

Supporting Information

Promoting Solution Discharge of Li-O₂ Batteries with Immobilized Redox Mediators

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Materials.

Commercially available reagents of dimethoxyethane (DME, Sigma-Aldrich, 99.9%) and acetonitrile (MeCN, Sigma-Aldrich, 99.9%) were distilled under Ar over CaH₂ and then further dried for several days over freshly activated molecular sieves (type 3Å) resulting in a final water content of ≤ 10 ppm (determined by Mettler-Toledo Karl Fischer titration apparatus). Battery grade lithium perchlorate (LiClO₄, Sigma-Aldrich) was dried under vacuum (buchi oven) at 120°C for 24 h. All materials were stored in an Ar-filled glove box (Mbraun, both H₂O and O₂ < 0.1 ppm).

The 9,10-dioxo-9,10-dihydroanthracene-1-diazonium tetrafluoroborate (AQD) was synthesized according to a published procedure.^{1,2} Briefly, 1-aminoanthraquinone (200 mg), HCl (36%, 2.5 ml) and H₂O (1 ml) were mixed in a flask on top of an ice bath for ~ 30 min, then NaNO₂ (90 mg) dissolved in 10 mL water was added in dropwise manner to the flask, which was followed by the addition of NaBF₄ (115 mg) dissolved in 1 mL water, producing the final products precipitated on the bottom of the flask. The precipitate was collected by filtration and thoroughly washed successively with cold water and ether. The synthesized products were dried under vacuum and kept in a freezer at 0°C for future use.

Electrode preparation and Li-O₂ cell assembly.

Gas diffusion layer (GDL, H2315, Quintech) was used as the oxygen cathode. The porosity of the GDL is ~80%, and the Brunauer–Emmett–Teller surface area is below 1 m² g⁻¹.³ Before use, the GDL were heated under an Ar:H₂ (95:5 v/v)

atmosphere at 900 °C for three hours. Three pieces of GDL (diameter=4 mm) were stacked to construct the oxygen cathode. The electro-grafting process was conducted in a glass electrochemical cell containing 2 mM AQD in 0.1 M TBAP MeCN, and repeated potential scan between 3.8 and 2.0 V vs. Li/Li⁺ for three cycles was applied to the model electrodes and the GDL. Afterwards, the electrode potential was held at 2.2 V for 5 min to further increase the surface concentration of immobilized AQs on the GDL electrode. At the end of electro-grafting, the PAQ-coated GDL electrode were rinsed with alcohol and dried under Ar stream.⁴

Swagelok-type Li-O₂ cells, comprised of a lithium or protected lithium anode, pristine GDL or PAQ-coated GDL cathode, and 0.1 M LiClO₄ MeCN or 0.1 M LiClO₄ DME electrolyte, were assembled and operated under 1 atm of O₂. The protected lithium anode was a lithium foil (80 μm thick) coated by a LiPON film (specifically, 2.0 μm thick Li_{3.3}P_{1.0}O_{3.9}N_{0.17}) that was prepared by radio frequency sputtering, and the obtained LiPON film has a Li⁺ ion conductivity of ~ 2x10⁻⁶ S cm⁻¹.⁵ The protected lithium anode was used only in MeCN solution and not in DME electrolyte.

Electrochemical and DEMS measurements.

Electrochemical measurements were conducted using a Biologic VMP3 electrochemical workstation. A standard three-electrode electrochemical cell consisting of a gold electrode (Au, diameter=2mm) as the working electrode, a platinum wire as the counter electrode, and a filamentary silver as the reference electrode was used throughout. The pristine and the PAQ-coated electrodes were

subjected to cyclic voltammetry in O₂ saturated 0.1 M TBAP MeCN or 0.1 M LiClO₄ MeCN, and the sweep rate was typically 100 mV s⁻¹. At the end of each measurement, CV of the redox of Fc/Fc⁺ couple was conducted to measure the potential of the silver quasi reference electrode. All the reported potentials are transformed to the Li/Li⁺ scale.

In situ differential electrochemical mass spectrometry (DEMS) was conducted with a modified Swagelok-type Li-O₂ cell,⁶ which has two glued PEEK capillary tubes as purge gas inlet and outlet and is linked to a commercial mass spectrometer (Hiden HPR-20) by a homemade gas-purging system. The flow rate of the purge gas was 1.5 mL min⁻¹. During the discharge process, a mixed gas of Ar/O₂ (mass ratio 1:4) was used to quantify the oxygen consumption, in which Ar acted as the internal trace gas with a known constant flux. The DEMS cell was electrochemically controlled with a Princeton PARSTAT 4000 electrochemical workstation.

Instruments and characterization.

