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

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S *Supporting Information*

ABSTRACT: Owing to its high theoretical specific energy, the Li-oxygen battery is one of the fundamentally most promising energy storage systems, but also one of the most challenging. Poor rechargeability, involving the oxidation of insoluble and insulating lithium peroxide (Li_2O_2), has remained the "Achilles' heel" of this electrochemical energy storage system. We report here on a new redox mediator tris[4-(diethylamino)phenyl]amine (TDPA), that—at 3.1 V— exhibits the lowest and closest potential redox couple compared to the equilibrium voltage of the Li-oxygen cell of

those reported to date, with a second couple also at a low potential of 3.5 V. We show it is a soluble "catalyst" capable of lowering the Li_2O_2 charging potential by >0.8 V without requiring direct electrical contact of the peroxide and that it also facilitates high discharge capacities. Its chemical and electrochemical stability, fast diffusion kinetics, and two dynamic redox potentials represent a significant advance in oxygen-evolution catalysis. It enables Li−O$_2$ cells that can be recharged more than 100 cycles with average round-trip efficiencies >80%, opening a new avenue for practical Li-oxygen batteries.
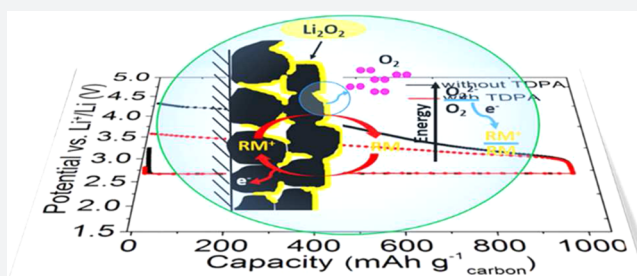
INTRODUCTION

Among all the rechargeable electrochemical energy storage systems, nonaqueous Li−O$_2$ batteries have generated unprecedented attention due to their high specific energy, which if accessed, could revolutionize electrical transportation.[1,2] To tap into the true potential of Li-O$_2$ batteries, however, there are some major scientific and technical challenges to overcome.[3,4] A significant scientific setback lies in the oxygen evolution or charge reaction (OER),[3−5] which would ideally result in the oxidation of the discharge product, Li_2O_2, at the positive electrode with quantitative O$_2$ evolution for reversible cell operation. Furthermore, a near equilibrium (2.96 V vs Li/Li$^+$) discharge and charge reaction is a prerequisite for an energy-efficient system. In practice, discharge is associated with a small ∼0.3 V overpotential, whereas charge involves a high overpotential of 1−1.5 V for the oxidation of solid and electrically insulating Li_2O_2 and side-products formed during discharge.[6,7] Very poor overall round trip energy efficiency results. The large overpotential on charge promotes further electrolyte decomposition[8] and oxidatively corrodes the active oxygen positive electrode (or "cathode") interface.[9] This deposits highly insulating Li$_2$CO$_3$ at the oxygen electrode interface and on Li_2O_2, which drives the charge overpotential even higher and severely affects the reversible and sustainable cell operation.[9]

Minimizing the charge polarization is a vital step toward realizing a practical Li-O$_2$ electrochemical storage device. The utilization of either coated or non-carbonaceous positive electrode supports[10−14] has been recently explored to try to overcome this problem, along with clever solid catalysts. The

fact that OER proceeds via a solid solution regime involving Li$_{2−x}$O$_2$[15] suggests that solution-based catalysis can play a critical role toward this goal. A soluble redox active additive is a catalyst which is electrochemically oxidized at the positive electrode interface and—in turn—chemically oxidizes the insoluble Li_2O_2. Using this approach, high recharging rates are possible, and the peroxide can be oxidized without direct contact with the oxygen electrode. The strategy has been pioneered with three such "redox mediator (RM)" systems that have been investigated in Li−O$_2$ cells for OER to date: tetrathiafulvalene (TTF) in dimethyl sulfoxide (DMSO) using a nanoporous gold electrode,[16] the I$_3^−$/I$_2$ redox couple in tetraethylene glycol dimethyl ether (TEGDME) using aligned nanotube "air" electrodes,[17] and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) with a carbon black-based oxygen electrode.[18] These seminal studies represent major steps forward in solving the problem of charging Li_2O_2 at low potentials, and a recent paper has importantly elucidated the complex concentration-dependent chemistry of the iodine mediator.[19] Our recent study on aprotic metal-O$_2$ batteries confirms previous views that redox mediators are, in fact, essential for the Li−O$_2$ cell.[20] Additionally, a bifunctional approach has been used to combine catalysts, i.e., RMs, for ORR and OER.[21]

