Enhanced Li-O₂ Battery Performance in a Binary “Liquid Teflon” and Dual Redox Mediators

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Low capacity, poor rechargeability, and premature cell death are major setbacks in the operation of Li-O₂ battery, hindering its practical application. A promising approach of meeting those challenges is via the use of redox mediators (RMs), promoting Li₂O₂ solution phase formation upon cell discharge and an efficient oxidation on charging. The use of dual RMs decouples the electrochemical reactions at the cathode with formation/decomposition of Li₂O₂, resulting in improved discharge capacity, lower charge overpotential, and cycle stability. Although Li-O₂ cell performance is no longer mitigated by an insulating Li₂O₂, a major inherent barrier to implement viable and functioning Li-air batteries lies in both limited O₂ mass transport and pores clogging. Here, a record discharge capacity of 6 mAh cm⁻² (60% increase), by combining dual RMs with “liquid Teflon” type perfluorocarbons binary system, is demonstrated. The combination of the two materials in the cell contributes to the enhanced cell performance manifested also in lower charge overpotential values throughout dozens of cycles. This is also attributed to the unique compact and an exceptionally smooth morphology of the Li₂O₂ deposit layers at both ends of the air cathode.

Li-O₂ battery is considered a promising energy storage device for future electric propulsion technology because of its exceptionally high theoretical specific energy of 3500 Wh kg⁻¹.[1,2] Successfully harvesting merely a third of the Li-O₂ theoretical specific energy could potentially deliver a battery that exceeds Li-ion technology. Li-O₂ cells usually comprise a lithium metal anode and porous carbonaceous O₂-cathode, separated by ether-based electrolyte. On discharge, oxygen reduction takes place at the cathode to produce lithium peroxide, Li₂O₂, an insulating and insoluble product. Li₂O₂ formed on the surface of the electrode pores leads to low rates, low capacities, and early cell death.[2-4]

However, the use of redox-mediating molecules to exchange electrons between the electrode surface and the growing (on discharge) and decomposing (on charge) of Li₂O₂ leads to higher operation rates and capacities of a few mAh cm⁻².[5-17] 2,5-Di-tert-butyl-1,4-benzoquinone (DBBQ) has been employed to mediate the reduction of O₂ to form Li₂O₂ from solution and is no longer mitigated by an insulating Li₂O₂, a major inherent barrier to implement viable and functioning Li-air batteries lies in both limited O₂ mass transport and pores clogging. Here, a record discharge capacity of 6 mAh cm⁻² (60% increase), by combining dual RMs with “liquid Teflon” type perfluorocarbons binary system, is demonstrated. The combination of the two materials in the cell contributes to the enhanced cell performance manifested also in lower charge overpotential values throughout dozens of cycles. This is also attributed to the unique compact and an exceptionally smooth morphology of the Li₂O₂ deposit layers at both ends of the air cathode.

The need to evenly deliver O₂ throughout the electrode volume and increase oxygen accessibility is an important step toward enhanced discharge capacity with high rate capabilities.[19-21] This motivated the introduction of the “liquid Teflon” type perfluorocarbons (PFCs). PFCs are organofluorine compounds, containing only carbon and fluorine bonded together, that is, CₓFᵧ, with high oxygen dissolving capacity, extreme inertia, and are hydrophobic with a lipophobic character.[22-24] Introducing PFC additive, which possess >5 times higher oxygen solubility than tetraethylene glycol dimethyl ether (TEGDME), was reported to form a uniform and intimate Li₂O₂ deposit, being evident at areas further away from the electrode/gas interface.[25-26] Here, we present that improved oxygen availability and a better surface area utilization demonstrated extensively higher discharge capacity in TEGDME electrolytes containing both dual RMs and PFC. Moreover, changing the morphology and hence increasing the surface area of Li₂O₂ is reported here to substantially ease the charging process. This is mainly an
inner-sphere process, involving adsorption of the mediator on peroxide surface, leading to a lower charge overpotential in this advance cell, compared with PFC-free Li-O2 cells.

