

Supplementary Information

Revealing the Catalytic Pathway of Quinone-Mediated Oxygen Reduction Reaction in Aprotic Li-O₂ Batteries

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Materials and Chemicals

Tetraethyleneglycol dimethylether (TEGDME, 99%, TCI) and lithium bis(trifluoromethane) sulfonimide (LiTFSI, 99.95%, trace metals basis, Sigma-Aldrich) were used as solvent and Li⁺ salt for the preparation of supporting electrolyte, respectively. Duroquinone (DQ, 97%, Aladdin) was used as the redox mediator. PVDF-Nafion membranes were fabricated as the selective separator according to the previous literature.¹ Carbon felt (GFD2.5 EA, SGL Group) was used as the cathode. The anode material consisted of lithium iron phosphate (LiFePO₄, BTR). Prior to use, LiTFSI and DQ were vacuum dried at 100 °C overnight, and TEGDME was treated with 4 Å molecular sieve for at least 3 days. All the above chemicals were stored in an argon-filled glove box without exposure to air. 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, DOJINDO Laboratories) was used as the spin trap for O₂⁻ and was stored under -20 °C prior to use. Dimethyl ether (DME, 99%, Energy Chemical) was used to clean the collected cathode from batteries and was stored in an Ar-filled glove box.

Electrochemical Measurements

Cyclic voltammetry (CV) was conducted with a typical three-electrode system. Planer Au (3 mm in

diameter) was used as the working electrode after polished with 0.05 μm Al_2O_3 powder. 10 mM Ag/AgNO_3 was used as the reference electrode and was priorly calibrated with ferrocene as the internal reference.² A $2 \times 2 \text{ cm}^2$ Pt plate was used as the counter electrode. O_2 was bubbled to the electrolyte for 10 min to prepare 3-ml O_2 -saturated samples. All the CV measurements were conducted with BioLogic-VMP3 at room temperature.

Battery Assembly

All battery tests were conducted with a custom-designed static battery device reported in our previous study.³ Both the anode and cathode endplates are made of Ti. LiFePO_4 and carbon felt were used as the anode and cathode, respectively. A 50 mg slurry containing LiFePO_4 , super P, and PVDF (80:10:10 in wt.%) was dropped on the endplate as the anode material, followed by vacuum dry at 120 $^\circ\text{C}$ overnight. A piece of PVDF-Nafion membrane was used as the selective separator to separate the two electrodes and to prevent the crossover of redox mediators. The size of the electrodes was $2 \times 2 \text{ cm}^2$. The anolyte and reference electrolyte consisted of 1 M LiTFSI in TEGDME. 1 ml of the above electrolyte solution with/without 10 mM DQ was added as the catholyte. The theoretical capacity of the added DQ is 0.268 mAh. The batteries were assembled in an Ar-filled glove box with O_2 and the water content below 0.1 ppm, followed by transferring to a O_2 testing container with water content below 0.1 ppm without exposure to air. All batteries were tested in a galvanostatic mode with a Neware battery cycler (CT-9002-5V5A-204, Shenzhen, China) at room temperature.

Characterizations

Scanning electron microscopy (SEM) images were obtained on a TESCAM MIRA3 scanning electron microscope. Prior to the imaging, the discharged batteries were disassembled in an Ar-filled glove box, and the collected carbon felts were washed with DME for three times, followed by vacuum dry overnight at room temperature.

Electron paramagnetic resonance (EPR) spectra were recorded on Bruker EMXplus-10/12. Solution samples were sealed in 50- μ l micropipettes (Blaubrand, 7087-33) at 298 K. The measurements were carried out with a frequency of 9.84 GHz, center field of 3500 G, sweep width of 120 G, microwave power of 20mW, modulation amplitude of 0.5 G, modulation frequency 100 kHz, and receiver gain of 30.