Herein, we report that tris[4-(diethylaminophenyl]amine (TDPA) is a new, efficient soluble catalyst for Li_2O_2 oxidation. TDPA belongs to the triphenylamine class of molecules,[22] which have been utilized as redox shuttle additives for

overcharge protection in Li-ion batteries.[23] The average redox potential of these molecules varies between 3.8 and 4.5 V vs Li depending on the substituent. In TDPA, the electron-donating diethylamino group at the para position of the phenyl rings lowers an otherwise high redox potential to a value suitable for practical charge mediation in a Li−O$_2$ cell. The presence of the diethylamino groups bestows steric stability upon the molecule to prevent the dimerization of the radical cation that occurs for triphenylamine.[22] Moreover, the tertiary amine groups allow for *two* redox couples that can act in concert to oxidize Li$_2$O$_2$ within the stability window (≤4.5 V) of the glyme-based electrolytes. The first couple lies at 3.1 V, which is desirably closer to the equilibrium potential than any other RM studied to date.[16−18] The principle is shown in Scheme 1, and the redox

Scheme 1. TDPA-Mediated Li$_2$O$_2$ Oxidation
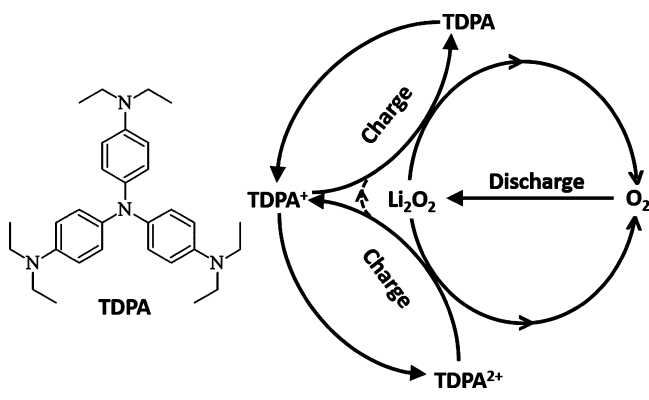
couples are depicted in Figure 1. As we report here, TDPA also exhibits excellent RM properties because of favorable O$_2$ solubility,[18] without any potential corrosion problems common to halides.[24] It thus represents a promising path forward in the quest for reversible Li−O$_2$ cell behavior.

■ RESULTS AND DISCUSSION

Redox Properties of TDPA. To prove the suitability of TDPA as a mediator for Li−O$_2$ cells, its redox properties were determined by cyclic voltammetry (CV) using 0.1 M LiTFSI + 5 mM TDPA in TEGDME as the electrolyte in a three electrode cell (see methods, SI). The reversibility of the TDPA redox couples was examined under both an Ar and O$_2$ atmosphere. The CV under Ar exhibits two reversible peaks corresponding to the redox couples TDPA/TDPA$^+$ (E_{p1}) and TDPA$^+$/TDPA^{2+} (E_{p2}) (Figure 1a). The reduction/oxidation peaks are similar, with cathodic (E_{pc}) to anodic peak (E_{pa}) current ratios of ∼1 for both couples, confirming the stability of the oxidized molecule. By averaging the cathodic and anodic peak potentials, a value of 3.1 and 3.5 V is obtained for the TDPA/TDPA$^+$ and TDPA$^+$/TDPA^{2+} couples, respectively. Thus, a Li−O$_2$ cell employing TDPA as a charge mediator is predicted to showcase a low OER potential, close to the equilibrium potential of the Li−O$_2$ cell (2.96 V). The corresponding redox potentials are shown schematically in Figure 1b. The reversibility of the electrochemical oxidation of TDPA in an oxygen-saturated electrolyte is also evident from the CV (Figure 1a). In the 2.5−4.25 V window (red dotted line) only the TDPA redox peaks appear, but between 2 and 4.25 V (solid red line), a broad oxygen reduction (ORR) peak is visible near 2.2 V (E_{pc0}). This is shifted down in the potentiodynamic sweep compared to the typical ORR potential
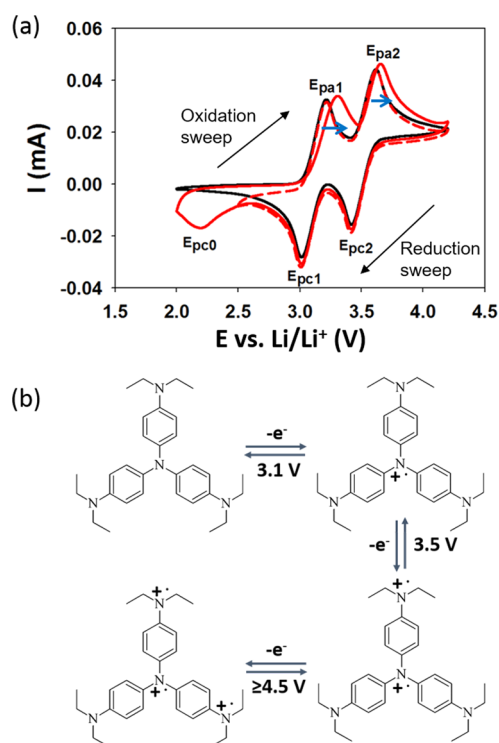