Methods of analysis and measurements performed in this study as well as Li-O2 cells construction are described in the Experimental Section (Supporting Information). In short, excess amount of LiFePO4 was used as anode instead of lithium metal to avoid undesired reactions involving the latter. It should be noted that the potential of LiFePO4, 3.45 V versus Li+/Li, would not result in a practical cell voltage. A lithium anode protected by a Li+ conducting membrane is required in practical Li-O2 cells. A metal-free binder-free gas diffusion layer (GDL) served as the carbonaceous air cathode, while 15 \times 10^{-3} \text{ M} DBBQ-15 \times 10^{-3} \text{ M} TEMPO-1 \text{ M LiTFSI} in tetruglyme was utilized as the electrolyte. The concentration of DBBQ and TEMPO was fixed at 15 \times 10^{-3} \text{ M} due to the solubility of DBBQ in tetruglyme and to avoid the mediators being the rate determining factors.

In order to study the influence of dual mediators and the compatibility of DBBQ and TEMPO in the electrolyte, cyclic voltammetry (CV) tests were conducted on DBBQ, TEMPO, and DBBQ/TEMPO under Ar and O2, respectively (Figure 1).

In the absence of dual RMs, Li-O2 cells containing the PFC additive exhibit a negligible discharge capacity and an early cell death. Cells with only dual RMs discharged under the same conditions show a typical discharge plateau around 2.7 V versus Li+/Li, a substantially higher discharge capacity and low charge potential on the order of 3.6 V versus Li+/Li, in accordance with recent observations, indicating Li2O2 film suppression and a predominant solution growth mechanism. When a binary system composed of both PFC and dual RMs was introduced, the Li-O2 cell capacity at a discharge process, in a current density of 50 \mu A \text{ cm}^{-2}, increases by slightly more than 60%, from 3.6 to 5.9 mAh cm^{-2}, while the effect was alleviated at higher current density of 500 \mu A \text{ cm}^{-2}, with the capacity rising from 1.5 to 1.7 mAh cm^{-2}. A binary system with lithium anode protected by a Lithium Superionic CONDuctor disc (LiSICON, Ohara) was also discharged to compare the performance with LiFePO4 (Figure S2, Supporting Information). Considering the iR (current \times resistance) loss across the LiSICON, the results are very similar to those with LiFePO4 as the anode, indicating no shutting effect between LiFePO4 and the mediators. The abrupt, rather than gradual, voltage decrease observed for both dual RMs Li2O2 systems indicates a similar failure mechanism of low oxygen diffusion rather than high resistance Li2O2 layer. In nonaqueous Li2O2 batteries, the electrolyte wets the carbonaceous electrode and floods the pores, and thus oxygen availability is determined by the concentration of O2 dissolved in the electrolyte solution. As a result, Li2O2 is mainly deposited at the electrode side, close to the oxygen reservoir, leaving a large portion of the electrode unused. Although GDL, as the porous air electrode, is an excellent gas diffusion layer electrode in aqueous medium, it fails to fulfill its role in nonaqueous electrolyte solutions, leading to substantially reduced current densities being driven from the cell. Introducing PFCs allows better oxygen distribution and more efficient air cathode utilization, as demonstrated in an extended discharge profile and enhanced capacity. However, mitigating the poor O2 mass transport can only support a limited and quite restricted improvement in Li2O2 battery performance.

By deliberately limiting the cell capacity to 1 mAh cm^{-2} at a current density of 500 \mu A \text{ cm}^{-2}, a step that is being adopted previously to prevent pore clogging at the oxygen/electrode interface. 

