Supporting Information for

A Highly Active Low Voltage Redox Mediator for Enhanced Rechargeability of Lithium-Oxygen Batteries

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Experimental Details:

Chemicals
Tris[4-(diethylamino)phenyl]amine (TDPA, 99%) and tetraethylene glycol dimethyl ether (TEGDME, >99%) were purchased from Sigma Aldrich and lithium-bis(trifluoromethylsulfonyl)imide (LiTFSI, 99%) was obtained from Solvionic. TEGDME was distilled over Na metal under vacuum and stored over activated 4 Å molecular sieves in an Ar filled glove box. LiTFSI and TDPA were dried at 150°C for 2 days and 70°C for 2 days, respectively, in a Büchi oven under vacuum. The TEGDME had a water content of < 1 ppm and all the other electrolytes had a total H₂O content of ≤ 4 ppm (Karl Fischer Titration). Glass fiber separators were dried at 300°C for 24 h under dynamic vacuum prior to use.

Cyclic Voltammetry and Rotating Disk Electrode (RDE) Tests
Cyclic voltammetry was performed with a three-electrode cell gas-flow enabled setup. The working electrode was a glassy carbon rotating disk (Pine Instruments Co., 0.2475 cm²) and the counter electrode was a Pt wire. A strip of lithium foil submerged in 0.1 M LiTFSI/TEGDME and separated from the bulk electrolyte solution with a Vycor glass frit served as the reference electrode. A solution of 0.1 M LiTFSI + 5 mM TDPA in TEGDME constituted the electrolyte. Argon or oxygen was bubbled through the electrolyte solution before and over the solution during the experiments. The experiments were controlled with a VMP3 potentiostat and EC-Lab® software (Bio-Logic Science Instruments) and the rotation rate of the working electrode was controlled with a modulated speed rotator (Pine Instruments Co.).

Galvanostatic Studies
Electrochemical performance was assessed using a hermetically sealed Swagelok type cell with the positive electrode head space filled with dry O₂ (<0.5 ppm) at 1.5 atm. For positive electrode fabrication, an ink obtained by blending 75% Ketjenblack with 25% polytetrafluoroethylene (PTFE) suspension was coated on stainless steel mesh (mesh size: 100 x 100, 30% open area) of 1 cm² geometric area. The electrodes were then dried at 60°C for 1 h in air followed by 12 h at 300°C under dynamic vacuum. Typical loading of the electrodes were 0.4 - 0.6 mg cm⁻². Electrochemical cells were assembled in an Ar filled glove-box (O₂ < 0.5 ppm, H₂O < 0.5 ppm) with 0.1 M LiTFSI-propylene carbonate (PC) pretreated Li metal foil as the negative electrode and one glass fiber membrane (Millipore, 0.7 mm) as the separator. 60 µL of 0.5 M LiTFSI in TEGDME with and without 50 mM of TDPA was used as the electrolyte with a single glass fiber separator (Millipore). Galvanostatic cycling was performed using a BT2000 battery cycler (Arbin Instruments). All the current densities reported in this work are based on the geometric electrode area.

Mass Spectrometry
The residual gas analysis was performed with a modified design based on an OEMS apparatus reported by Tsiouvaras et. al (J. Electrochem. Soc. 2013, 160, A471-A477). A commercial electrochemical flow cell (EL-Cell, ECC-DEMS) was attached in-line with a
gas flow controller (Bronkhorst, F-200CV) and a quadrupole mass spectrometer (Stanford Research Systems, RGA 200). During cell operation a controlled flow of Ar (5.0 Grade) sweeps the evolved gases from the cell to the MS entrance chamber where the gas enters the quadrupole through a fused silica capillary (50 um ID). The pressure inside the MS chamber is 2 x 10^{-6} torr during operation. Prior to measurement, the mass spectrometer is calibrated to establish a relationship between the measured ion current (A) and target gas concentration (ppm). With the use of known gas concentrations (from 2000 ppm O_2/Ar balance and 2000 ppm CO_2/Ar balance mixtures) mixed with different amounts of Ar, a linear relationship between the gas concentration and ion current is established. Quantification is performed with the use of Mathworks Matlab software.

