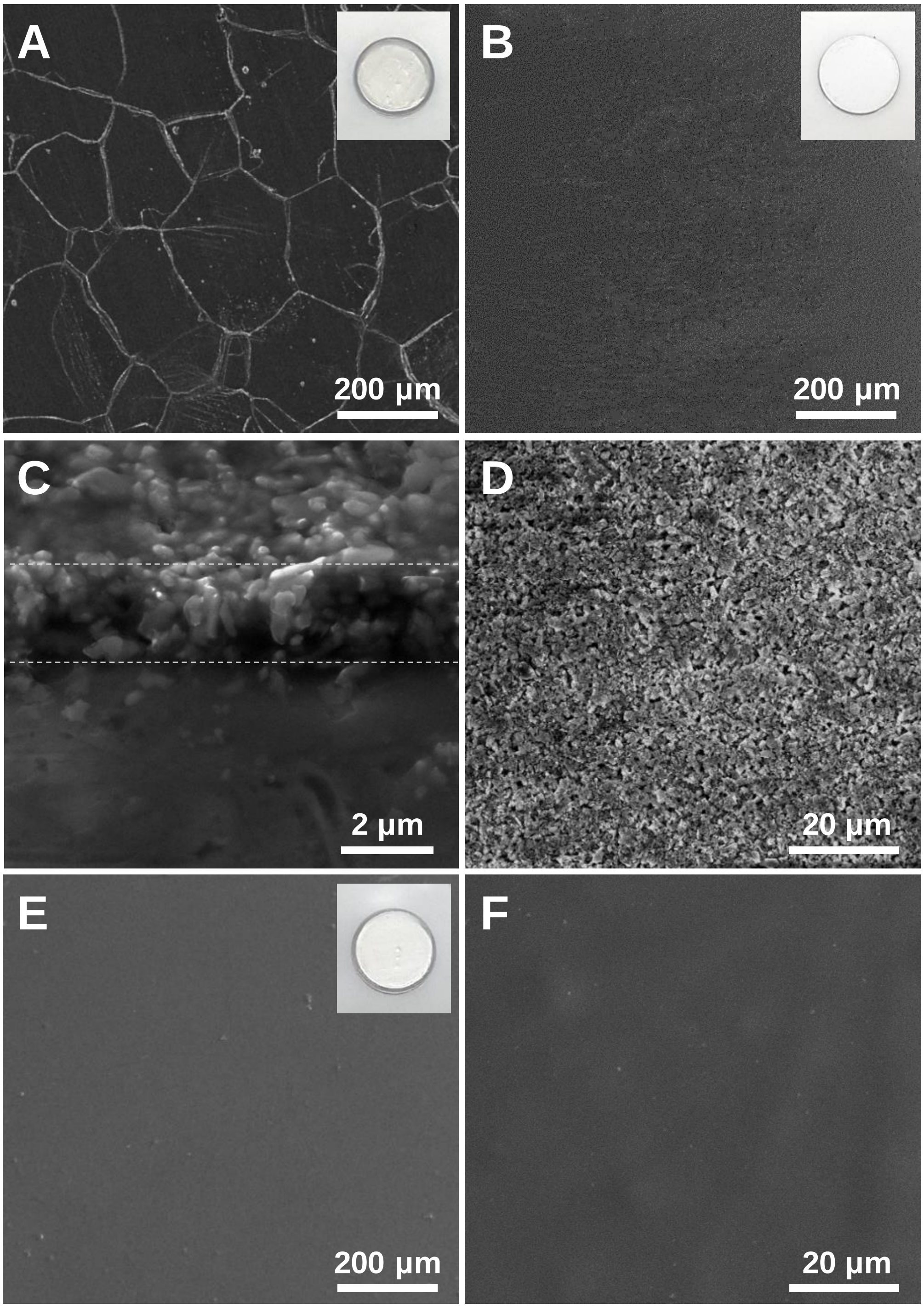

Fig. S1 Scanning electron microscopy (SEM) images of (A) Li metal, (B–D) NCL-coated Li metal, and (E, F) Nafion-coated Li metal without Al_2O_3. Inset photographs in Fig. S1 (A, B, and D) are representative of Li metal, NCL-coated Li metal, and Nafion-coated Li metal, respectively.