The XPS data were acquired with an ESCALAB 250 system using the Al K α source under high-vacuum. XRD study of the cathodes was conducted with a Bruker D8 Advance powder X-ray diffractometer with the Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The discharged cathodes were housed in a homemade airtight sample chamber during measurement. FTIR measurements were carried out on a Nicolet iS5 spectrometer (Thermo Fisher Scientific) housed in an Ar-filled glove box and operated in transmission mode. Field emission scanning electron microscopy (FESEM) images were obtained with a XL-30 E-SEM. Raman Spectroscopy was performed by using a

customized LabRAM HR Evolution Raman system (HORIBA Scientific) with an excitation wavelength of 532 nm.

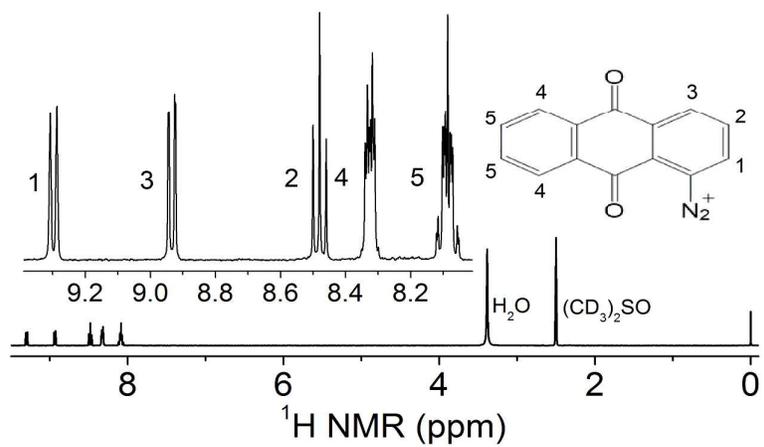


Figure S1. ^1H NMR spectrum of 9,10-dioxo-9,10-dihydroanthracene-1-diazonium tetrafluoroborate.

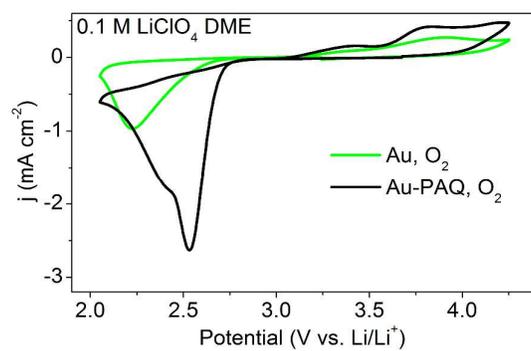


Figure S2. CVs of the redox of O₂/Li₂O₂ in 0.1 M LiClO₄ DME on pristine Au and PAQ-coated Au electrode.

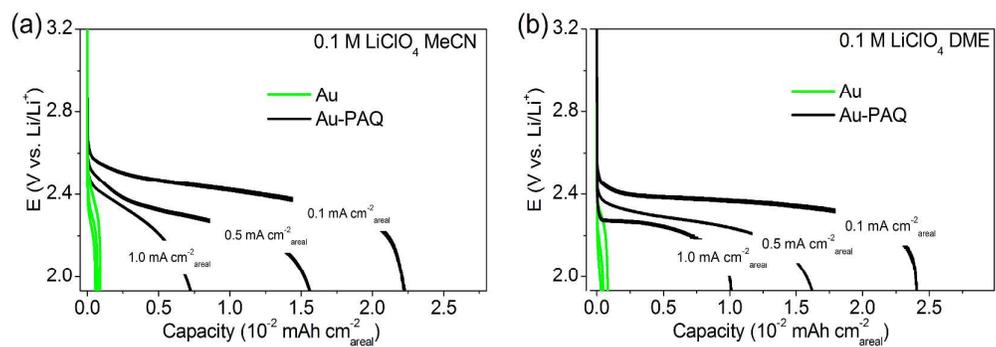


Figure S3. Discharge curves of Li-O₂ batteries on pristine Au (green) and PAQ-coated Au (black) cathodes at various current densities in 0.1 M LiClO₄ MeCN (a) and 0.1 M LiClO₄ DME (b).

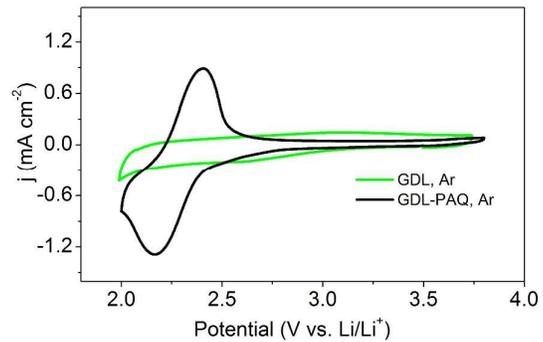


Figure S4. CVs of a pristine GDL (green) and a PAQ-coated GDL (black) electrode in Ar-saturated 0.1 M TBAClO₄ MeCN. The scan rate is 0.01 V s⁻¹.

