On the Utilization of Cobalt Bis(terpyridine) Metal Complex as Soluble Redox Mediator in Li-O_2 Batteries

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ABSTRACT

Redox mediators hold significant promise in reducing the large overpotentials pervasive upon charging of lithium-oxygen (Li-O_2) cells. Cobalt bis(terpyridine) ($Co(Terp)_2$) was investigated as mediator of the Li-O_2 charging reaction using electrochemical, XRD and mass spectrometry measurements and benchmarked against tetrathiafulvalene (TTF). Significant reductions in reversible potential versus Li^+/Li are measured for $Co(Terp)_2$ and TTF from diglyme to Pyr_{14}TFSI:diglyme to Pyr_{14}TFSI, attributable to upward shift in the Li^+/Li electrode, due to weakening Li^+ solvation in this solvent order. Lowering of the reversible potentials has noticeable gains on the kinetics of the charge reaction and greater reduction in charge overpotential are observed with the cobalt complex. However, using differential electrochemical mass spectrometry reveal that less than 25% of the O_2 consumed on discharge is recovered on charge in presence of $Co(Terp)_2$, while TTF enables up to 32% O_2 recovery on charge. CO_2 is a significant charging product at voltages greater than 4.0 V vs. Li^+/Li because of electrolyte decomposition. Further work is required in order to develop mediators with 100% of oxygen evolution efficiency, and the present finding of the possibility to tune the reversible redox potential of the mediator by changing the solvent will be very useful to achieve this formidable task.

1. INTRODUCTION

Li-O_2 or Li-air batteries have the potential to revolutionize energy storage with an estimated practical gravimetric energy density three times greater than current Li-Ion batteries.[1] These batteries store the electrochemical energy of the reaction between lithium and oxygen, typically forming Li_2O_2 ($2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$). The smaller molecular weight of gaseous oxygen compared to transition metal oxides culminate in greater theoretical gravimetric energy densities for Li-O_2 (3500 $Wh \cdot kg^{-1}_{Li2O2}$) compared to contemporary Li-Ion (544 $Wh \cdot kg^{-1}_{LiFePO4}$, 548 $Wh \cdot kg^{-1}_{LiMn2O4}$, and 1013 $Wh \cdot kg^{-1}_{LiCoO2}$ as reported by Lu et al.[2]).

A key bottleneck in the development of Li-O_2 batteries is the inefficiency of the charging process. The discharge product Li_2O_2 is nominally an electronic insulator (~10^{-12} $S \cdot cm^{-1}$)[3-4] and the oxygen evolution reaction from its oxidation has sluggish kinetics; therefore, high overpotentials are required to charge Li-O_2 cells. High charging voltages, in turn, induce several undesired reactions such as electrolyte degradation[5-8] and corrosion of carbon containing electrodes.[9-13] The combination of high charging voltage and parasitic degradation result in poor round trip efficiencies and limited cycling.

It has been shown that certain soluble redox agents (referred to as redox mediators), enhance the charging kinetics of Li-O_2 cells by mediating the electron transfer from Li_2O_2 to the electrode surface. The soluble redox agent (denoted M in reactions (1) and (2) below) is first oxidized on exposed carbon surfaces. Then, the oxidized form of the mediator chemically oxidizes Li_2O_2 evolving oxygen and releasing Li^+ cations into the electrolyte.[14-15]

$$M \rightarrow M^+ + e^- \quad (1)$$

$$2M^+ + Li_2O_2 \rightarrow 2M + O_2 + 2Li^+ \quad (2)$$

Since chemical oxidation of Li_2O_2 is initiated by the electro-oxidation of the redox agent, it is expected that the charging potential of the cell will be close to the reversible potential of the redox agent, $E^0(M^+/M)$. For the chemical reaction (2) to proceed, it is necessary that $E^0(M^+/M)$ be greater than the reversible potential of ($2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$), i.e 2.96 V_{Li}.

Several redox mediators have been demonstrated such as TTF,[15] TEMPO,[16] transition metal phthalocyanines,[17] iodine,[18-27] and tris[4-(diethylamino)phenyl]amine[28] with varying degrees of efficiency on enhancing the kinetics of the charge reaction. The requirements for efficient redox mediators are: i) fast and reversible electron transfer kinetics, ii) fast reaction with Li_2O_2 to evolve oxygen, iii) absence of degradation reactions, and iv) formal potential $E^{0'}(M^+/M)$ higher than 2.96 $V_{Li,}$ but not too high so as to afford low charging potentials (see the discussion below). The conditions in which Li-O_2 batteries operate (high voltages and presence of oxygen and reactive reaction intermediates such as superoxide) make it difficult to find redox reagents with long term stability (absence of degradation reaction). In addition, enhancing the rate of reaction of Li_2O_2 with the redox agent (reaction 2) is complicated by poor understanding of the reaction mechanism. Although, to first order, this reaction rate is expected to increase with increasing $E^{0'}$of the redox agent, since the driving force for the electron transfer reaction between the redox agent and Li_2O_2 (reaction 2) will increase. On the other hand, if the redox potential of the redox agent is too high, charging of the Li-O_2 cell will require high voltages, where significant electrolyte breakdown takes place. Comparison of the effectiveness of different mediators is hindered by the different conditions (electrolyte, oxygen electrode structure, mediator concentration) under which each literature experiments are carried.