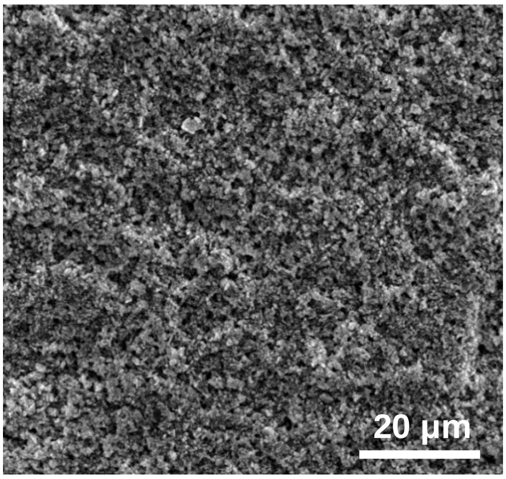

Fig. S2 SEM image of a composite protective layer (CPL, Al_2O_3-PVdF mixture)-coated Li metal.

There are no morphological differences between NCL and CPL.

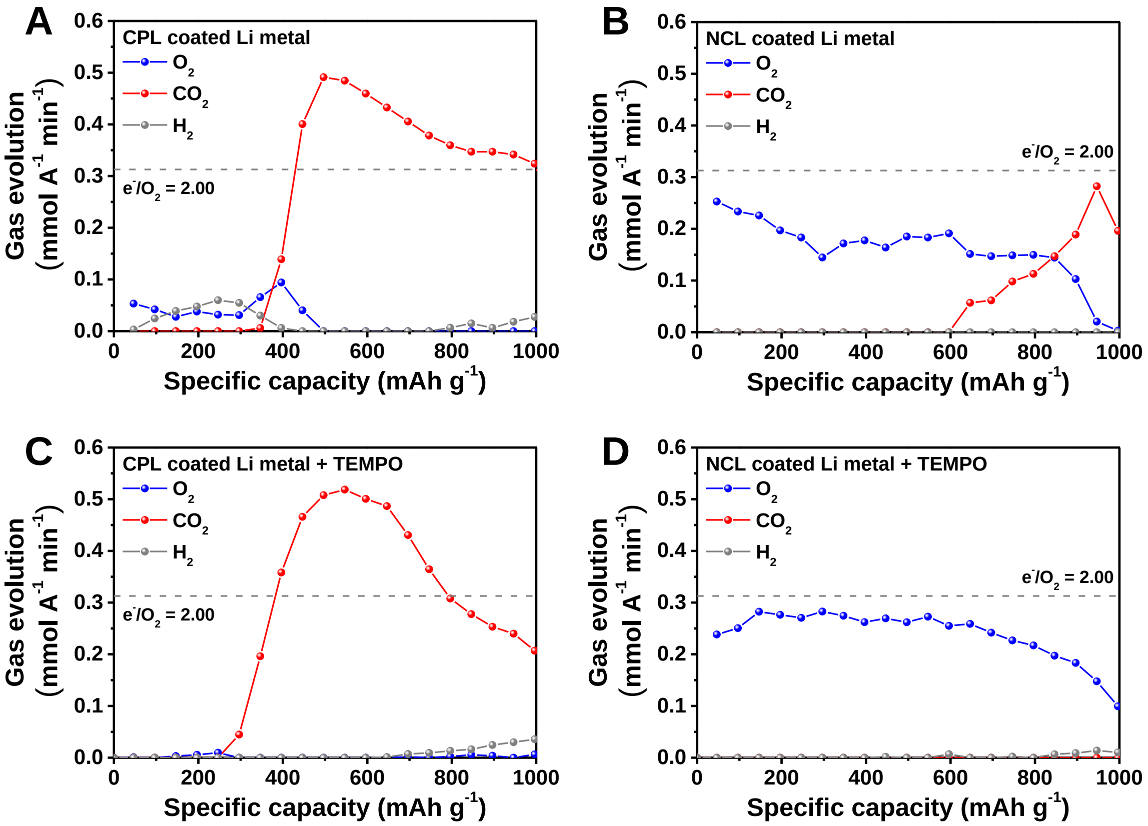

Fig. S3 Gas evolution profiles during charge of Li-O_2 cells with (A, C) CPL and (B, D) NCL for Li-metal protection with 1 M LiTFSI in TEGDME. A TEMPO (0.3 M) redox mediator was additionally included in (C) and (D). Before charging process, discharge was performed at a fixed capacity of 1000 mAh g^{-1}. The blue and red dotted lines, and grey dashed lines denote the O_2, CO_2, and H_2 evolution profiles, respectively. The horizontal dashed line refers to an e^-/O_2 gas evolution with the rate of 2.