The EPR samples were prepared with a three-electrode cell. A piece of porous carbon felt which has an uptake of \sim 0.5 ml solution was used as the working electrode for sample collection. 10 mM Ag/AgNO₃ and Pt plate were used as reference and counter electrode, respectively. DQ sample was prepared by dissolving 10 mM DQ in supporting electrolyte (0.1 M LiTFSI-TEGDME). DQ⁻ sample was prepared by applying a potential of 2.4 V (*vs.* Li/Li⁺) to the above electrolyte, and oxygen was subsequently supplied to it to produce DQ⁻ + O₂. 100 μ l sample was added to 10 μ l DMPO right before the tests. ORR product without DQ was prepared by applying a potential of 2 V (*vs.* Li/Li⁺) to an O₂-saturated supporting electrolyte. As for the attenuation tests, 1 ml TEGDME was additionally added to each sample to mitigate the sensitivity of EPR measurements. DMPO was added after the relaxation.

The averaged intensity of the first peak and valley at each relaxation time was chosen to present the retention information.

Raman spectra were collected on a Renishaw Via Raman Spectrometer (wavelength: 633 nm and power: 0.5 mW). The washed and dried carbon felt was sealed in a home-made Teflon box with a quartz window on the top for laser access.

Calculation & Simulation

All calculations including the structure and free energy were performed with the Gaussian 16 package using the DFT/B3LYP/6-311 basis set. Solvent effects were taken into account via the Solvation Model Based on Density (SMD) model⁴ using a dielectric constant of 7.9 for TEGDME solvent.⁵

EPR fitting was performed with the EasySpin software,⁶ using a spin Hamiltonian taking into account the electron Zeeman (g-value) and hyperfine (A-value) interactions, as implemented in the software. The fitting was performed prior to the calibration of the magnetic field, so that the range is different from that in the figures in the manuscript.

Figures

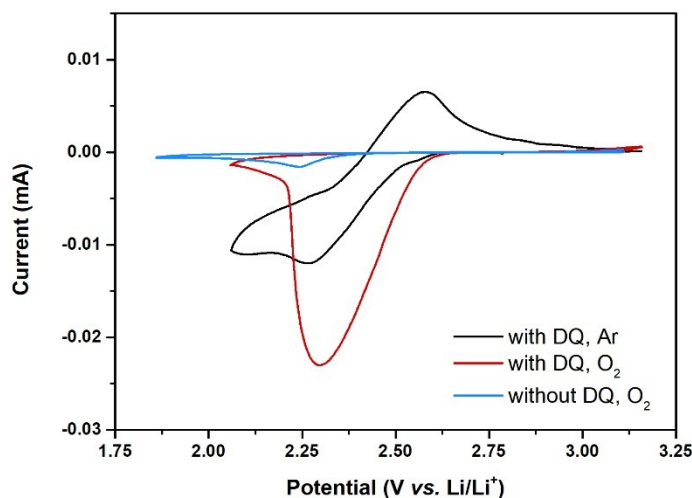


Figure S1. CV curves of duroquinone (DQ) in Ar (black) and O₂ (red), and that of reference electrolyte in O₂ (blue). The supporting electrolyte was 0.1 M LiTFSI-TEGDME. The scan rate was 10 mV s⁻¹.

Discussion: DQ functions as an electron shuttle during the cathodic ORR process. DQ receives an electron from the working electrode to become DQ⁻, followed by transferring it to the dissolved O_{2(sol)}, chemically reducing O₂ to LiO₂. With the regeneration of DQ by O₂, the reduction current increases. The lack of the reduced species, DQ⁻, leads to the disappearance of anodic peak.