In this work, we compare under similar experimental conditions the cobalt bis(terpyridine) ($Co(Terp)_2$) complex and the well-known tetrathiafulvalene (TTF)[15] as redox mediators in Li-O_2

cells using electrochemical characterization, X-ray diffraction (XRD) and differential electrochemical mass spectrometry (DEMS) measurements. $Co(Terp)_2$ was selected because, as other metal complexes, it undergoes fast and reversible electron transfer reaction. Having cobalt as the metal center is suitable as the Co^{II} to Co^{III} process is located in a potential window where the mediated oxidation of Li_2O_2 is thermodynamically favorable, ie. $E^{0'}(Co^{II}/Co^{III})$ in $Co(Terp)_2$ is higher than 2.96 V_{Li}. Cobalt complexes are known to undergo changes in their coordination sphere, between octahedral and tetrahedral geometries, during electron transfer reactions.[29] Therefore, a tridentate ligand such as bis(terpyridine) was chosen in order to strengthen the metal-ligand interaction and to minimize possible side-reactions such as de-complexation and formation of cobalt oxide. Herein, we show that the redox potential of metal complexes can be easily tuned by changing the solvent. This effect is related to the shift in potential of the lithium counter electrode,[30] and therefore, applicable to most mediators, including TTF. By carefully changing the solvent composition, the onset of the charging reaction of Li-O_2 cells can be decreased to ca. 3.2 V_{Li}. However, some shortcomings of both $Co(Terp)_2$ and TTF were elucidated using DEMS as discussed in detail below.

2. EXPERIMENTAL

2.1 Reagents

Cobalt (II) bis(terpyridine) bis(trifluoromethane)sulfonylimide was synthesized according to the literature.[31] An aqueous solution of cobalt (II) chloride ($CoCl_2$, Puriss ≥ 98.5 %, Fluka) was added drop wise to solution of 2,2':6',2"-terpyridine (Terp, 98 %, Sigma-Aldrich) in the molar ratio 1:2. This produced a yellow solution. Excess lithium bis(trifluoromethane)sulfonylimide (LiTFSI, 99.95 %, Sigma-Aldrich) in water was then added, causing a red/brown product to precipitate out of solution. The product was then washed with water and dried overnight under

vacuum at 80 ˚C before being stored in a dry glove box. Commercially available tetrathiafulvalene (97%) was purchased from Sigma-Aldrich and used after drying at 70 ˚C under vacuum in a Buchi B585 glass oven.

2.2 Electrolytes solutions

LiTFSI used in the preparation of electrolyte solutions was dried under vacuum at 120 ˚C for 48 h. The ionic liquid pyrrolidinium bis(trifluoromethane)sulfonylimide ($Pyr_{14}TFSI$, 99.5%, IoLiTec) was dried under vacuum at 120 ˚C for 48 h. Diethylene glycol dimethyl ether (diglyme, anhydrous 99.5 %, Sigma-Aldrich) was dried using molecular sieves (3 Å, beads, 4-8 mesh, Sigma-Aldrich). Electrolyte solutions of 1 M LiTFSI in diglyme, 1 M LiTFSI in $Pyr_{14}TFSI$:diglyme = 1:1 (volume ratio), and 0.1 M LiTFSI in $Pyr_{14}TFSI$ were prepared in an argon-filled glove box (H_2O < 0.1 ppm and O_2 <0.1 ppm).

2.3 Cyclic voltammetry

Cyclic voltammetry (CV) experiments were carried out in a two electrode split cell. Lithium metal (30 mm diameter, 150 μm thick, RockWood Lithium Inc.) was used as a counter and reference electrode and was housed in the negative electrode compartment of the cell. In all cases the electrolyte in the negative electrode compartment did not contain either of the mediators $Co^{II}(Terp)_2$ or TTF. A 3 mm diameter glassy carbon electrode was used as the working electrode and was housed in the positive electrode compartment of the cell with an electrolyte consisting of LiTFSI in varying concentrations depending on the solvent and 2 mM $Co^{II}(Terp)_2$ or TTF. CVs were recorded under an Ar atmosphere at 20 $mV \cdot s^{-1}$ from 2 to 4 V_{Li}.

2.4 Li-O_2 cell testing

Electrolytes with 50 mM of a redox mediator ($Co^{II}(Terp)_2$ or TTF) dissolved in 1 M LiTFSI/diglyme or 1 M LiTFSI/$Pyr_{14}TFSI$:diglyme were prepared for the purpose of Li-O_2 cell

testing. Electrochemical cells consisted a "2-compartment cell"[32] of the following stack: lithium foil (15 mm diameter, 150 μm thick, RockWood Lithium Inc.), battery membrane separator (18 mm diameter, C480, Celgard) wetted with 50 μL 1 M LiTFSI/diglyme, a Lithium-Ion Conducting Glass-Ceramic electrolyte (19 mm diameter, 150 μm thick, LICGC™, Ohara Corp.), Whatman GF/A separator wetted with 200 μL of electrolyte (1 M LiTFSI/diglyme or 1 M LiTFSI/Pyr_{14}TFSI:diglyme with or without 50 mM of redox mediator), free standing vertically aligned carbon nanotubes (CNT, 1 cm^2 square geometry, 0.4 to 1.2 mg),[33] and stainless steel current collector. The Ohara glass electrolyte in the "2-compartment cell" configuration suppresses the crossover of redox mediator from cathode to anode which may result in an undesired internal electrochemical shuttling.[34] All cell assembly and pressurization with O_2 was carried within an argon-filled glovebox. All galvanostatic discharge and charge of thus assembled cells was performed at a rate of 200 $mA \cdot g^{-1}_{CNT}$ using a research-grade multi-channel potentiostat (VMP3, BioLogic Inc.)