Figure 1. (a) Cyclic voltammetry plots recorded at a scan rate of 10 mV S^{-1} on a glassy carbon electrode for 0.1 M LiTFSI + 5 mM TDPA in TEGDME under argon (black) and oxygen (red) in 2−4.25 V window. The dashed red line is the CV curve under oxygen in 2.5−4.25 V window, without the ORR process. (b) The TDPA redox couples and the corresponding redox potentials.

of 2.7 V observed in a Li−O$_2$ cell under galvanostatic control.[25] The fact that the integrated anodic peak areas are very similar regardless of whether ORR occurred or not (red dashed vs red solid trace) implies that the direct unmediated oxidation of Li$_2$O$_2$ (Li$_2$O$_2$ → Li$^+$ + e$^-$ + 1/2 O$_2$) is insignificant. In other words, E_{pa1} and E_{pa2} correspond to the electrochemical oxidation of the RM (which in turn chemically oxidizes the peroxide), and this redox-mediated pathway is dominant. The reversibility and similarity of the CVs of TDPA under both Ar and in the presence of O$_2$ and reactive oxygen intermediates furthermore suggest that this RM is completely stable in a Li−O$_2$ cell. This is confirmed by NMR studies (see below).

Deposition of Li$_2$O$_2$ in the ORR sweep leads to a positive shift in the anodic peak potentials: 0.1 V for the TDPA/TDPA$^+$ couple and 0.05 V for the TDPA$^+$/TDPA^{2+} compared to the non-ORR profile (indicated by the arrows). The shifts are the result of ohmic resistance owing to the insulating peroxide. The cathodic peaks do not display any shift on the subsequent reduction, indicating the insulating peroxide is removed during the oxidation sweep. Because the second peak (E_{pa2}) is also shifted, it clearly shows that the first couple (E_{pa1}) does not completely oxidize the peroxide from the surface. We note that E_{pa1} at 3.1 V is the lowest redox couple compared to other Li−O$_2$ cell RMs reported to date,[16−18] and very close—while necessarily above—the thermodynamic equilibrium potential for oxidation of Li$_2$O$_2$ (E^0 = 2.96 V). Whereas the first redox couple should be sufficient for RM function, because of kinetic lag, we believe the second redox couple also plays an important role in completely oxidizing the peroxide. Under typical conditions where kinetic overpotentials occur—either owing

to high current density and/or impedance from peroxide deposits—the voltage is easily driven above equilibrium. We note that TTF, another very highly promising redox mediator, also shows two redox couples corresponding to oxidation to TTF$^+$ (at 3.6 V) and TTF^{2+} (at 3.8 V);[16] however, the higher voltage of both couples relative to E^0 probably results in the second not being invoked. Using an RM with two couples at lower voltage provides a suitable alternative and better energy efficiency compared to an RM with a higher voltage couple.