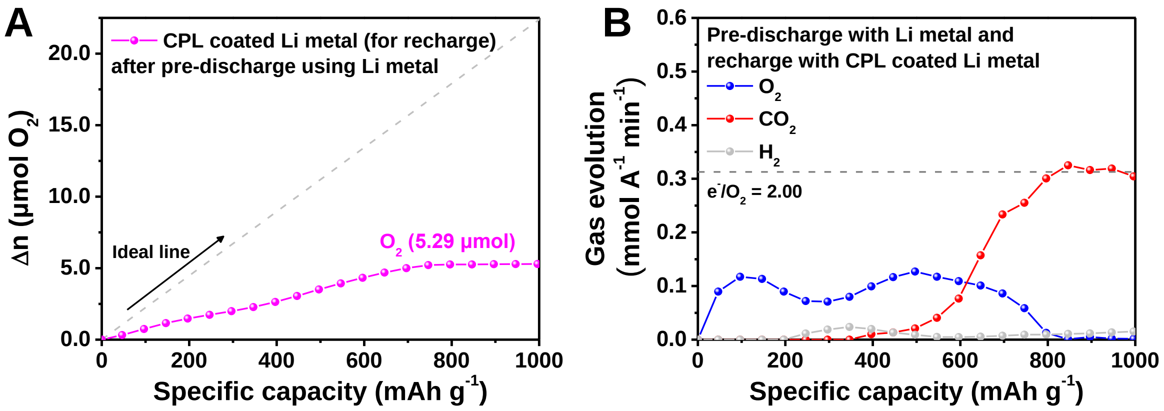

Fig. S4 The OEMS gas analysis of Li–O_2 cell where a naked Li metal was used during discharge with a fixed capacity of 1000 mAh g^{-1}. This Li anode was replaced with a CPL-coated Li metal in an Ar-filled glove box after discharge, and charge process was continuously carried out. (A) Cumulative evolution of O_2 gas and (B) gas evolution profiles during charge. The blue, red and grey dotted lines in (B) denote the O_2, CO_2, and H_2 evolution profiles, respectively. The dashed line in (A) indicates the ideal amount of O_2 gas. The horizontal dashed line in (B) refers to an e^-/O_2 gas evolution with the rate of 2.