2.5 Differential electrochemical mass spectroscopy (DEMS)

A custom-made DEMS based on a configuration reported by McCloskey et al.[7] and Harding et al.[35-36] was used for measurement of oxygen consumption during discharge and gas evolution on charge at 200 $mA \cdot g^{-1}_{CNT}$. Oxygen consumption during galvanostatic discharge was quantified via pressure drop monitoring at two second intervals. O_2, CO, CO_2, and H_2O evolution during charge was quantified at 15-minute intervals using a mass spectrometer coupled with pressure monitoring. Details of DEMS and cell technical construction are available online.[35] Li-O_2 cells for DEMS underwent the following electrochemical sequence: 12-hour rest period, 5-hour discharge to 1000 $mAh \cdot g^{-1}_{CNT}$, 10-hours rest, and charging to 4.5 V_{Li} cut-off.

3. RESULTS AND DISCUSSION

Results of cyclic voltammetry investigation of $Co(Terp)_2$ and TTF on a glassy carbon electrode in 3 different solvents: diglyme, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$), and $Pyr_{14}TFSI$:diglyme = 1:1 (volume ratio) are shown in Figure 1. The peak cathodic and anodic currents decrease in the order diglyme (η = 2.96 mPa·s) > $Pyr_{14}TFSI$:diglyme (η = 20.7 mPa·s) > $Pyr_{14}TFSI$ (η = 79 mPa·s) both for $Co(Terp)_2$ (Figure 1a) and TTF (Figure 1b). This result is the immediate consequence of increasing solvent viscosity, η: peak current during CV is approximately proportional to $\eta^{-1/2}$ under the reasonable reversibility of the analytes herein (Figure S1).

More interestingly, the solvent produces a marked effect on the measured potentials of the Co^{III}/Co^{II}, Co^{II}/Co^{I}, TTF^{I}/TTF^{0}, and TTF^{II}/TTF^{I} as summarized in Figure 1c. Anodic to cathodic peaks separation for $Co(Terp)_2$ and TTF were found to vary between 66 and 80 mV (Table S1). These values are reasonably close to the 59 mV expected for a reversible one electron processes.[37] Variation in the formal potential could be due to (i) a shift in the absolute potential of the redox agent or/and (ii) a shift in the absolute potential of the Li^{+}/Li reference electrode. Changing the solvent produces similar shifts in the redox process of $Co(terp)_2$ and TTF (Figure 1c), thus suggesting that the main cause of the shift is a variation of the potential of the lithium reference electrode. Indeed, very similar shifts in potential with solvents were observed in the voltammograms of the ferrocene/ferrocenium couple (Figure S2), which is often used as reference to compare between different solvents since ferrocene-based couples are known to interact only weakly with solvents.[30, 38] On the contrary, there is a strong interaction between the solvent and lithium cations, which affects the activity of lithium cations, and with this, the potential of the Li^{+}/Li reference electrode. Solvent-induced shifts in the potential of the lithium electrode versus the standard hydrogen electrode have been reported and are correlated to the

strength of lithium solvation.[39] Solvation of lithium cations in diglyme containing electrolytes are stronger than in the ionic liquid $Pyr_{14}TFSI$; consequently, $E^{0'}(Li^+/Li)$ is lower in diglyme containing electrolytes, and as a result, the measured redox potential of $Co(Terp)_2$ and TTF measured vs. Li^+/Li decreases with the addition of more $Pyr_{14}TFSI$ (see Figure S3 for schematic description).