For the measurements in Figure 3, positive electrodes were prepared with a 75:25 weight percent of Ketjenblack : PTFE. The contents were spread onto a stainless steel mesh (2 cm^2/100 mesh size) and dried under vacuum at 300 °C for 12 hours. The cells were assembled with 200 uL of 0.5M LiTFSI in TEGDME or 0.5M LiTFSI + 50 mM TDPA in TEGDME, two glass fiber separators and 0.1 M LiTFSI-PC pretreated lithium metal foil as the counter electrode. Discharge was performed at 100 uA cm^{-2} under a 5% O_2/balance Ar flow for 12 h. Charging of the cell was performed at 100 uA cm^{-2} after a 5 hour rest period at OCV. The e^-/O_2 values were determined from the total accumulated amount of O_2 corresponding to the fixed capacity of 2.4 mAh.

**Analytical Methods**

**XRD:** For the ex-situ analysis of the discharged and charged oxygen electrodes, cells were disassembled in an Ar filled glove-box and the electrodes were washed with dry acetonitrile (<1 ppm) and dried in a vacuum chamber. Powder X-ray diffraction was performed on a PANalytical Empyrean equipped with PIXcel detector, using Cu-Kα radiation (λ= 1.5405Å) in the range from 30° to 60° (2θ) at a step size of 0.025° using Bragg-Brentano geometry. The oxygen electrodes were mounted on a zero background silicon sample holder for the XRD analysis. In addition to a Kapton® film covering the sample holder, a drop of paraffin oil was applied on top of the sample for atmospheric protection.

**Li_2O_2 Quantification by Iodometry:** In a chemical reaction involving H_2O_2 and I-, the former is reduced to water and the latter is oxidized to iodine, which can then be titrated using standard thiosulfate solution to quantify the peroxide concentration. The net reaction between peroxide and iodide can be written as follows:

\[ \text{H}_2\text{O}_2 + 3\text{I}^- + 2\text{H}^+ \leftrightarrow 2\text{H}_2\text{O} + \text{I}_3^- \]

This reaction is slow without a catalyst but can be quite fast in the presence of catalysts such as Mo(VI) and excess I^- that forces the reaction to proceed to the right resulting in the formation of I_3-. The I_3^- is titrated using thiosulfate based on the following reaction:

\[ \text{I}_3^- + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

In a standard iodometric estimation of H_2O_2, the peroxide is reacted with excess iodide in an acidic media. However, acid is known to cause chemical disproportionation of peroxide
to water and oxygen, and iodide is prone to oxidation at acidic pH. Both these processes are likely to introduce significant error in the peroxide quantification. Therefore, in our work, we have adopted a modified iodometric method employing a pH neutral iodide-phosphate buffer reaction media that maintains steady supply of protons for the peroxide-iodide reaction, while maintaining a constant pH. Neutral pH suppresses peroxide disproportionation along with suppressing the oxidation of iodide. The inhibition of iodide oxidation was evident from the unchanged color of the post titration solution (colorless) even days after the titration. In a standard iodometric procedure, the post titration solution turns blue quickly from the oxidation of I⁻ to I₂, which binds to starch.

The buffer-catalyst solution was prepared by dissolving 65 mg of (NH₄)₆Mo₇O₂₄•4H₂O (ammonium heptamolybdate) along with 0.11 mol of H₂PO₄⁻ and 0.03 mol of HPO₄²⁻ in 500 ml of Millipore water. Adding 67 g of KI to this buffer solution and diluting it to 1 L resulted in the reagent buffer solution, which was freshly prepared before use. For the Li₂O₂ quantification, the discharged/charged positive electrodes were transferred to a glass vial to which 5 ml of Millipore water was added and shaken vigorously. The content of the vial was transferred to a conical flask with an extra 5 ml of water that was used to rinse the vial. To this mixture, 10 ml of water and 25 ml of buffer catalyst solution was added. The mixed solution immediately turned yellow indicating the liberation of iodine, which was titrated with standardized thiosulfate solution until a straw yellow color was achieved. The titration was continued after adding starch indicator solution, with the end point showing a color change from blue-violet to colorless.