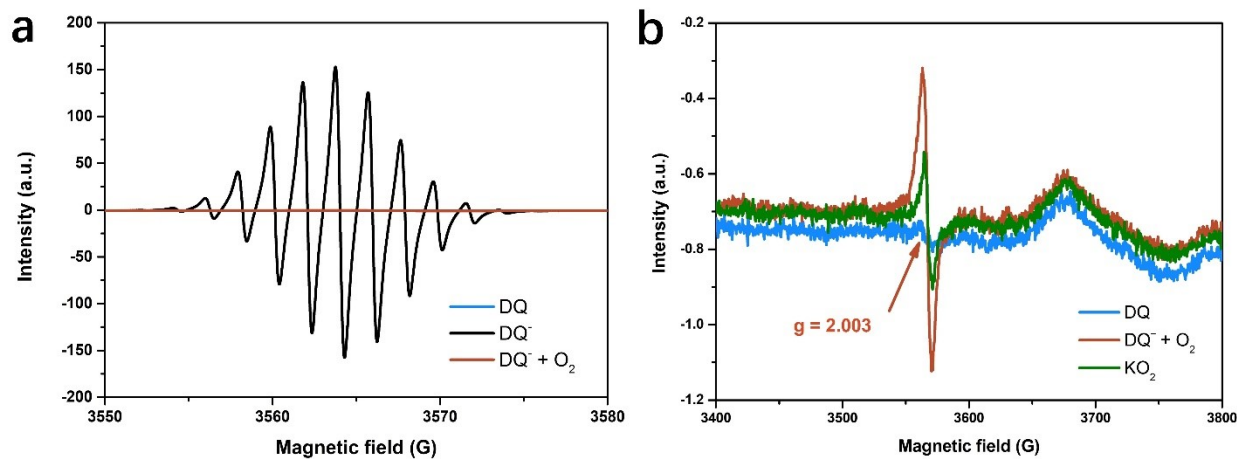


Figure S2. (a) EPR spectra of pristine DQ (blue), reduced DQ⁻ (black) and the reaction product of DQ⁻ and O₂ (red). (b) EPR spectra of pristine DQ (blue), the reaction product of DQ⁻ and O₂ (red) and KO₂ (green) in broader magnetic field range.

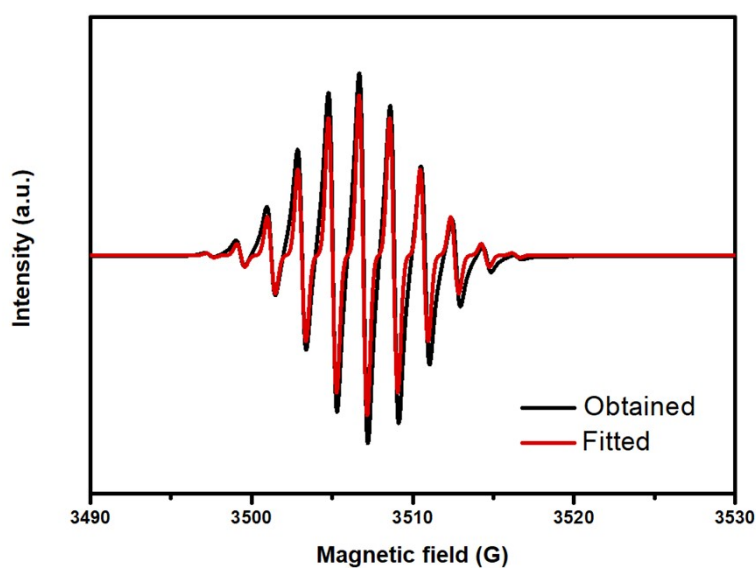


Figure S3. Obtained (black) and fitted (red) EPR spectra of DQ⁻ in TEGDME.

Discussion: The obtained and fitted EPR spectra correspond to the hyperfine splitting of the twelve hydrogen atoms from the four methyl groups. The result is in accordance with the previous report.⁷