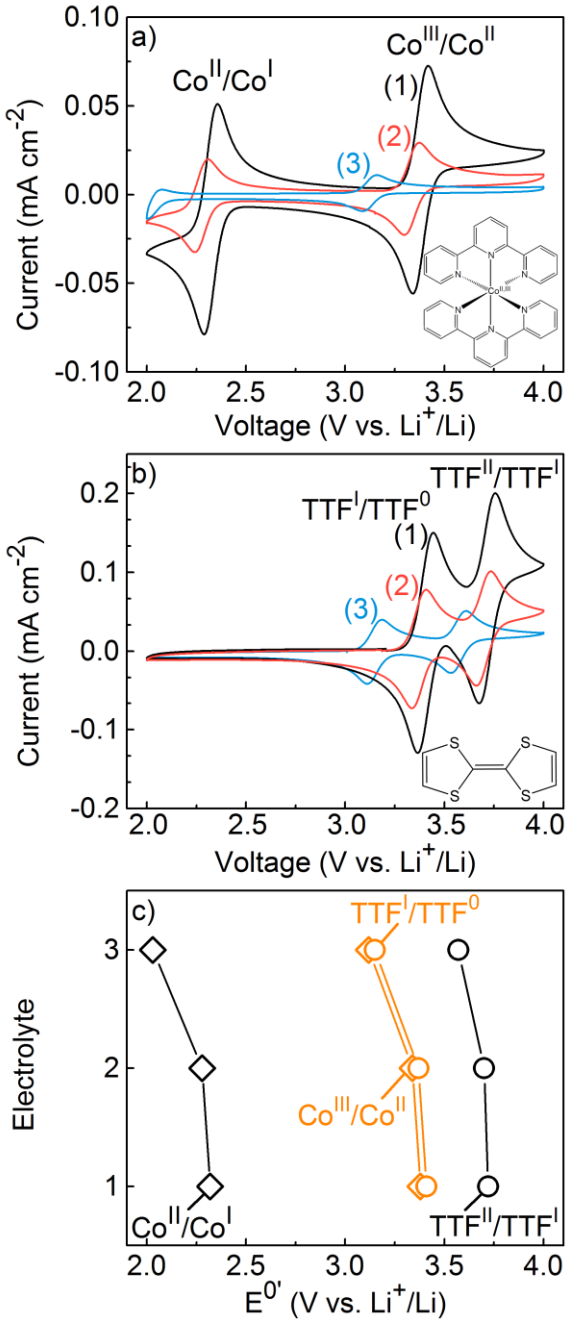

Figure 1. Voltammograms at 20 mV·s^{-1} using a glassy carbon electrode of 2 mM $Co^{II}(Terp)_2$ (a) and TTF (b): (1) 1 M LiTFSI in diglyme, (2) 1 M LiTFSI in Pyr_{14}TFSI:diglyme = 1:1 (volume ratio), and (3) 0.1 M LiTFSI in Pyr_{14}TFSI. (c) Reversible redox potential of mediators in respective electrolytes annotated with redox couples. Numbers on y-axis correspond to electrolyte formulations listed for (a) and (b).

In order to mediate the oxidation of Li_2O_2, the formal potential of the metal complex *vs.* Li^+/Li should be higher than the reversible potential $E^0(O_2/Li_2O_2)$ = 2.96 V vs. Li^+/Li.[14] The range of potential of interest for $Co(Terp)_2$ and TTF are highlighted in orange in Figure 1c. The formal potential of Co^{III}/Co^{II} in $Co(Terp)_2$ were found to be 3.38, 3.34, and 3.12 V_{Li} in diglyme, Pyr_{14}TFSI:diglyme, and Pyr_{14}TFSI, respectively. Similarly, the formal potential of TTF^I/TTF^0 were found to be 3.41, 3.37, and 3.15 V_{Li} in the same order of electrolyte solvents. Preliminary studies in unary Pyr_{14}TFSI electrolyte showed only a minor effect of $Co(Terp)_2$ on the charge reaction likely because the potential (3.15 V_{Li}) was too close to the thermodynamic potential of Li_2O_2 oxidation (2.96 V_{Li}), and therefore, the driving force for the mediated Li_2O_2 oxidation (reaction 2) was small. Consequently, the following studies were restricted to diglyme and Pyr_{14}TFSI:diglyme.

Unlike TTF,[15, 40-41] no prior report treats $Co(Terp)_2$ as a redox mediator in Li-O_2 batteries; therefore, we first probed the efficiency gain in Pyr_{14}TFSI:diglyme (with an intermediate formal potential of $Co(Terp)_2$ of 3.34 V_{Li}). Carpets of carbon nanotubes (CNT) served as the positive electrode and the first galvanostatic cycle at 200 $mA \cdot g^{-1}_{CNT}$ is reported in Figure 2a. No major effect of $Co(Terp)_2$ was resolved on the discharge to 2.0 V_{Li}. Although, the capacity of the CNT electrode in presence of $Co(Terp)_2$ appeared smaller than in its absence, capacity variations are common in different Li-O_2 cells. On charge, the average cell voltage with $Co(Terp)_2$ was ~3.8 V_{Li} versus ~4.1 V_{Li} without the mediator. This result indicates $Co(Terp)_2$ may have been enhancing cell charging per its intended use as a redox mediator.

