

Utilization of Cobalt Bis(terpyridine) Metal Complex as Soluble Redox Mediator in Li-O₂ Batteries

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Viscosity measurements

Viscosity measurements were carried out using a Cannon-Fenske Viscometer (Ace Glass, size 200). The kinematic viscosity of the electrolytes was determined by measuring the efflux time of each electrolyte when flowing through the viscometer. The kinematic viscosity of the electrolyte was then calculated by multiplying by the viscometer constant (dependant on viscometer size, $0.1 \text{ cSt} \cdot \text{s}^{-1}$ for a size 200 viscometer). It was then possible to determine the dynamic viscosity (cP) of the electrolyte by multiplying the kinematic viscosity (cSt) by the density ($\text{g} \cdot \text{cm}^{-3}$) of the electrolyte.

Viscosity data of electrolytes used for cyclic voltammetry

Electrolyte	Kinematic viscosity ($\text{mm}^2 \cdot \text{s}^{-1}$)	Density ($\text{g} \cdot \text{ml}^{-1}$)	Dynamic Viscosity ($\text{mPa} \cdot \text{s}$)
1 M LiTFSI in diglyme	2.65	1.12	2.96
1 M LiTFSI in Pyr ₁₄ TFSI:Diglyme	15	1.36	20.4
100 mM LiTFSI in Pyr ₁₄ TFSI	54	1.46	78.8

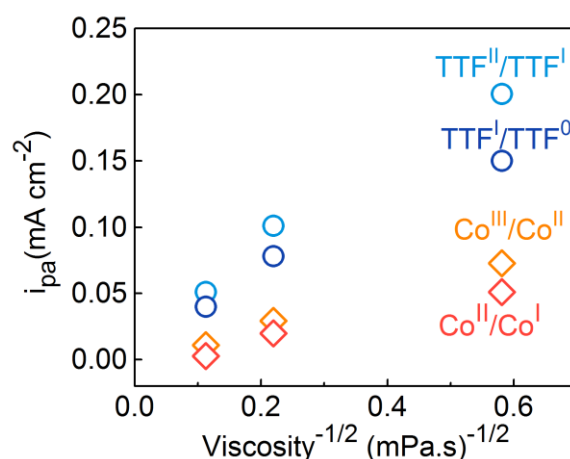


Figure S1. Values of anodic peak current per redox couple during CV at $20 \text{ mV} \cdot \text{s}^{-1}$, plotted as a function of the inverse of the square root of the dynamic viscosity.

Relation of peak current and solvent viscosity

For a reversible system, the peak current density recorded on a cyclic voltammetry experiment is a function of the number of electrons exchanged (n), the diffusion coefficient of the analyte (D), the scan rate (ν), and the analyte bulk concentration (c^*)

$$i_p = (2.69 \cdot 10^{-5}) \cdot n^{\frac{3}{2}} \cdot D^{\frac{1}{2}} \cdot \nu^{\frac{1}{2}} \cdot c^*$$

In addition the Stokes-Einstein hard sphere diffusion equation states:

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot a}$$

where k_B , T , η , and, a are the Boltzmann constant, temperature, solution dynamic viscosity, and the hydrodynamic radius of the diffusing species respectively.

As a consequence, the peak current density is expected to increase with the inverse of the square root of the dynamic viscosity.

Table S1. Peak separation in mV for Co(Terp)₂ and TTF redox processes

Units (mV)	Co ^{III} /Co ^{II}	Co ^{II} /Co ^I	TTF ^{II} /TTF ^I	TTF ^I /TTF ⁰
1 M LiTFSI in diglyme	78.5	65.8	79.6	76.9
1 M LiTFSI in Pyr ₁₄ TFSI:Diglyme	71.5	66.7	70.6	67.6
100 mM LiTFSI in Pyr ₁₄ TFSI	66.6	--	72.7	70.7

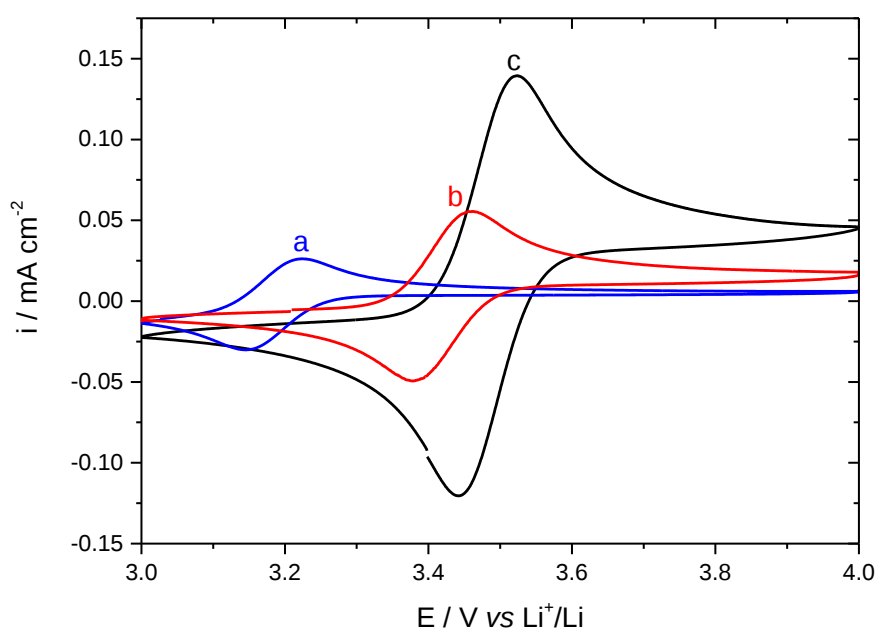


Figure S2. Voltammograms of a glassy carbon electrode in: a) 1 M LiTFSI + 2 mM ferrocene in diglyme, 1 M LiTFSI + 2 mM ferrocene in a 1:1 mixture of Pyr₁₄TFSI and diglyme, and c) 100 mM LiTFSI + 2 mM ferrocene in Pyr₁₄TFSI. Scan rate: 20 mV/s.