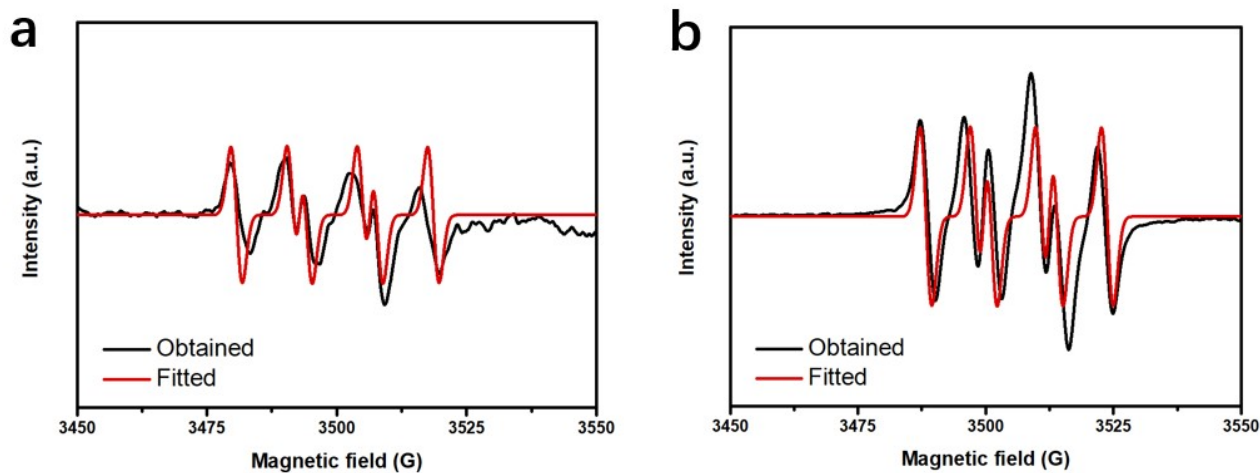


Figure S4. Obtained (black) and fitted (red) EPR spectra of (a) ORR without DQ and (b) $\text{DQ}^- + \text{O}_2$ in TEGDME. 10 μl DMPO was added prior to the measurements. The fitting suggests DMPO-O_2^- for both cases.

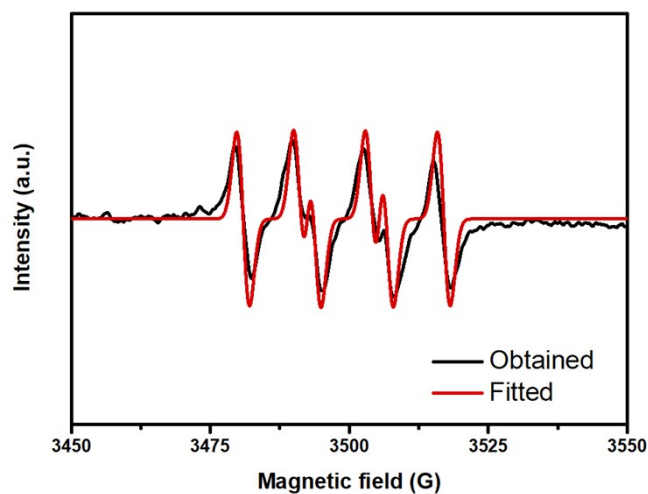


Figure S5. Obtained (black) and fitted (red) EPR spectra of KO_2 -saturated electrolyte. The solvent was TEGDME and 10 μl DMPO was added prior to the measurement. The fitting suggests DMPO-O_2^- .