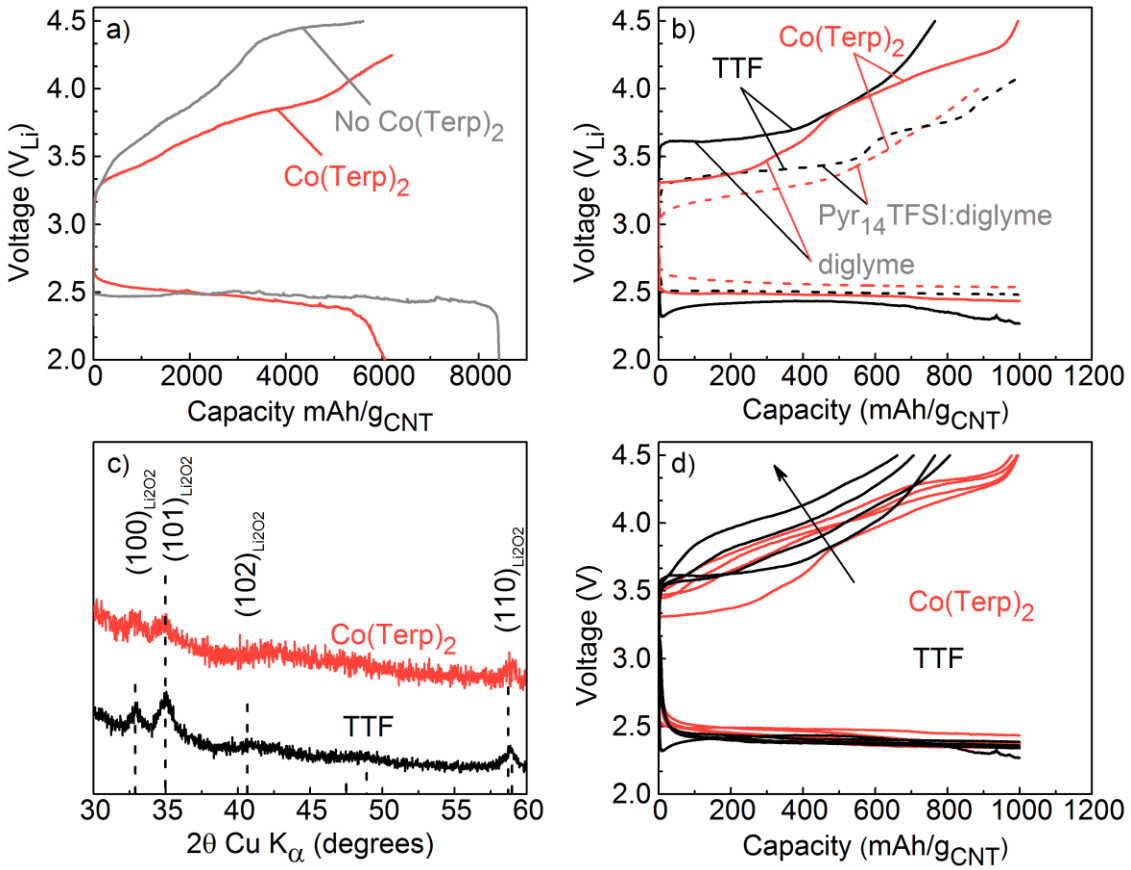

Figure 2. (a) Galvanostatic discharge (to 2.0 V_{Li}) and charge at 200 $mA{\cdot}g^{-1}_{CNT}$ of Li-O_2 cells in 1 M LiTFSI in Pyr_{14}TFSI:diglyme (1:1 volume ratio), with and without 50 mM $Co(Terp)_2$. (b) First cycle galvanostatic discharge and charge at 200 $mA{\cdot}g^{-1}_{CNT}$ of Li-O_2 cells using 1 M LiTFSI in diglyme (solid line) and Pyr_{14}TFSI:diglyme (dashed line) in presence of 50 mM $Co(Terp)_2$ or TTF. Capacities were limited to 1000 $mAh{\cdot}g^{-1}_{CNT}$. (c) XRD patterns of CNT electrodes after discharge in 1 M LiTFSI in diglyme with 50 mM $Co(Terp)_2$ and TTF. (d) Electrochemical discharge and charge during cycling under DEMS at 200 $mA{\cdot}g^{-1}_{CNT}$ of Li-O_2 cells in 1 M LiTFSI in diglyme in presence of 50 mM TTF or $Co(Terp)_2$. Cells discharge capacities were limited to 1000 $mAh{\cdot}g^{-1}_{CNT}$ and charging was limited to a 4.5 V_{Li} voltage cut-off. Arrow indicates the general direction of charge curves with increasing cycles.

We proceed to compare the electrochemical behavior at 200 $mA \cdot g^{-1}_{CNT}$ of $Co(Terp)_2$ and TTF in diglyme and $Pyr_{14}TFSI$:diglyme (Figure 2b). Once again, little influence of the mediators was observed on discharge. Also, no robust trend can be claimed regarding the discharge voltage profile from diglyme to $Pyr_{14}TFSI$:diglyme; the apparent higher discharge voltage with $Pyr_{14}TFSI$:diglyme compared to diglyme is likely within experimental error. All previous studies of redox mediators for the Li_2O_2 oxidation such as TTF,[15] TEMPO,[16] LiI,[23, 25-26] TDPA[28] similarly report negligible influence of the mediator on the discharge voltage. On charge, overpotentials seen when using $Co(Terp)_2$ appeared to be consistently less than those of TTF in each solvent. This is in line with $E^{0'}(Co^{III}/Co^{II})$ being lower than $E^{0'}(TTF^{I}/TTF^{0})$ as seen in (Figure 1c). We also note that charging in the presence of the mediators also displayed lower potentials in $Pyr_{14}TFSI$:diglyme than in diglyme, which is likely associated with lower values of $E^{0'}(Co^{III}/Co^{II})$ and $E^{0'}(TTF^{I}/TTF^{0})$ in the former solvent. Noteworthy, the reduction in charging potential within the cell (Figure 2b) are significantly greater than the variations in $E^{0'}$ (Figure 1c). This observation is likely a result of the effects of the formal potential on the electrochemical step (1) convoluted with its effect on the chemical step (2). Additionally, the higher of viscosity $Pyr_{14}TFSI$:diglyme compared to diglyme may favor proximity of the oxidized mediator produced in reaction (1) to the Li_2O_2 surface for reaction (2). This phenomenon will be the subject of further studies.

It is paramount to understand the actual chemistry associated with these electrochemical processes in Li-O_2 cells. Therefore, XRD and DEMS were performed to elucidate product formation and gas consumption and evolution. Although better overall performance seems to occur in cells using $Pyr_{14}TFSI$:diglyme, we elected to investigate the chemical processes occurring in the presence of a redox mediator using the unary ether electrolyte commonly

employed in Li-O_2 reports. Figure 2c shows the XRD of CNT electrodes discharged to a low cut-off of 2.0 V_{Li}. Formation of Li_2O_2 during discharge in the presence of TTF has been reported by Raman spectroscopy[15, 41] and electrochemical quartz crystal microbalance[40]. Similar to TTF, we report formation of Li_2O_2 as the discharge product in the presence of $Co(Terp)_2$. This initial result suggests the presence of $Co(Terp)_2$ allows the main discharge reaction ($2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$) to proceed. DEMS results discussed below provide more details of the O_2 consumption in presence of these mediators.