![Figure 1. A,B] Cyclic voltammograms for DBBQ (black), TEMPO (blue), and DBBQ/TEMPO (red) in tetruglyme under Ar and O2. The mediator concentrations was 15 \times 10^{-3} \text{ M}, and cyclic voltammograms were carried out on 3 mm planar Au electrodes; scan rate 50 mV s^{-1}.
cells cycled under 1 atm of O2 with PFC show a clear and evident improvement in overall cycle performance, compared to the PFC-free cells, as shown in Figure 3. The discharge plateau, at ≈2.65 V versus Li+\text{/Li}, recorded during the first 10 cycles was hardly influenced by the addition of PFC, indicating that PFC additive did not affect the electrochemical reduction at the cathode surface. During the first 10 cycles, the charge voltage profile steadily increased toward a plateau of 3.7 V versus Li+/Li for both of the dual RMs cells due to oxidation of Li2O2 by oxidized TEMPO, with a continuously increasing voltage between 3.7 and 4.5 V versus Li+/Li due to the oxidation of TEMPO in the absence of Li2O2 at the final stage of charge, similar to the observations made in previous studies.[34] This trend is a symptom to a problem attributed to the electrochemical oxidation of carbon and/or electrolyte.[35]

Figure 2. First full discharge profile of Li-O2 cells with PFC additive (blue), dual RMs (black), and binary PFC dual RMs (red). a,b) The cells were discharged to 2.2 V at the current density of 50 and 500 µA cm⁻².

Figure 3. Represented cycle performance of Li-O2 cells with (red line) and without PFC additive (black line) with a capacity limited to 1 mAh cm⁻² between the potentials of 2.2 and 4.5 V at the current density of 500 µA cm⁻².
During the proceeding cycles, a continuous and gradual increase on the charging potential from 3.7 V (10th cycle) to 4.1 V (25th cycle) and 4.35 V (50th cycle) was observed for the Li-O₂ cell that did not utilize PFC. Li-O₂ cells with PFC showed a much less charge overpotential during the first 50 cycles, from 3.7 V (10th cycle) to 3.75 V (25th cycle) and 4.1 V (50th cycle). Although TEMPO alone allows cycling with a reduced charging potential, the addition of PFC further improves both cycle performance and the round-trip efficiency, demonstrated by a plateau-like charging curve at a lower charging voltage. This, in turn, will potentially lead to less side products formation and accumulation at the air cathode. Lower oxidation voltage can be attributed to a more efficient oxidation of Li₂O₂ due to its morphology and higher contact area between TEMPO and the discharge products. Nevertheless, high charging voltage of 4.1 V at the 50th cycle (Figure 3d) could not be avoided through the use of PFC, due to the accumulation of side products, associated with the reactivity of Li₂O₂, carbon, and the electrolyte degradation processes, leading to the increase in the electrode's resistance and thus, a rise in the overcharge potential.[36]

In an effort to comprehend the morphology of the deposited Li₂O₂ and better understand the associated mechanisms, identical cells (with or without PFC) were discharged to 2.2 V versus Li⁺/Li followed by an extraction of the air cathodes from the cells and their examination by a scanning electron microscopy (SEM). The SEM images presented in Figure 4 clearly demonstrate differences in Li₂O₂ morphology as a function of PFC content and distance from the oxygen reservoir. In all cases, solution growth of Li₂O₂ is promoted, attributed to the presence of DBBQ, showing little evidence of a film growth on the electrode surface.[37] In a PFC-free Li-O₂ cell containing dual RMs, toroidal Li₂O₂ particles with an average diameter of 500 nm are sparsely distributed on the carbon fibers and in the pores of the electrode, whereas a denser ≈1 µm thick layer of products are intimately formed near the carbon electrode surface in the presence of PFC. As PFC has higher O₂ solubility, once DBBQ is reduced on the electrode surface, it will form Li₂O₂ near the carbon surface, leading to the formation of a thick layer. It should be noted that in the presence of DBBQ in the electrolyte and PFC with high O₂ solubility, Li₂O₂ formed as a thick layer near the electrode rather than on the electrode surface and the electrode surface remained clean.