Diffusion Coefficient of TDPA. Linear sweep voltammetry experiments were performed with a rotating disk electrode at different rotational speeds (ω; Figure S1a) to obtain a diffusion coefficient for TDPA of 1.2×10^{-6} cm^2 s^{-1} determined from the plot of limiting current vs $\omega^{1/2}$ (Figure S1b). A similar value of 1.0×10^{-6} cm^2 s^{-1} was also obtained from analysis of the voltammograms in Figure 1 (see SI). This is comparable to the good O$_2$ diffusivity (2.17×10^{-6} cm^2 s^{-1}) in LiPF$_6$-TEGDME based electrolytes.[26] High diffusion kinetics of the mediator is essential to avoid mass transport limitations and hence voltage polarization.[20]

Chemical Reactivity of Oxidized TDPA with Li$_2$O$_2$. Direct proof of the capability of TDPA$^+$/TDPA^{2+} to oxidize Li$_2$O$_2$ comes from its reactivity (Figure 2). TDPA dissolved in
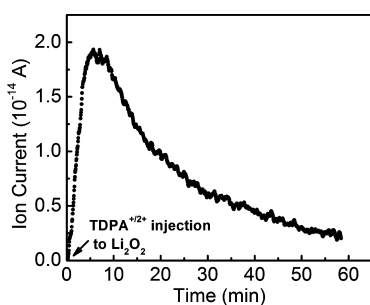
Figure 2. Mass spectrometry analysis of the O$_2$ evolution from the direct chemical reaction between oxidized TDPA and Li$_2$O$_2$.

0.1 M LiTFSI-TEGDME was oxidized under Ar at a constant voltage of 3.4 V (against Li dipped in 0.1 M LiTFSI-TEGDME reference electrolyte) at a carbon electrode in a two-chamber "H-cell" equipped with a diaphragm separating the chambers. The amount of oxidized TDPA was determined from the coulombs passed. A known aliquot of the oxidized TDPA solution was then injected into a vial containing a large excess of Li$_2$O$_2$, and O$_2$ evolution was monitored by mass spectrometry. O$_2$ evolution was observed instantaneously, and the integrated response was quantitative ($\sim$2.2 e$^-$/O$_2$) based on the quantity of oxidized mediator injected. The small deviation from the ideal 2 e$^-$/O$_2$ ratio is likely due to the cumulative error associated with the intricate experimental process.

Effect of TDPA on the Li–O$_2$ Cell Performance. The highly improved reversibility and energy efficiency conveyed by TDPA is evident in the galvanostatic discharge–charge profiles presented in Figure 3a. Cells employing 0.5 M LiTFSI-TEGDME electrolyte with and without 50 mM of the TDPA mediator were compared. This concentration is in the range suitable for practical Li–O$_2$ batteries. For the electrochemical studies, carbon coated on stainless steel mesh was used as the positive electrode, and a lithium metal foil pretreated in 0.1 M LiTFSI-PC served as the counter (negative) electrode. To prevent reduction of the mediator by lithium, other redox
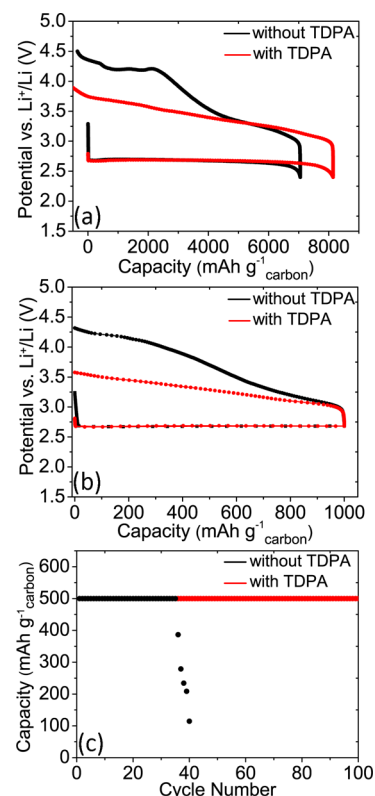
Figure 3. (a) Galvanostatic discharge–charge profile with and without TDPA using 0.1 mA cm^{-2} of current density without capacity limitation; (b) galvanostatic discharge–charge profile with and without TDPA at 0.1 mA cm^{-2} for 1000 mAh g^{-1} of capacity; (c) cyclability with and without TDPA at 0.1 mA cm^{-2} of current density for 500 mAh g^{-1} capacity.

mediator studies have employed LiFePO$_4$ as the counter electrode,[16] but it cannot be used here as its redox potential (3.4 V) is higher than the 3.1 V potential of TDPA/TDPA$^+$. The pretreatment provides a sufficiently protected Li surface to stabilize the lithium metal against oxygen, and as reported previously, together with a positive electrode of tortuous porosity that traps the in situ generated RM, the reduction of oxidized TDPA molecules is effectively suppressed.[18] In a practical cell, a lithium-ion conducting membrane would be utilized, but this is beyond the scope of our work. At the same positive electrode loading and current density, the discharge voltage was identical with or without TDPA (2.7 V), confirming that it does not participate directly in ORR.