In order to probe the chemical efficacy of $Co(Terp)_2$ and benchmark it against TTF, 2-compartment cells[32] were cycled at 200 $mA \cdot g^{-1}_{CNT}$ for four cycles under DEMS using a 1 M LiTFSI diglyme electrolyte. Results of the cycling are summarized in Figure 2d. Similar to the observations on the first cycles mentioned above, the discharge profiles of $Co(Terp)_2$ during cycling (Figure 2d) are close to that of TTF and match the ~2.5 V_{Li} plateau characteristic of unmediated CNTs at 200 $mA \cdot g^{-1}_{CNT}$ (see Figure 2a). Electrochemical differences between $Co(Terp)_2$ and TTF, without regard to DEMS, were apparent mostly on charge where $Co(Terp)_2$ maintained lower charging voltages compared to TTF throughout cycling.

Probing of the O_2 consumption and evolution revealed considerable differences between the two mediators investigated. Figure 3 summarizes the measurements of O_2 consumption during discharge in presence of $Co(Terp)_2$ (panel a) and TTF (panel b) by monitoring the pressure decay of the O_2 atmosphere within the cell. Since formation of desired Li_2O_2 is a 2 e^-/O_2 reaction ($2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$), a close match between O_2 consumption and half of the faradaic current is expected. In the first cycle, less O_2 was consumed in the $Co(Terp)_2$ cell than expected from the half-current line (Figure 3a-1), especially at the beginning of discharge. Similar under-stoichiometric consumption of O_2 in cells with $Co(Terp)_2$ was noted for the subsequent three

cycles (Figure 3a-2,3,4), where the number of electron per O_2 was found to be between 2.3 and 2.8 e^-/O_2 (Figure S4a). On the other hand, TTF displays a good match between the half-current and O_2 consumption on the first cycle (Figure 3b-1). A relatively small over-consumption of O_2 was observed at the beginning of discharge on the second through fourth cycles of TTF (Figure 3b-2,3,4) which might warrant further investigation (e^-/O_2 values between 1.9 and 2 recorded in Figure S4a). The excess current as compared to O_2 consumed occurring during discharge with the addition of $Co^{II}(Terp)_2$ can be attributed to the reduction of Co^{II} to Co^{I} in the 50 mM $Co(Terp)_2$ used. Electrolysis of all the $Co^{II}(Terp)_2$ present in the working electrode compartment would contribute a capacity of 307 $mAh \cdot g^{-1}_{CNT}$ which would account for ~1.54 hours of discharge at 200 $mA \cdot g^{-1}_{CNT}$. This excess of current could increase the overall capacity of the battery, which would act as a combined Li-O_2 and redox battery.