Accumulation of discharge products in a dense-layer configuration is advantageous with respect to effectively utilizing the surface area for higher discharge capacity. Oxygen evolution reaction (OER) is also affected by the current density as well as the identity and morphology of the discharge products.[38,39] PFC dual RMs Li-O₂ cells potentially ease Li₂O₂ oxidation, due to a larger contact area between the dissolved mediator and the discharge products. It is postulated that an increase in oxygen concentration due to PFC addition may have broken the delicate balance between O₂ diffusion, DBBQ, and TEMPO and their concentrations. Higher oxygen concentration, attributed to PFC introduction, may have shifted the limiting factor from mediator mass transport to O₂ mass transport. Albeit the thick-layered structure of Li₂O₂ and its relatively efficient oxidation suggest otherwise, as it is found to be advantageous for solution-operating mediators.

Powder X-ray diffraction (PXRD) and infrared spectroscopy were obtained in order to inspect and evaluate the identity of the particles observed in Figure 4. PXRD pattern collected from the GDL after discharge with PFC exhibits peaks associated with Li₂O₂, as the primary discharge product and LiOH as a minor by-product (Figure S3, Supporting Information). Although tetraglyme is considered as a relatively stable electrolyte, decomposition products (lithium carbonate, formate, and acetate) were reported.[37,40] Such products are undetectable in the XRD but clearly visible in infrared spectroscopy (Figure S4, Supporting Information), where the presence of Li₂O₂ is confirmed. In addition, minor by-products as Li-acetate, Li-formate,
It is clear from the SEM that the thick layer disappeared after SEM (Figures S4 and S5, Supporting Information, respectively). were investigated by Fourier transform infrared (FTIR) and carbon electrode, forming lithium acetate/formate and Li$_2$CO$_3$ at 250 µm, advantageous not only for

and Li$_2$CO$_3$ are also detected. After charging, the electrodes were investigated by Fourier transform infrared (FTIR) and SEM (Figures S4 and S5, Supporting Information, respectively). It is clear from the SEM that the thick layer disappeared after charging, suggesting the complete removal of Li$_2$O$_2$ on charge. Some fine particles are observed on the charged electrode surface at the end of charge, which, according to FTIR, is lithium carbonate, and organic carbonate due to some side reactions between Li$_2$O$_2$, the electrolyte, and the electrode.

Further investigation on the impact of PFC during operation of a binary PFC dual RMs Li$_2$O$_2$ cell was performed by the application of in situ differential electrochemical mass spectrometry (DEMS), enabling the detection of gas consumption and evolution. No gas was detected, except only for O$_2$ during discharge in the dual RMs Li$_2$O$_2$ cell with and without PFC, as shown in Figure 5 and Figure S6 (Supporting Information). The total O$_2$ consumed and total charge passed were calculated, and the integral provided a ratio of electrons passed per O$_2$ consumed of 2.04 e$^-$/O$_2$ with PFC and 2.05 e$^-$/O$_2$ without PFC, corresponding to a dominant two-electron reduction in both systems, leading to the formation of Li$_2$O$_2$ [34,41,42]. Upon charging and as common in Li$_2$O$_2$ cells without PFC, an evidence of both O$_2$ and CO$_2$ evolution was detected (Figure S6, Supporting Information). During the transition from the first charging plateau at 3.7 V, corresponds to the oxidation of Li$_2$O$_2$ by TEMPO [34] to the second plateau above 4.0 V, a strong evolution of CO$_2$ was detected, associated with an oxidation of decomposition products. With the addition of PFC, it did not eliminate the side reactions between Li$_2$O$_2$, electrolyte, and carbon electrode, forming lithium acetate/formate and Li$_2$CO$_3$ and subsequently did not eliminate their oxidation to CO$_2$ above 4.0 V (Figure 5). However, the CO$_2$ evolved was halved comparing to that without PFC, suggesting a much less side reaction due to the contribution of PFC to Li$_2$O$_2$ morphology enabling a favorable OER at lower potentials.