TDPA, however, reproducibly (over five cells) provided 10–15% higher discharge capacity (8000 mAh g^{-1} vs 7000 mAh g^{-1} in the TDPA-free or "reference" cell). Because RMs such as TEMPO have the opposite effect on discharge capacity,[18] we propose that TDPA may improve O$_2$ solubility and/or O$_2$ diffusivity. The oxygen solubility and transport properties of the electrolyte are of great significance in determining discharge capacity and rate capability, even at these current densities.[27] As shown later, TDPA also improves the performance of the cell at higher rates, which also corroborates our claim. Most significantly, the charging voltage is significantly reduced by $\sim$0.8 V with TDPA. The slightly sloping charge profile is complete by $\sim$3.7 V, which is also much lower than that of the $\sim$4.0 V afforded by TEMPO (where only about 60% charge is achieved by 3.7 V) (Figure S2). The small overcharge at the end represents further oxidation of the TDPA, which will

continue until all the TDPA$^+$ molecules are oxidized to TDPA^{2+}. The charge profile for the TDPA cell is expected to be governed by both TDPA/TDPA$^+$ and TDPA$^+$/TDPA^{2+} redox couples as they are both active in the 3.1–3.7 V window. During the first ~10−20% of charge, the profile is somewhat similar for the two cells and represents oxidation of amorphous Li$_2$O$_2$ and/or LiO$_2$ nanodomains.[15] Without the redox mediator, the voltage rises sharply past this point. In its presence, above 3.1 V, TDPA is oxidized at the positive electrode to TDPA$^+$. The cation diffuses to the Li$_2$O$_2$ surface, chemically oxidizing the lithium peroxide to oxygen and converting back to TDPA. If all the TDPA$^+$ fails to react, at slightly higher potential (~3.5 V) it will be oxidized to TDPA^{2+} at the electrode. This converts peroxide and release oxygen either by a direct 2e$^-$ process, or via a 1e$^-$ process that regenerates yet more active TDPA$^+$ directly at the peroxide surface (see Scheme 1). Thus, overlapping electrochemical processes are involved: initial Li$_2$O$_2$ oxidation without the RM, and the dynamic biredox couples of the mediator. These operate in concert to give rise to the gently sloping profile. Cells operated with a capacity cutoff of 1000 mAh g^{-1} (Figure 3b) and 500 mAh g^{-1} (Figure S3) show very similar behavior and slightly lower charge potentials below 3.5−3.6 V.

This dynamic charge mechanism is reflected in the good cycling performance of the TDPA/Li−O$_2$ cells. Restriction on the specific capacity enables faster cycling and a lower charging voltage that additionally suppresses parasitic processes. Figures 2c and S4a compare the performance to the non-TDPA Li−O$_2$ cells. The 500 mAh g^{-1} cell attained more than 100 cycles (Figure 3c), 3-fold higher than the TDPA-free Li−O$_2$ cell, which failed after 35 cycles. Nonetheless, an increase in the charging voltage was recorded for the TDPA cell with cycling over extended periods (Figure S4a). This is due to the accumulation of electrolyte degradation products such as acetates and formates that are formed from the reaction of the discharge product Li$_2$O$_2$ or LiO$_2$/O$_2^-$ intermediates with the electrolyte and are not removed completely upon oxidation, thus raising the charge transfer impedance. Such carboxylate species are formed even at the end of first discharge as detected by NMR and account for the deviation from a 100% Li$_2$O$_2$ yield (see below). Typically insulating carbonate species (see below) are also formed by increased parasitic processes triggered at the higher charging voltages required in the absence of the RM. This results in much earlier cell death (Figure S4b), and is also apparent for 1000 mAh g^{-1} capacity cells (Figure S4c). The influence of higher current density on galvanostatic discharge and charge performance is shown in Figure S5. At both 0.2 mA cm^{-2} and 0.4 mA cm^{-2}, TDPA ensures complete rechargeability below 4 V for 1000 mAh g^{-1} capacity cells. The low polarization even at the higher current density further demonstrates the fast diffusion kinetics of TDPA. This is essential for the oxidation of insoluble solid Li$_2$O$_2$ far from the positive electrode interface. Without the redox mediator, the Li−O$_2$ cell could not discharge to 1000 mAh g^{-1} at 0.4 mA cm^{-2} without severe polarization, suggesting that the TDPA also improves oxygen solubility and diffusivity as described above.