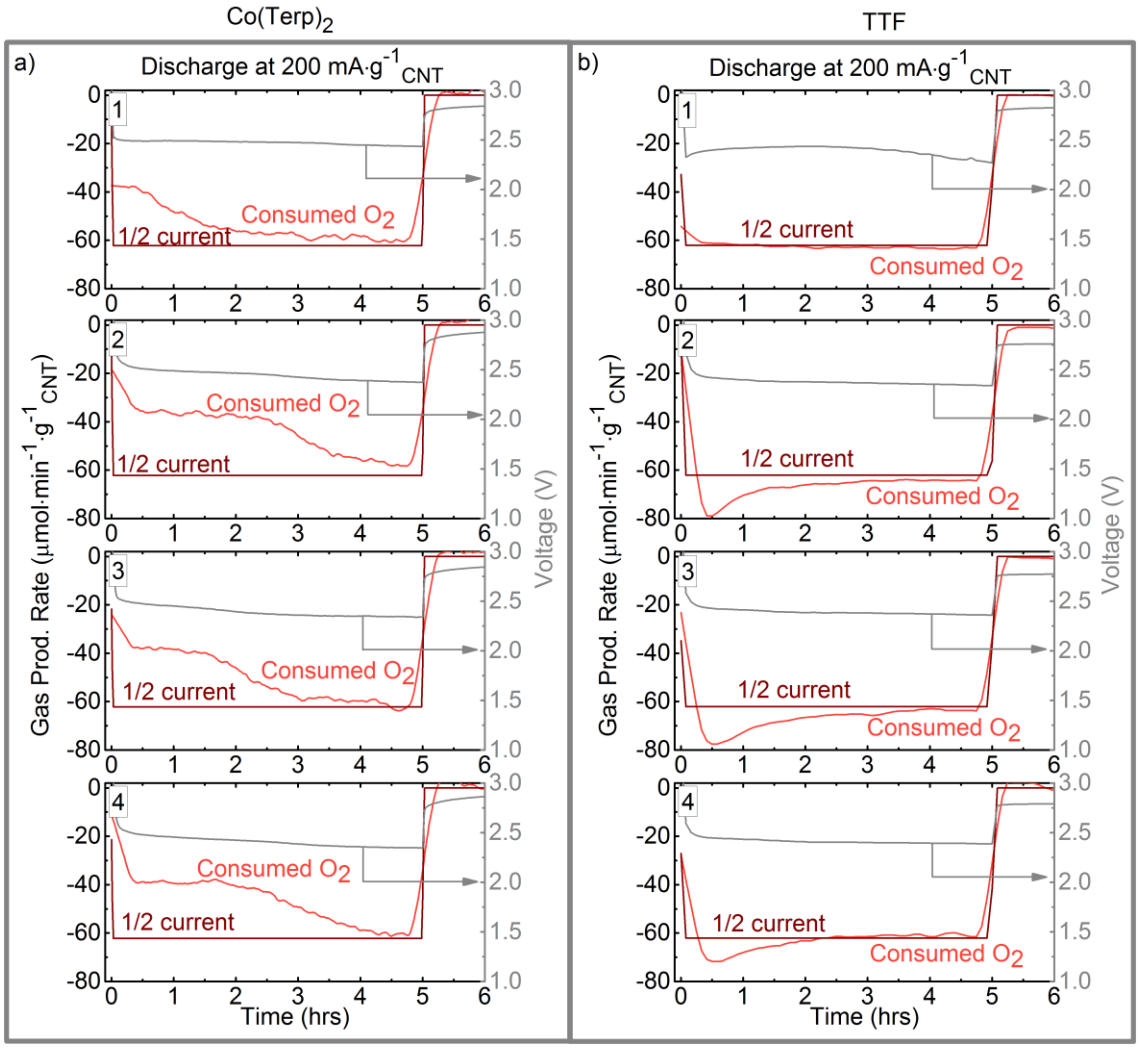

Figure 3. Galvanostatic discharge at 200 mA·g^{-1}_{CNT} of Li-O_2 cells in 1 M LiTFSI in diglyme in presence of 50 mM $Co(Terp)_2$ (a) and TTF (b). Faradaic current is aligned to the production rate axis according to the 2 e^-/O_2 expected reaction. Cell discharges were limited to 1000 mAh·g^{-1}_{CNT}. Panel numbering corresponds to cycle number for $Co(Terp)_2$ and TTF separately. Discharge voltage profiles are the same shown in Figure 2d.

We report the DEMS monitoring of gases evolved during galvanostatic charging, at 200 mA·$g^{-1}_{CNT,}$ of Li-O_2 cells in the presence of $Co(Terp)_2$ and contrast this with TTF in Figure 4. First, we note that no CO or H_2O was evident in DEMS spectra for all four cycles of the two mediators investigated. O_2 evolution was observed in the early stages of charging at potentials as low as

~3.4 V_{Li} for $Co(Terp)_2$ and ~3.6 V_{Li} for TTF. These low onset voltages of O_2 evolution from Li_2O_2 oxidation show that these redox mediators can effectively reduce the overpotential required for Li_2O_2 oxidation in Li-O_2 batteries. Noticeably, when increasing voltages to ~4.0 V_{Li} and greater, CO_2 was found as the predominant gas evolved in presence of $Co(Terp)_2$ as well as TTF which can be assigned to decomposition of ether solvents at those potentials.[42-43] This observation suggests that "galvanostatic charging followed by potentiostatic holding at voltages lower than 4.0 V_{Li}" of Li-O_2 cells with these redox mediators would be effective to oxidize Li_2O_2 with reduced potentials without triggering parasitic decomposition of electrolyte to CO_2. For both mediators, the amount of O_2 measured on charge was lower than that consumed on discharge. The amount of O_2 evolved on charge in the presence of $Co(Terp)_2$ was between 10% and 23% of the O_2 consumed in the preceding discharge, OER/ORR, while in presence of TTF values between 10% and 32% were measured (Figure S4b). This OER/ORR was found to decay with cycle number, with TTF outperforming $Co(Terp)_2$ and showed better round-trip O_2 recovery. Furthermore, more CO_2 (at greater than ~4.0 V_{Li}) was measured relative to O_2 evolved in presence of $Co(Terp)_2$ compared to TTF in Figure 4. Figure S4c confirms this assessment with a generally larger CO_2/O_2 ratio in cells with $Co(Terp)_2$ versus TTF. In the case of TTF in Figure 4b, O_2 accompanies CO_2 evolution above 4.0 V_{Li}, while O_2 and CO_2 evolutions do not overlap in presence of $Co(Terp)_2$ (Figure 4a).