**NMR Studies:** NMR experiments were conducted using D₂O or CDCl₃ as the solvent using a Bruker Advance 300 MHz spectrometer. ¹H spectra were referenced to the HDO peak at 4.78 ppm (TSP at 0 ppm) in D₂O or the residual CHCl₃ peak at 7.26 ppm in CDCl₃. Discharged oxygen electrodes were vacuum dried and extracted with 0.7 ml of D₂O. For the ¹H NMR analysis of the electrolyte after repeated discharge-charge cycling, separators of the cycled cell were extracted with 0.7 ml of CDCl₃. 200 µL of electrolyte and two glass fiber separators were used for these cycling experiments.
Supplementary Figures:

**Figure S1.** (a) Linear sweep voltammograms at 5 mV/s on a glassy carbon disk in (5 mM TDPA + 0.1 M LiTFSI)/TEGDME electrolyte under an argon atmosphere and the corresponding Levich plot (b).

**Discussion of Figure S1: Diffusion Coefficient Calculation for TDPA**

The diffusion coefficient (D) can be estimated using the Levich equation below:

$$I_L = 0.620nFAD^{2/3}Cv^{-1/6}\omega^{1/2}$$

The slope of the Levich plot ($I_L/\omega^{1/2} = 1.4347\times10^{-5}$) displayed in Figure S1b and the known constants: $n$ (number of electrons transferred = 1), $F$ (Faraday’s constant = 96485 C mol$^{-1}$), $A$ (electrode surface area = 0.2475 cm$^{2}$), $C$ (concentration of TDPA = 5x10$^{-6}$ mol cm$^{-3}$), $v$ (kinematic viscosity of TEGDME = 0.04014 cm$^{2}$ s$^{-1}$) $^{[1]}$ were used to calculate a value of 1.2x10$^{-6}$ cm$^{2}$ s$^{-1}$.

Alternatively, the Randles-Sevcik equation (below) can be applied to the cyclic voltammograms in Figure 1a (manuscript).

$$i_p = 0.4463nF\left(\frac{nF}{RT}\right)^{1/2}AD^{1/2}Cv^{1/2}$$

Assuming a 1-electron oxidation of TDPA $\rightarrow$ TDPA$^+$ + e$^-$, $i_{pa1}$ was used from the CV under argon atmosphere (black curve). A similar value was obtained using this equation: 1.0x10$^{-6}$ cm$^{2}$ s$^{-1}$. 

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Figure S2. Galvanostatic discharge-charge profiles for the Li-O₂ cells containing 50 mM of TEMPO (black)/TDPA (red) in 0.5 M LiTFSI-TEGDME electrolyte with a Ketjenblack based positive electrode at 0.1 mA cm⁻² current density without capacity limitation.

Figure S3. Galvanostatic discharge-charge profile of the Li-O₂ cells with and without TDPA using 0.1 mA cm⁻² current density to 500 mAh g⁻¹ capacity.
Figure S4. The discharge/charge voltage at the end of each cycle for the TDPA (a) and non-TDPA (b) Li-O₂ cells cycled at 0.1 mA cm⁻² of current density for 500 mAh g⁻¹ of capacity. (c) cyclability with and without TDPA at 0.1 mA cm⁻² for a 1000 mAh g⁻¹ capacity cell, showing early death at 15 cycles without TDPA.
**Figure S5.** (a) First galvanostatic discharge-charge cycle with and without TDPA at 0.2 mA cm$^{-2}$ of current density for a capacity of 1000 mAh g$^{-1}$. (b) First discharge-charge cycle with TDPA at 0.4 mA cm$^{-2}$ of current density for a restricted capacity of 1000 mAh g$^{-1}$.