Physicochemical Investigations of the Li−O$_2$ Cells. Additional evidence of the improved rechargeability conveyed by TDPA is provided by *ex-situ* analyses of the positive electrode after a galvanostatic cycle. For this study, the cells with and without TDPA were discharged to 1 mAh and recharged to the equivalent capacity. Although the degradation

product—Li$_2$CO$_3$—was readily detected by XRD after charge in the positive electrode for the reference cell, the cell with TDPA yielded a pattern free of impurities (Figure S6). This is also reflected in the improved reversibility and sustainability of the TDPA Li−O$_2$ cell, confirmed by quantitative oxidation of the peroxide of charged positive electrodes via iodometric titration (see SI, Table S1 for details and quantitative results). The cells discharged to 1 mAh of capacity showed a ~89% peroxide yield, comparable to that obtained by McCloskey et. al with a carbon electrode.[28] Some Li$_2$O$_2$ (or superoxide) is consumed by side reactions with the carbon electrode[9,29] and electrolyte,[30] producing mainly lithium formate and acetate (see Figure S7). Clearly, there is no influence of the redox mediator on the discharge (Li$_2$O$_2$) yield, as it does not operate on discharge. The effect of the TDPA is very significant on OER, however. After cells were charged to 1 mAh (completed below 4 V), while iodometric analysis detected no remaining Li$_2$O$_2$ for the TDPA cell, the reference cell still contained >1/3 of the Li$_2$O$_2$. Stability of the TDPA mediator in the Li−O$_2$ cell environment was confirmed from the ^{1}H NMR spectrum of the electrolyte extracted from the cell after multiple discharge−charge cycles, which showed no evidence of TDPA decomposition (see SI, Figure S8).

Mass Spectrometry Investigation of the Influence of TDPA on Li−O$_2$ Cell Chemistries. To further quantify the role of TDPA for OER, coulometry was combined with in situ gas analysis using quantitative online electrochemical mass spectrometry (OEMS). The cells were galvanostatically discharged to a capacity of 2.4 mAh under 5% O$_2$/Ar flow and then charged under an Ar flow at 0.1 mA cm^{-2} for the OEMS studies. By comparing the coulombs passed per mole of O$_2$ consumed or evolved, e$^-$/O$_2$ values are obtained. The e$^-$/O$_2$ ratios obtained on discharge of 1.98 ± 0.04 (with TDPA) and 2.06 ± 0.04 (without TDPA) are in accord with previous reports[31] and indicate peroxide formation is governed by the expected 2 e$^-$/O$_2$ ratio (Figure S9a). We conclude that TDPA does not significantly alter ORR—aside from improving the slight deviation from the stoichiometric 2 e$^-$ reduction indicative of parasitic processes—and does not react with the superoxide intermediate or peroxide. The high effectiveness of TDPA for the OER was demonstrated by charging the cells to their original discharge capacity and monitoring the accompanying gas evolution (Figure 4). The TDPA cell exhibits a gentle voltage rise closer to an ideal flat potential, where steady O$_2$ evolution corresponds to 2.25 e$^-$/O$_2$ (Figure 4a). The small change in the initial rate of O$_2$ production corresponds to the point where the RM becomes active at 3.15 V, as indicated by the dotted line. Above ~3.5 V, O$_2$ evolution gradually diminishes and stops at termination of the 2.4 mAh charge. The slight rise in voltage at the end coincides with a miniscule release of CO$_2$, which ideally would be zero. In comparison, the cell without TDPA exhibits a slightly lower O$_2$ evolution rate corresponding to 2.4 e$^-$/O$_2$ in the initial stages of charge (3−3.5 V), followed by a steeper voltage rise and a rapid decay in O$_2$ evolution (Figure 4b). By 4 V only about 70% of the total charge reaction is completed (Figure S9b), which is in agreement with the iodometric analysis result of the non-TDPA cell electrode after charging to 4 V. Here, a much higher potential is required to complete the charge, and accordingly, very significant CO$_2$ evolution is observed. It even exceeds O$_2$ production between 4.2−4.5 V, owing to exacerbated electrolyte decomposition, producing carbonate-type byproducts that are decomposed at higher charging voltages and detected as
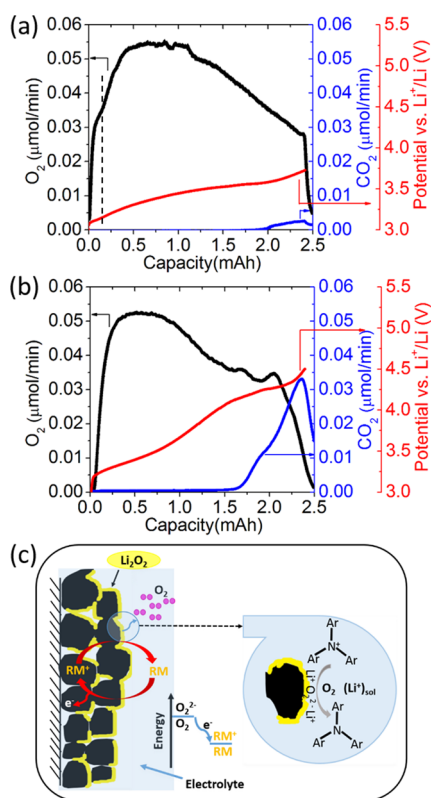
Figure 4. Charge voltage curve (red) and the corresponding O_2 (black) and CO_2 (blue) evolution profile for the $Li-O_2$ cell (a) with and (b) without 50 mM TDPA in the 0.5 M LiTFSI-TEGDME electrolyte. (c) Proposed scheme for the solution based OER catalysis by TDPA/TDPA$^+$ (RM).