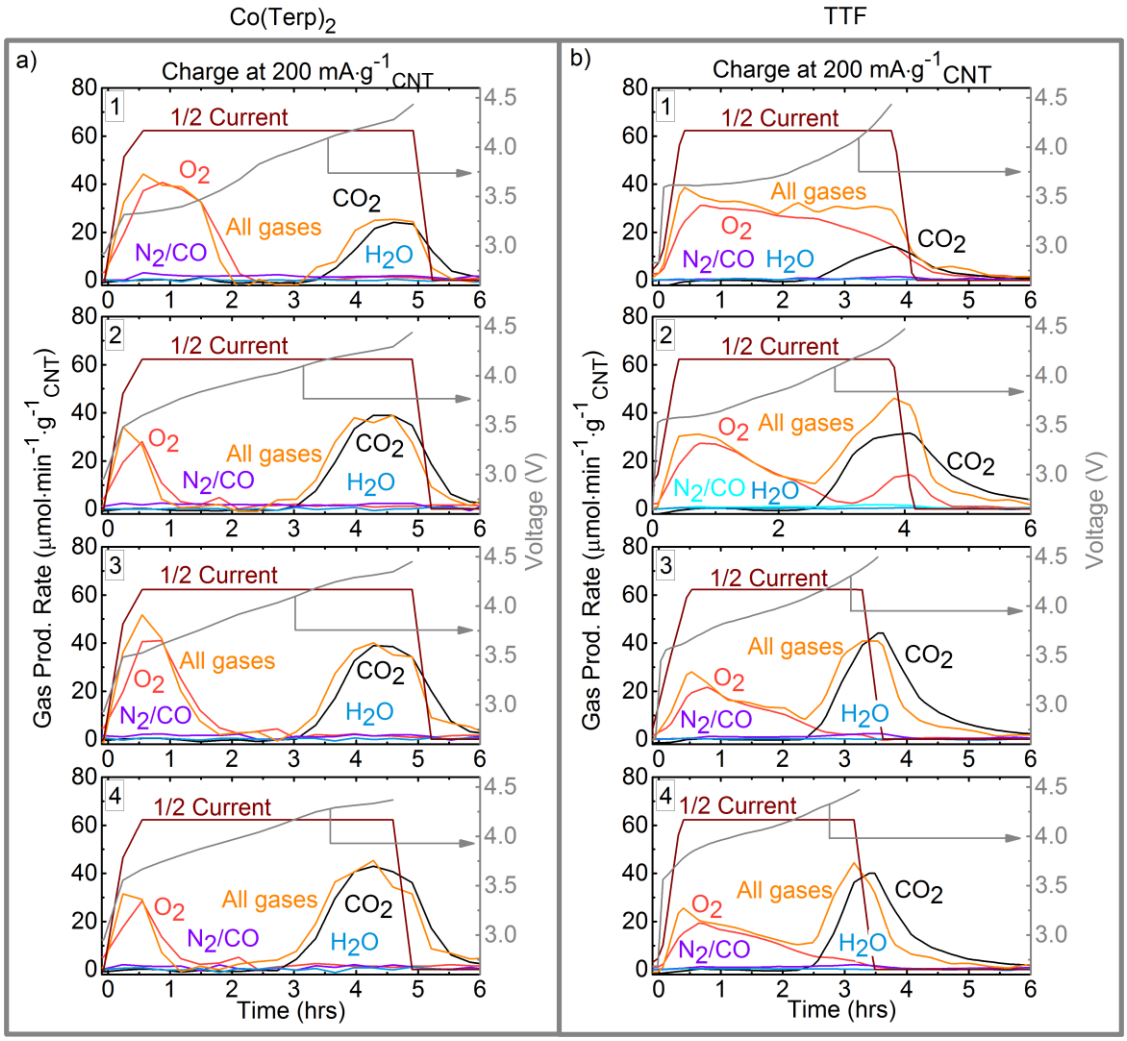

Figure 4. Galvanostatic charging at 200 mA·g$^{-1}_{CNT}$ of Li-O_2 cells in 1 M LiTFSI in diglyme in presence of 50 mM $Co(Terp)_2$ (a) and TTF (b). Faradaic current is aligned to the production rate axis according to the 2 e^-/O_2 expected reaction. Charging voltages were limited to 4.5 V_{Li}. Panel numbering correspond to cycle number for $Co(Terp)_2$ and TTF separately. Voltage profiles are the same shown in Figure 2d.

4. CONCLUSIONS

The effect of cobalt bis(terpyridine) on the electrochemical performance of Li-O_2 cells was characterized by cyclic voltammetry and galvanostatic cycling, XRD and DEMS and benchmarked against TTF. It has been found that the redox potential of redox mediators such as

Co^{III}/Co^{II} and TTF^{I}/TTF^{0} redox couple measured vs. Li^{+}/Li decreases from unary diglyme to $Pyr_{14}TFSI$:diglyme to unary $Pyr_{14}TFSI$ due to weakening of Li^{+} solvation causing an upward shift of the Li^{+}/Li electrode potential. The change in redox potential is reflected in the value of the charging potential of Li-O_2 batteries, with lower charging voltages measured in $Pyr_{14}TFSI$:diglyme compared to diglyme in presence of either of the two mediators. The effect of $Co(Terp)_2$ has been compared to that of TTF, a well-known mediator of the Li_2O_2 oxidation in Li-O_2 cells.[14] Upon charging, although galvanic data showed faster charging kinetics with $Co(Terp)_2$, differential electrochemical mass spectrometry measurements reveal only partial O_2 recovery and significant CO_2 evolution above 4.0 V_{Li}. Similarly, partial O_2 recovery and CO_2 evolution occurred with TTF; however, the efficacy of TTF was found superior to the cobalt complex. In summary, the present detailed investigation of $Co(Terp)_2$ indicates it is not a suitable candidate for utilization as metal complex redox mediator for Li-O_2 batteries charging. Future efforts could be centered on the design of the ligand field of the metal complex in order to further understand the effect of formal potential on the two-step reaction involved in redox mediation and potentially discover optimal mediators. Nonetheless, the systematic methodology here applied and the possibility of tuning the redox potential of a redox mediator by choice of electrolyte solvent are important tools and approaches for future research in the field.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.xxxxxxx

Anodic peak vs. viscosity (Figure S1); Derivation of dependence of peak current and viscosity; Values of peak separations during cyclic voltammetry of $Co(Terp)_2$ and TTF (Table S1); Voltammograms of ferrocene in various solvents (Figure S2); summary of e^-/O_2, O_2 recovery, and CO_2 evolution measured by DEMS (Figure S4).

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The authors declare no competing financial interest.

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