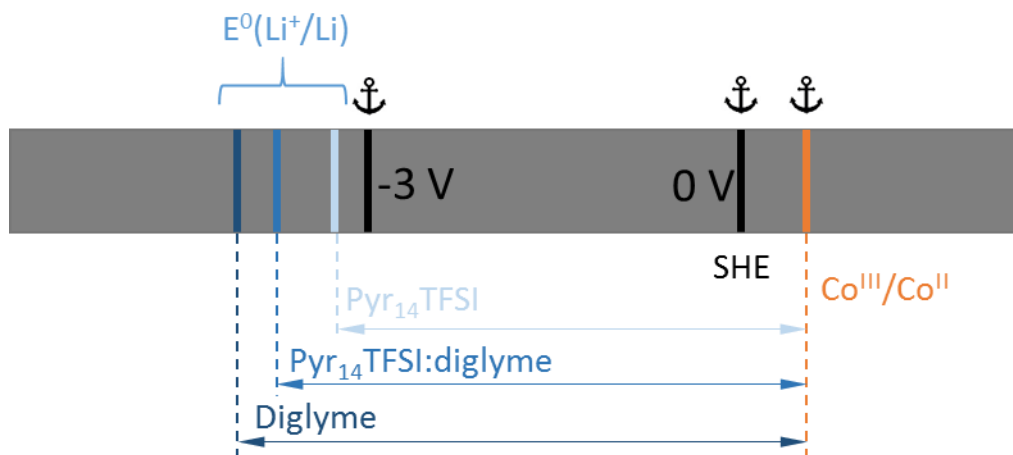


Figure S3. Schematic visualization of Li⁺/Li potential downshift with addition of Pyr₁₄TFSI in diglyme.

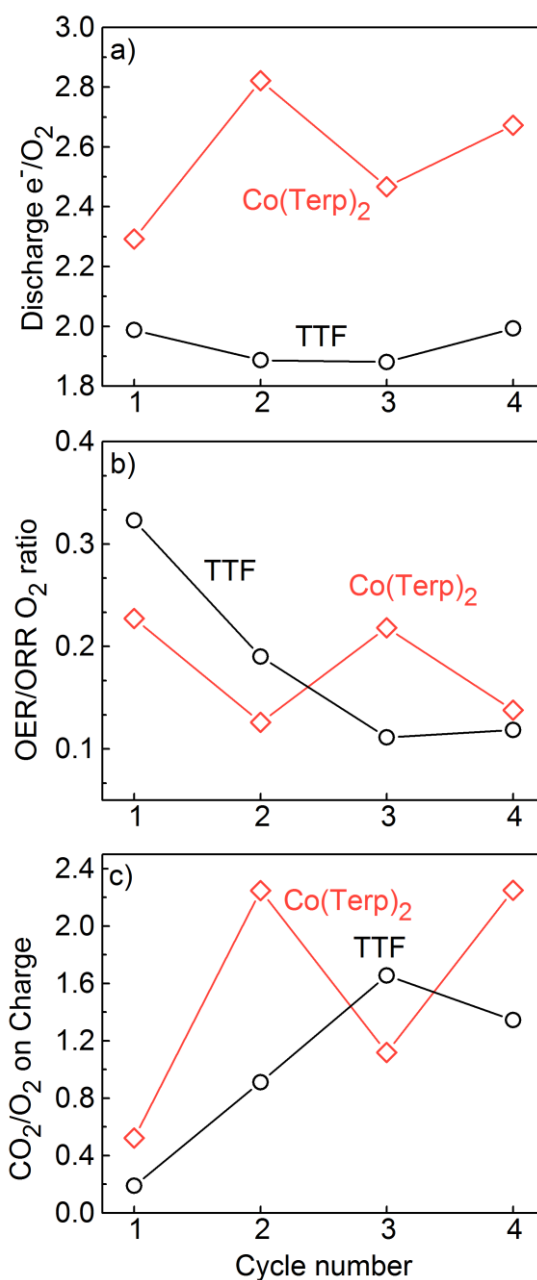


Figure S4. Summary of DEMS cycling at 200 mA·g⁻¹_{CNT} of Li-O₂ cells in 1 M LiTFSI in diglyme in presence of 50 mM Co(Terp)₂ and TTF. Cells discharge are limited to 1000 mAh·g⁻¹_{CNT}. Charging voltages are limited to 4.5 V_{Li}. (a) Number of electrons per O₂ on discharge. (b) Ratio of O₂ evolved on charge to O₂ consumed on discharge. (c) Ratios of CO₂ to O₂ evolved on charge as a function of cycle number. For these calculations, cumulative values of species were obtained by integration of the rate curves shown in Figures 3 and 4 of the main manuscript.

References:

- 1 Electrochemical Methods: Fundamentals and Applications. Allen J. Bard and Larry R. Faulkner