CO_2 evolution. A quantitative comparison of O_2 evolution vs charging potential for the two cells not only shows that the oxygen evolution is complete at a voltage 0.8 V lower in the presence of TDPA, but the TDPA cell also evolves 15% more O_2 than the non-TDPA cell (Figure S9b). The results unambiguously highlight the efficacy of TDPA as a soluble catalyst for Li_2O_2 oxidation. The overall function of the RM is summarized schematically in Figure 4c using TDPA/TDPA$^+$ as the example on the right (the second TDPA$^+$/TDPA^{2+} redox couple is not shown here for clarity). In addition to ensuring more reversible Li_2O_2 oxidation, the catalyst greatly improves the energy efficiency of the $Li-O_2$ cell by lowering the charge potential by ~0.8 V.

We note that the generic problems of electrolyte degradation associated with glyme-based electrolytes in $Li-O_2$ cells are still present in the mediator cell. Because of the reactivity of the discharge product Li_2O_2 and discharge intermediates LiO_2/O_2^- with the electrolyte (reflected in low Li_2O_2 yield even after the first discharge), insulating carboxylate side products such as lithium acetate and formate are formed during each discharge cycle even if the charge polarization is restricted to a lower voltage. These insulating byproducts, which are not removed during the charge step, keep amassing with every cycle triggering a slow but steady rise of the charge potential even in the presence of the charge mediator. In the absence of the mediator a much higher charge overpotential (0.8 V) leads to additional decomposition during charge which accelerates the charge voltage rise and cell failure. The use of a low voltage charge mediator like TDPA thus curbs the side reactions on charge and prolongs the cycle life. However, the use of a more

stable electrolyte is essential to explore very long-term cyclability of a $Li-O_2$ cell in the presence of a redox mediator and for the realization of a practical cell.

CONCLUSIONS

In conclusion, we introduce a novel low voltage redox mediator—TDPA—for enhanced rechargeability and improved cyclability of the aprotic $Li-O_2$ cell. Its excellent chemical and electrochemical stability, fast diffusion kinetics, and suitable redox potentials for solution-based OER catalysis show great promise. The low overpotential favors the OER process over parasitic side reactions, ensuring a significantly better cycle life. Furthermore, as indicated by the improved discharge capacity and discharge rate capability, TDPA appears to improve the oxygen solubility/diffusivity in the electrolyte. Discovery of this new amine class of molecule as a charge mediator leads to our anticipation that other molecules within this class may prove even more efficient in promoting quantitative peroxide oxidation with higher energy efficiency.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.5b00267.

Detailed electrochemical and analytical methods, TDPA diffusion coefficient calculation, supporting figures on electrochemical results and analytical characterizations (PDF)

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Notes
The authors declare no competing financial interests.

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