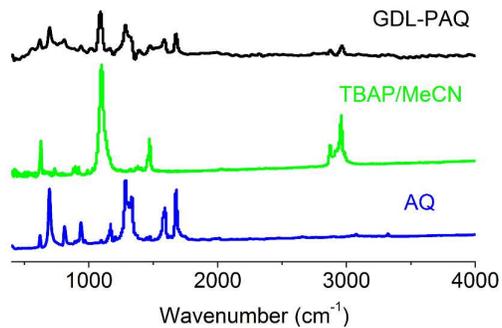


Figure S5. FTIR spectrum of PAQ-coated GDL electrode (black). The peaks were assigned as below: 1680 cm⁻¹ is the stretching of C=O (aryl ketone), 1595 and 1585 cm⁻¹ are the C=C aromatic stretching, and 1320 and 1275 cm⁻¹ are the ring stretching and C-H bending. For comparison, FTIR spectra of (green) 0.1 M TBAClO₄ MeCN and (blue) AQ are also included.

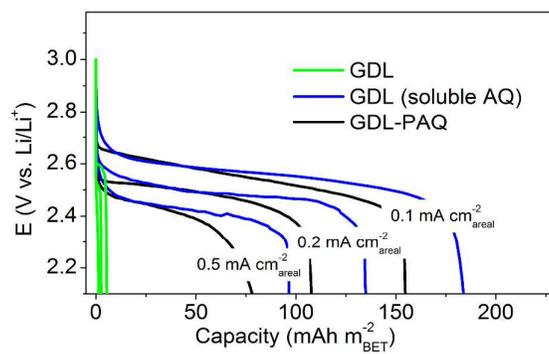


Figure S6. Discharge curves of Li-O₂ batteries with (green) pristine, (blue) soluble AQ-, and (black) PAQ-catalyzed GDL cathodes in 0.1 M LiClO₄ DME at various current densities.

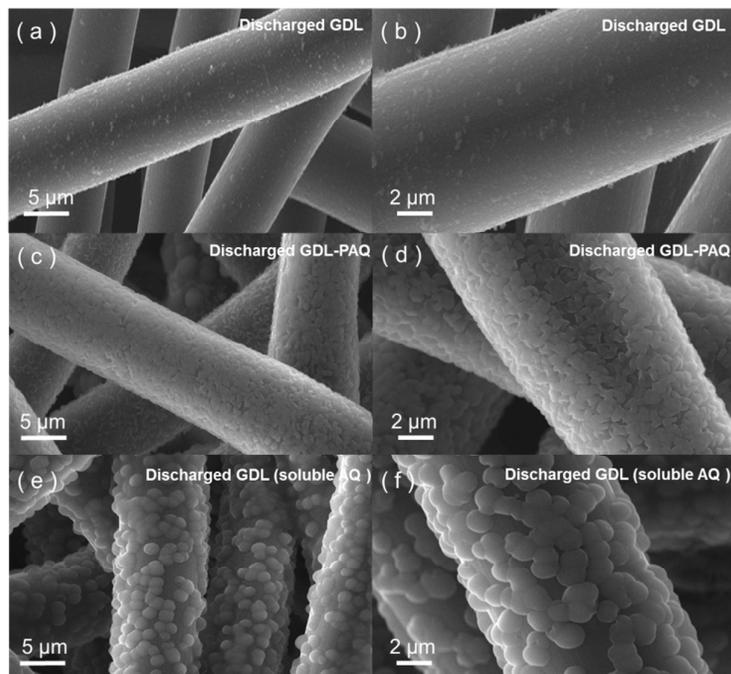


Figure S7. SEM images of the (a, b) GDL discharged in the absence of soluble AQ, (c, d) PAQ-coated GDL at the end of discharge, and (e, f) GDL discharged in the presence of soluble AQ at a current density of 0.1 mA cm^{-2} in $0.1 \text{ M LiClO}_4 \text{ DME}$.

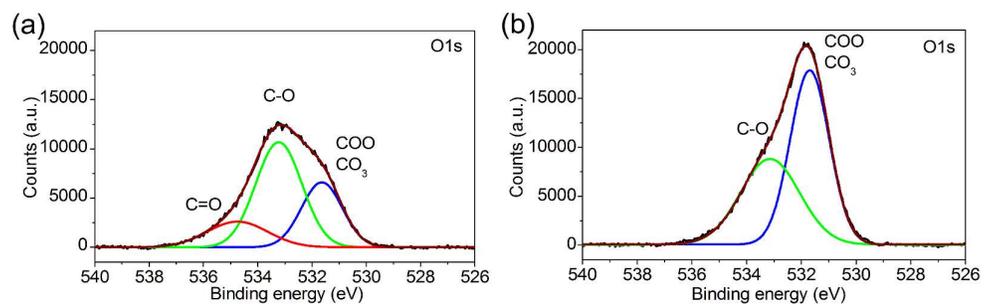


Figure S8. O 1s XPS spectra of the lithium metal anode of Li-O₂ cells containing 0.1 M LiClO₄ DME with (a) 2 mM soluble AQ and (b) immobilized AQ, respectively.

References

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