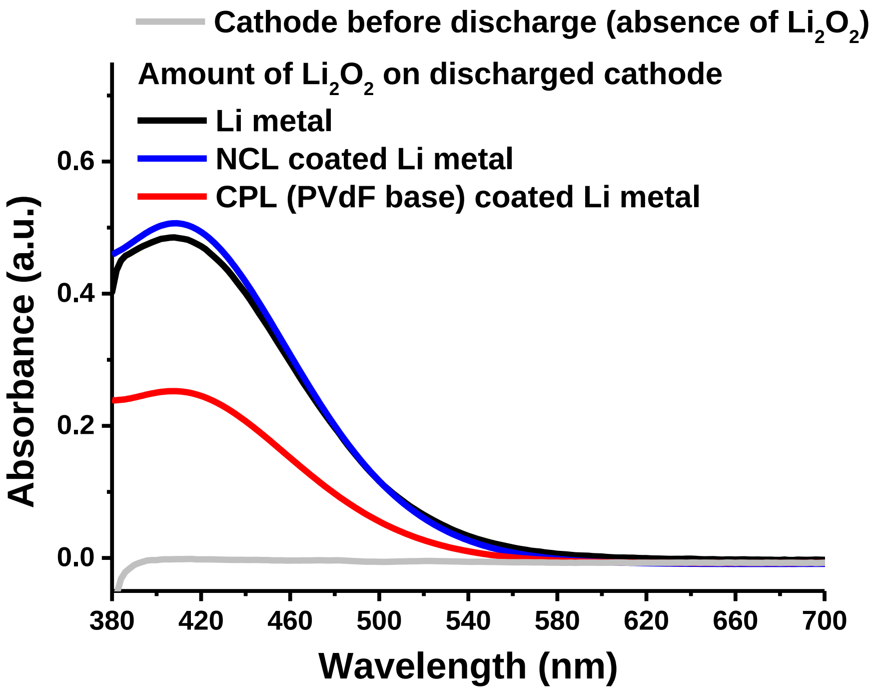

Fig. S5 UV-Vis spectra of discharged electrodes (0.1 mA – 20 h) immersed in a Ti^{4+} solution for titration of Li_2O_2. The electrodes were made of Li metal, NCL-coated Li metal, or CPL (PVdF-based)-coated Li metal.

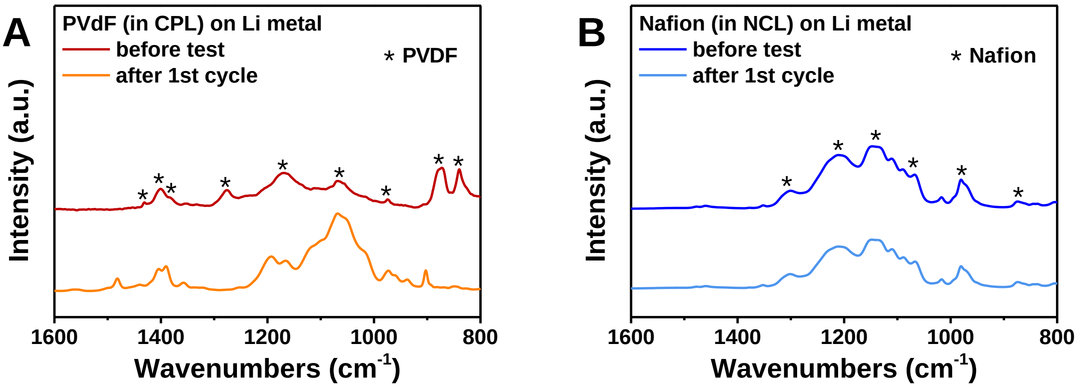

Fig. S6 ATR-FTIR spectra of the protective layers in Li-O_2 batteries before and after cycle tests to check the stability of (A) PVdF-based CPL-coated Li metal, and (B) NCL-coated Li metal in Li-O_2 batteries. All the data were used without fitting to exhibit changes in the peaks clearly.

