

Supporting Information

***In situ* visualization of synergistic effects between electrolyte additives and catalytic electrodes in Li-O₂ batteries**

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1. Experimental Section

Electrode and Electrolyte Preparation.

Freshly cleaved highly oriented pyrolytic graphite (HOPG) (ZYH type, Bruker Corp.) was used as the base of the working electrode. The Pt nanoparticles electrode was made by sputtering Pt on HOPG for 500 s using Leica EM SCD 500 High Vacuum Sputter Coater.

Dimethyl sulfoxide (DMSO) was purchased from Acros. Lithium bis(trifluoromethane sulfonimide) (LiTFSI) was purchased from Sigma-Aldrich and potassium bis(trifluoromethane sulfonimide) (KTFSI) was purchased from TCI. LiTFSI and KTFSI was used as received. The electrolyte was prepared by mixing 0.5 M LiTFSI and DMSO with or without 0.25 M KTFSI. The prepared electrolyte was stored in an Ar glovebox with <0.1 ppm of O₂ and <0.1 ppm of H₂O. All electrolytes were bubbled with dried O₂ (>99.999%) for 2 h in a homemade device before the experiments.

Electrochemical AFM

Li-O₂ model cells use a three-electrode system, with lithium wires for both counter and reference electrodes. HOPG or Pt nanoparticles electrode was used as the working electrode with an area of 0.5 cm² exposed to the electrolyte. The electrochemical AFM cell was assembled on the commercial AFM system (Bruker, Multimode 8 with Nanoscope V controllers) coupled with a potentiostat for *in situ* electrochemical AFM experiments in argon filled glovebox (MIKROUNA, Super (1220/750), < 0.1 ppm of H₂O and < 0.1 ppm of O₂). Cyclic voltammetric (CV) curves was performed in the voltage range 1.9 V - 4.4 V at a scan rate of 1 mV/s. During discharge, the potential was scanned negatively from OCP (~3.3 V) to 1.9 V and then positively to 4.4 V during the charging process. *In situ* AFM morphology images were obtained at different potentials during discharge at a scan rate of 1 mV/s. The scan rate for AFM imaging is scaled with scan size: 0.501 Hz for scan sizes 10 μm × 10 μm (about 8.5 mins each image), 0.868 Hz for scan sizes 5 μm × 5 μm (about 4.9 min each image), 0.601 Hz for scan sizes ≤ 3 μm × 3 μm (about 7 mins each image), 0.601 Hz for scan sizes ≤ 2 μm × 2 μm (about 7 mins each image), 0.601 Hz for scan sizes ≤ 1 μm × 1 μm (about 7 mins each image). After the discharge potential stopped at 2.5V, the sweep of the image is continued for half an hour to observe the evolution in the electrode surface. During charging, the potential is held while charging to 4.0V and the image keep sweeping to observe the product evolution. All the AFM images were gained in peak force tapping mode with an insulating triangular silicon nitride AFM tip (force constant of 5 N/m).

Characterization.

After discharging, the HOPG or Pt nanoparticles electrode was removed and the surface is cleaned of electrolyte with DMC and dried in an argon filled glove box (MIKROUNA, Super (1220/750), < 0.1 ppm of H₂O and < 0.1 ppm of O₂) before

Raman and XPS characterization. Raman spectroscopy (HORIBA LabRAM HR Evolution, 532 nm laser wavelength) was applied to characterize the chemical composition of the samples. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALab 250Xi (Thermo Fisher) using monochromated Al K α (1486.6 eV) with an energy of 150 W. The base pressure was approximately 3×10^{-9} mbar, and the binding energies were referenced to the sp³-hybridized carbon C 1s peak at 284.8 eV.