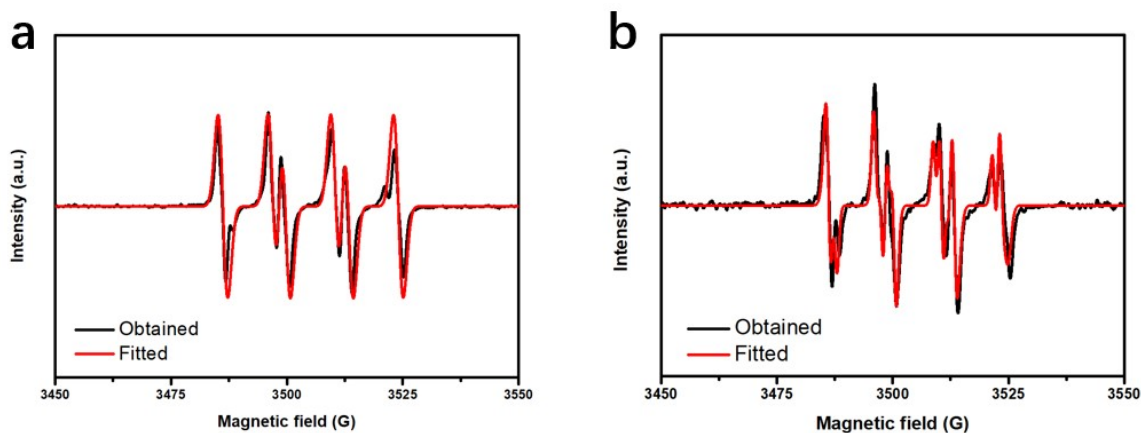


Figure S6. Obtained (black) and fitted (red) EPR spectra of ORR product (a) with and (b) without DQ in TEGDME at 0 min. 10 μl DMPO + 1 ml TEGDME was added prior to the measurements. The fitting suggests the mixture of DMPO- O_2^- and DMPO-OOH for both cases.

Discussion: the simulation results in Fig. S6 suggest a mixture of DMPO- O_2^- and DMPO-OOH for both cases. The absence of DQ $^-$ in Fig. S6a rules out the possibility that the reaction between the remaining DQ $^-$ and dissolved O_2 led to the high retention of O_2^- . In addition, considering the previous simulation in Fig. S4, the proton should not come from the ORR. Therefore, the proton may stem from the moisture contamination during the longer sample preparation time, including the electrochemical process, O_2 supply and relaxation period.

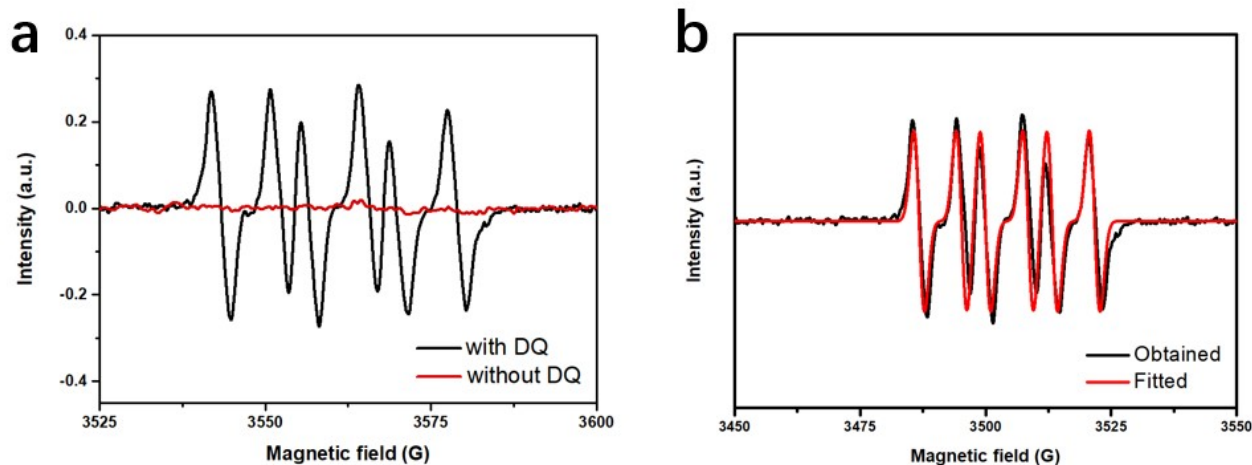


Figure S7. (a) EPR spectra with DMPO of extracted catholyte with (black) and without (red) DQ from Li-O₂ batteries discharged in an Ar-filled glove box. The batteries were discharged at 12.5 uA cm⁻² for 10 min. After discharge, the batteries were rested for 2 min before the extraction of catholyte. 10 μl DMPO was added prior to the measurements. (b) The obtained (black) and fitted (red) curves of the case with DQ in (a). The fitting indicates DMPO-O₂^{•-}.

Reference

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