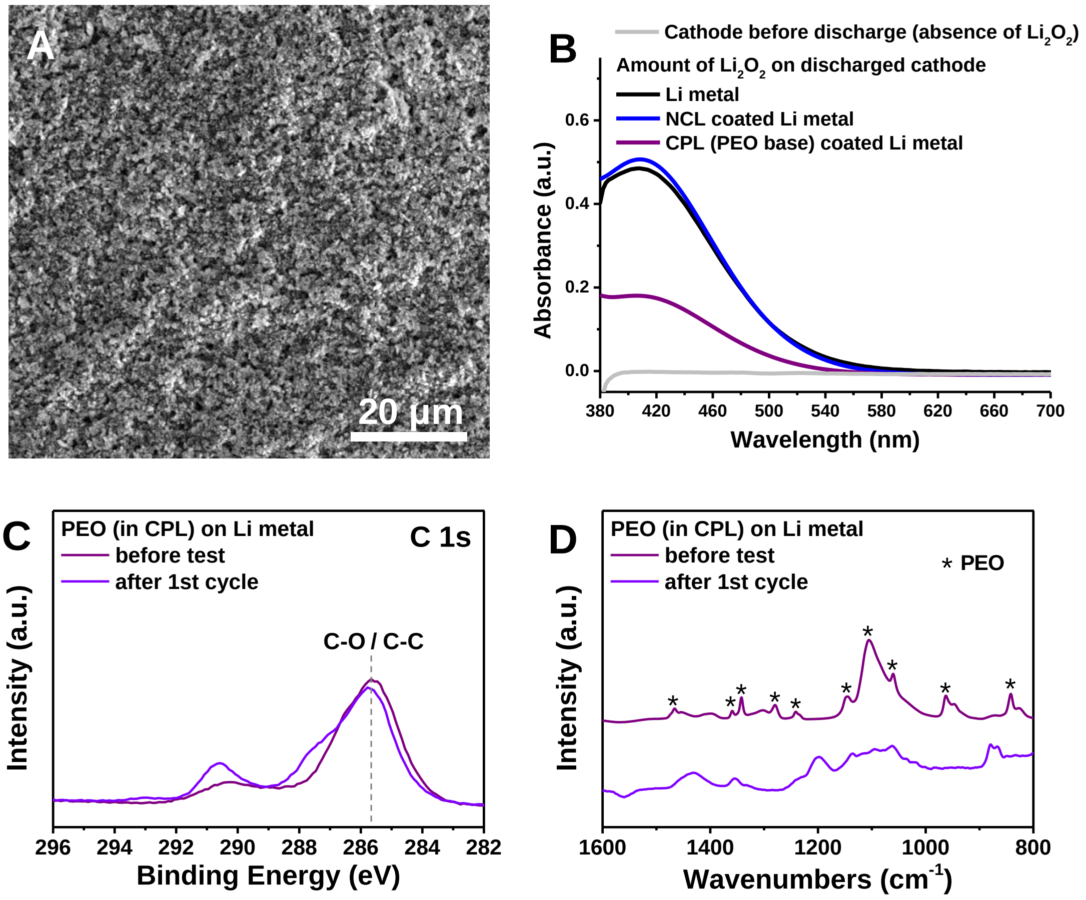

Fig. S7 (A) SEM analysis of PEO-based CPL (Al_2O_3-PEO mixture)-coated Li metal. This layer has the same morphology as NCL and PVdF-based CPL. (B) UV-Vis spectra of discharged electrodes (0.1 mA – 20 h) immersed in a Ti^{4+} solution for titration of Li_2O_2. The electrodes were made of Li metal, NCL-coated Li metal, or CPL (PEO-based)-coated Li metal.

(C) C 1s XPS spectra and (D) ATR-FTIR spectra of the protective layers in Li-O_2 batteries before and after cycle tests to check the stability of PEO-based CPL-coated Li metal in Li-O_2 batteries. All the data were used without fitting to exhibit changes in the peaks clearly.