2. Supplementary Figures

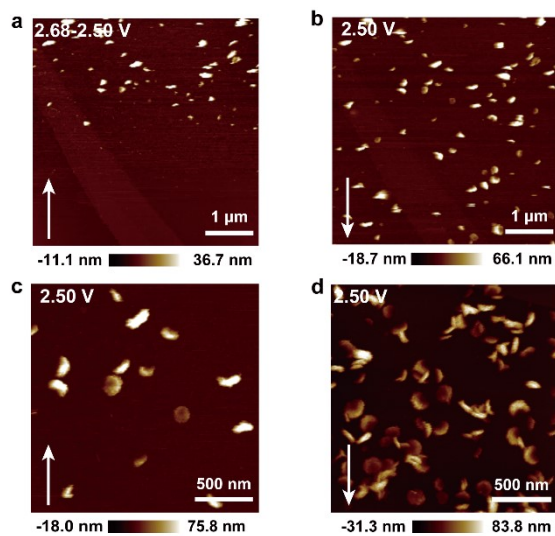


Fig. S1 *In situ* AFM images showing the topography on the HOPG in the electrolyte containing 0.5 M LiTFSI upon discharging at (a) 2.68-2.50 V with discharging time of ~700 s, 2.50 V with discharging time of (b) ~1000 s, (c) ~1400 s and (d) 1800 s. The white arrow in (a-d) indicates the scan direction.

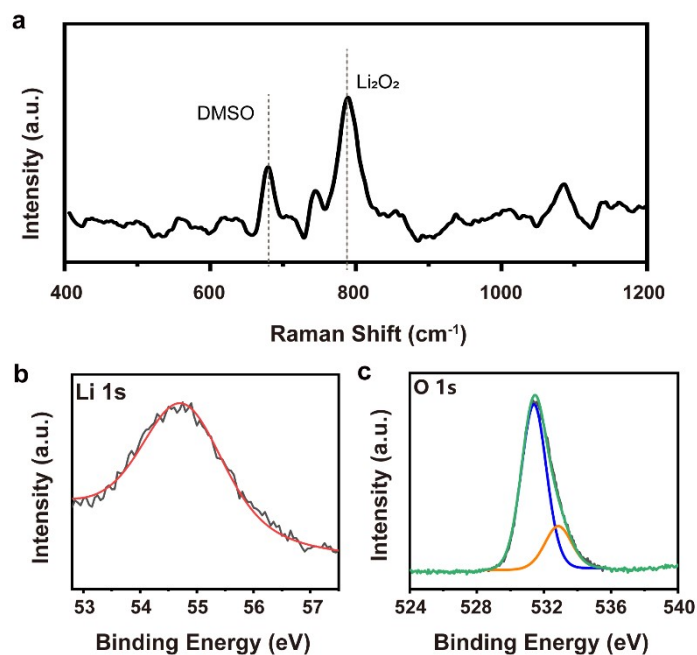


Fig. S2 Raman (a) and XPS (b, c) spectra of discharged HOPG electrode obtained in the electrolyte with 0.25 M KTFSI. Raman peak at 789 cm⁻¹ corresponds to Li₂O₂ and the peak at 680 cm⁻¹ corresponds to DMSO remaining on the electrode surface. The peak present in O 1s (c) at 531.5 eV represents Li₂O₂ and the peak at around 532.9 eV contains contributions from bound carbon–oxygen species.¹