**Figure S6.** X-ray diffraction patterns of the pristine positive electrode, discharged and charged positive electrodes cycled with and without TDPA. The cells were discharged to a capacity of 1 mAh and charged to an equivalent capacity before XRD measurement. The Li$_2$O$_2$ peaks are marked with asterisk.
Figure S7. $^1$H NMR spectra of discharged positive electrodes with and without the TDPA in LiTFSI-TEGDME electrolyte. $^1$H spectra are referred to HOD peak at 4.78 ppm. The peaks of formate and acetate, formed as side products, are marked in red.

Figure S8. $^1$H NMR analysis of the 0.5 M LiTFSI-TEGDME electrolyte before electrochemical cycling (a), after 5th discharge (b), and after 10th discharge (c) of Li-O$_2$ cells cycled at a current density of 0.1 mA cm$^{-2}$ for 0.3 mAh (~500 mAh g$^{-1}$) of capacity. (d), (e), and (f) are the corresponding $^1$H NMR spectra using 0.5 M LiTFSI-TEGDME
electrolyte with 50 mM TDPA in it. The intensities of all the spectra are normalized w.r.t. the intensity of the reference CHCl₃ peak at 7.26 ppm. Due to the very low concentration of TDPA in the electrolyte, a comparatively large amount of TDPA electrolyte with CDCl₃ was used to record the spectra (d) so that the ¹H NMR signals of the TDPA could be observed (marked with blue arrow; the peak around 1 ppm corresponds to the aliphatic protons, whereas the peak around 6.2 ppm is due to the aromatic protons). Therefore the intensities of the glyme peaks are also higher in this spectra. However, due to the low concentration, the TDPA peaks are not very visible in the NMR spectra of the cycled electrolyte. Interestingly, an increased concentration of acetone was detected in the electrolyte of the non-TDPA cell (* marked: 2.15 ppm, (b) and (c)) with cycling, unlike the TDPA cell for which the acetone concentration in the electrolyte did not increase with cycling (see (e) and (f)). Though the electrolyte degradation mechanism leading to acetone formation is not clear, it is evident that the degradation process is somewhat suppressed in the TDPA cell, which could be due to the better solvation and resulting stability of the reactive oxygen intermediates in the presence of TDPA molecules. Overall, the NMR study of the cycled electrolyte showed no sign of aggravated electrolyte decomposition in the presence of TDPA.

![Graph](image_url)

**Figure S9.** (a) O₂ consumption w.r.t. the charge passed for the discharge of the Li-O₂ cells with (solid blue) and without (dotted blue) 50 mM of TDPA in 0.5 M LiTFSI-TEGDME electrolyte for a Ketjenblack based positive electrode at 0.1 mA cm⁻² current density. (b) Comparison of the O₂ evolution w.r.t. the charge potential of the Li-O₂ cells with (black) and without (red) the mediator. We note that the non-TDPA cell exhibits an overall e⁻/O₂ ratio of 3.0 on charge, compared to 2.45 e⁻/O₂ for the cell with TDPA. The latter value is similar to cells charged with prefilled commercial Li₂O₂, which exhibit greatly reduced electrolyte degradation owing to lack of the discharge intermediates.
Table S1. Iodometric estimation of Li$_2$O$_2$ after Li-O$_2$ cell discharge and charge.

| Cell Type     | After discharge to 1 mAh capacity | After charge to 1 mAh or to 4 V against Li$^+$/Li |
|---------------|-----------------------------------|--------------------------------------------------|
|               | Titrated Li$_2$O$_2$ equivalent in capacity | Li$_2$O$_2$ yield (%) (titrated capacity/coulomb capacity)$^\times100\%$ | Charge capacity and voltage | Remaining Li$_2$O$_2$ equivalent in capacity |
| TDPA Cell     | 0.894 mAh                          | 89.4%                                             | 1 mAh, 3.65 V                | 0                                               |
| Non TDPA Cell | 0.887 mAh                          | 88.7%                                             | 0.61 mAh, 4V                 | 0.297 mAh                                       |

References

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