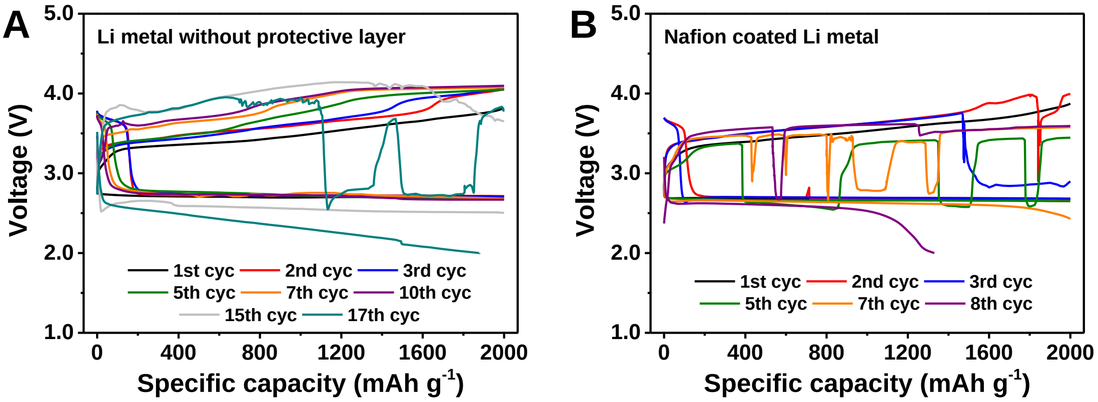

Fig. S8 Voltage profiles during galvanostatic cycling test of a Li-O_2 pouch cell using (A) Li metal and (B) Nafion-coated Li metal as anodes at the same conditions as the pouch cell in Fig. 4b. Poorer cycling performance of Li-O_2 pouch cell using Nafion-coated Li metal (Fig. S8B) than that of Li metal without coating material (Fig. S8A) results from mechanically unstable protective layer (NL without Al_2O_3) which causes deterioration of the cell due to abnormal accumulation of decomposed byproduct on the metal surface.

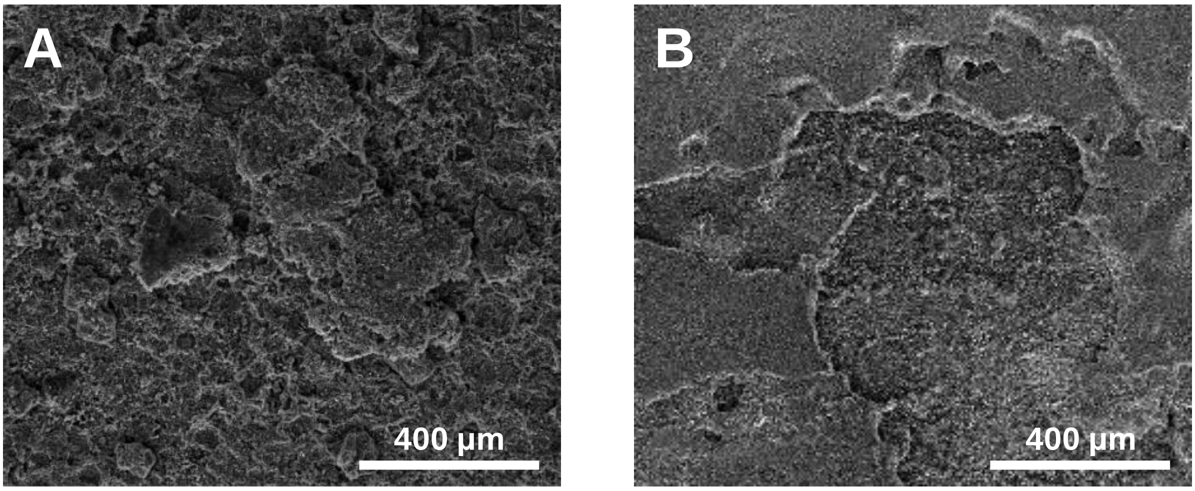

Fig. S9 SEM images of (A) Nafion-coated Li metal without Al_2O_3 and (B) CPL (PVdF-based)-coated Li metal after the cycling test of Li-O_2 cells.