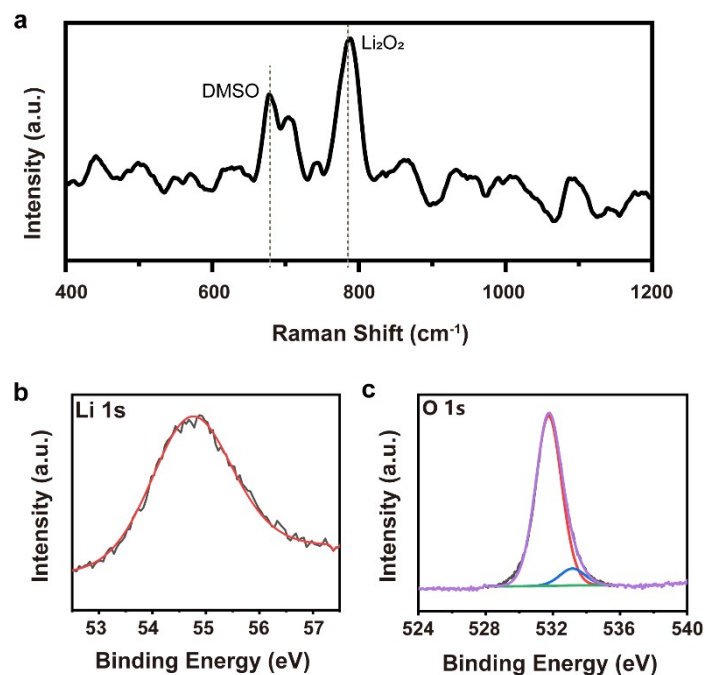


Fig. S3 Raman (a) and XPS (b, c) spectra of discharged Pt nanoparticles electrode obtained in the electrolyte without electrolyte additives. Raman peak at 789 cm⁻¹ corresponds to Li₂O₂ and the peak at 678 cm⁻¹ corresponds to DMSO remaining on the electrode surface. The peak present in O 1s (c) at 531.7 eV represents Li₂O₂ and the peak at around 533.1 eV contributions from various surface bound carbon–oxygen species.¹

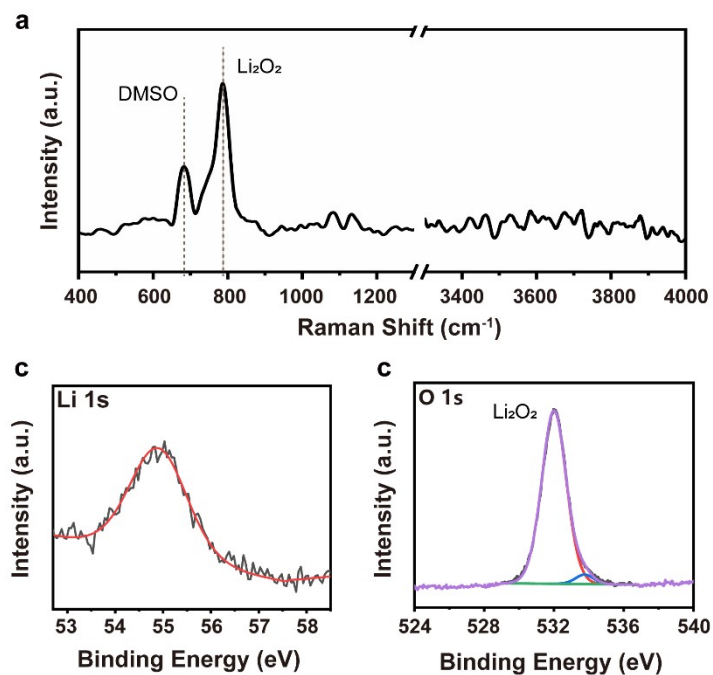


Fig. S4 Raman (a) and XPS (b, c) spectra of discharged Pt nanoparticles electrode in the electrolyte with 0.25 M KTFSI. Raman peak at 788 cm⁻¹ corresponds to Li₂O₂ and the peak at 679 cm⁻¹ corresponds to DMSO remaining on the electrode surface. The peak present in O 1s (c) at 531.6 eV represents Li₂O₂ and the peak at around 533.4 eV contributions from various surface bound carbon–oxygen species.¹

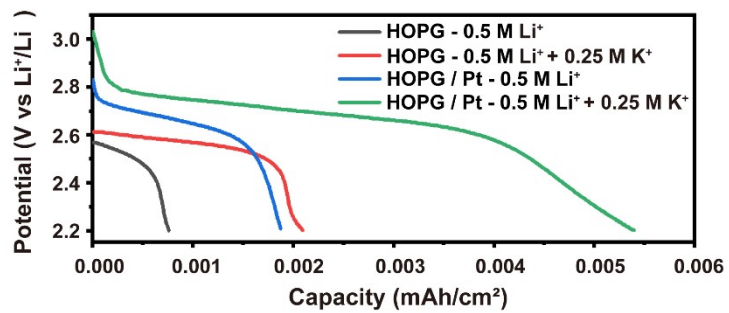


Fig. S5 Discharge profiles of Li–O₂ cells in different systems, obtained at a current density of 0.02 mA/cm² with a cutoff voltage of 2.2 V.

1. M. A. Schroeder, N. Kumar, A. J. Pearse, C. Y. Liu, S. B. Lee, G. W. Rubloff, K. Leung and M. Noked, *Acs Applied Materials & Interfaces*, 2015, 7, 11402-11411.