We studied the concept of binary dual RMs Li$_2$O$_2$ cells by incorporating oxygen carrier compound, that is, PFC, soaked in the GDL air electrode. SEM images alongside XRD, infrared, and DEMS analysis demonstrate that the increase in capacity is directly governed by a compact and efficient Li$_2$O$_2$ deposition. The formation of Li$_2$O$_2$ via a mediated solution mechanism is promoted by DBBQ. Nevertheless, PFCs introduce new oxygen channels through the entire volume of the GDL electrode with continuous and even O$_2$ transportation routes. The binary combination results in a dense thick layer of Li$_2$O$_2$ at both sides of the air electrode, as opposed to disconnected toroidal Li$_2$O$_2$ products, clogging the pores at the O$_2$/electrode interface in the absence of PFC. On charging, by introducing PFCs and changing the product morphologies, the charge voltage is reduced even further, and cycle life is improved accordingly. As the nature of oxidation process is highly influenced by the size and shape of Li$_2$O$_2$, new Li$_2$O$_2$ morphology is observed upon PFC addition, promoting an efficient oxidation due to higher surface area and possibly a better adsorption of the mediator on the peroxide surface [71]. Such phenomenon leads to a lower charge overvoltage and occurs without triggering carbon decomposition, which is commonly enhanced due to intimate contact between the carbon and the discharge products.

Mediated formation and decomposition of lithium peroxide is an advantageous approach to fulfill Li$_2$O$_2$ cell prospective as high specific energy power source. Nevertheless, Li$_2$O$_2$ cell with dual RMs has been shown to shift the cell limitation from insulating and insoluble nature of Li$_2$O$_2$ to O$_2$ mass transport and is associated with pores clogging. With the introduction of oxygen-carrier additive, namely, PFCs, the limitation of oxygen distribution throughout the entire volume cathode was mitigated, demonstrating over 60% increase in discharge capacity and improved cycling performance. The addition of the highly inert PFC compound directly to the GDL electrode supports the formation of artificial three-phase reaction zones, allowing continuous transportation of O$_2$ molecules to the entire electrode, without interrupting the process of mediating reduction and oxidation during discharge and charge, respectively. The improved capacity was attributed to product deposition in a denser and thicker layer of \approx 1 \mu m, advantageous not only for dissolved RMs operation but also for an efficient utilization of the surface area for a maximal product deposition with a minimal risk of pores clogging and restricted O$_2$ transportation and availability.

Even though previously dismissed as a suitable cathode material due to instability, carbon as the substrate material and main constituent in the air cathode is still an attractive material when coupled with dual RMs due to improved stability attributed to solution-based mechanism. Here, we resolve the challenge of carbon-based air cathodes associated with a flooding of all air channels that prevents an effective utilization of GDL air electrode. The introduction of oxygen-carrier additive, in the form of PFC, would alter the Li$_2$O$_2$ morphology, leading to a lower discharge/charge overpotential, also evident with a higher cycle number. Though electrolyte solution stability remains an acute challenge, the present work on the binary PFC dual RM cells, being a generic in its nature, allows the community to move a few steps closer to meet the market demand of high-capacity Li$_2$O$_2$ battery with a sustained cycling. Discovery and implementation of PFCs as complementary to the operation of dual RMs can be easily implemented and adopted once stable electrolyte solutions are to be found. The search for stable
electrolytes solutions is still an on-going task that eventually will allow improved Li-O₂ cell’s performance and enhanced cycling stability. Once such solutions are recognized and established, systems utilizing a binary PFC-dual RMs system would provide higher capacity, superior rate, and a stable cycle performance Li-O₂ battery.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
binary dual redox mediators, carbon air cathode, gas diffusion layer, Li-O₂ battery, “liquid Teflon” type perfluorocarbon (PFC) additive, rechargeability

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