

# Advances and Challenges for Aprotic Lithium-Oxygen Batteries using Redox Mediators

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Rechargeable aprotic Li–O<sub>2</sub> batteries that can deliver extremely high energy density have attracted worldwide attention. However, the practical use of this promising technology is hindered by an unsatisfactory cycling life and inferior energy efficiency (high discharge/charge voltage gap), although significant progress has been made in this area in the last decade. Recent reports indicate that soluble catalysts or redox mediators dissolved in aprotic electrolytes can catalyze Li<sub>2</sub>O<sub>2</sub> decom-

position and reduce the voltage gap between O<sub>2</sub> reduction reaction and O<sub>2</sub> evolution reaction. Here, a specific review on a series of suitable soluble catalysts for Li–O<sub>2</sub> batteries is provided. This review will highlight the underpinning chemistry and electrochemistry mechanisms of Li–O<sub>2</sub> batteries, as well as the recent progress and challenges of soluble catalysts, with the aim of motivating researchers to further explore applications in Li–O<sub>2</sub> cells and other energy storage and conversion systems.

## 1. Introduction

In the domain of next-generation energy storage systems, Li–O<sub>2</sub> cells have attracted great interest because of their exceptional theoretical energy density of ~3,500 Wh kg<sup>-1</sup><sup>[1]</sup> that is five times higher than that of Li-ion batteries of the same weight. If fully commercialized, these new batteries could revolutionize the battery industry and peoples' lives. However, the present development of Li–O<sub>2</sub> batteries faces a number of critical challenges, including unsatisfactory recyclability and energy inefficiency. The main issue lies in the charge reaction or oxygen evolution reduction process (OER), which would, in theory, oxidize and decompose the discharge product, Li<sub>2</sub>O<sub>2</sub>, at the cathode with O<sub>2</sub> gas evolution at an equilibrium voltage of 2.96 V vs. Li/Li<sup>+</sup>. In fact, it is formidable to proceed efficiently by virtues of the insulating nature of Li<sub>2</sub>O<sub>2</sub> and the sluggish kinetics of the OER process, which further leads to high charging overpotential, electrolyte decomposition, and corrosion of cathode materials.<sup>[2]</sup>

In order to minimize the charge polarization, various attempts have been explored to overcome this problem. Heterogeneous catalysts, for instance, noble metal, metal oxides, sulfides, and nitrides, are widely adopted and have resulted in some improvements.<sup>[3]</sup> However, these catalysts can only influence the OER process at limited and rigid contact sites (solid/solid interface) between the Li<sub>2</sub>O<sub>2</sub> and solid catalysts, resulting in sluggish kinetics of the electrocatalytic reactions. Soluble redox mediators (RMs) can promote oxidation of Li<sub>2</sub>O<sub>2</sub> at a considerably larger and dynamic interface through a

chemical reaction and is considered an appealing substitute to decrease the charging overpotential.<sup>[4]</sup>

The mechanism of the charge process for Li–O<sub>2</sub> cells with RMs is described below (Figure 1):



Figure 1. Reaction mechanism, category, advantages, feature and challenge for Li–O<sub>2</sub> cells with redox mediators.



During charging, RM is first electrochemically oxidized to RM<sup>+</sup> near the cathode surface (Step 1), and the discharge product, Li<sub>2</sub>O<sub>2</sub>, is subsequently oxidized by RM<sup>+</sup> to release O<sub>2</sub> through a chemical reaction. Therefore, the application of RM converts the charge reactions from electrochemical pathways into chemical ones, significantly curbing the charge overpotential. The reactive sites of the solution-phase catalyst can be anywhere at the Li<sub>2</sub>O<sub>2</sub> surface, resulting in better contact between the soluble RM catalyst and the solid Li<sub>2</sub>O<sub>2</sub>. However, solution-phase catalysts have lower electronic conductivity compared with solid-phase catalysts. The greatest advantage of soluble catalysts is their mobility. Therefore, a combination of low-viscosity electrolytes and cathode materials with consid-

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erable number of pores with RMs can ensure the acceleration of the diffusion rate. Moreover, RMs migrating from the cathode side can react with the Li metal anode, causing cell life degradation. In general, soluble RMs possess distinct and preeminent preponderance for advanced Li–O<sub>2</sub> batteries, meanwhile they are faced with some challenges. A comprehensive picture of RMs and updates on their progress are necessary for furthering the practical applications of the Li–O<sub>2</sub> batteries.

Soluble catalysts for Li–O<sub>2</sub> batteries can be classified into inorganic and organic compounds. Recently, research on dual mediators becomes a new research hot spot, and this part is also discussed. In addition, the fundamental mechanisms and influence of RMs on the Li<sub>2</sub>O<sub>2</sub> morphology and capacity are reviewed. Finally, we share our views and perspectives on the challenges and opportunities for soluble RMs in aprotic Li–O<sub>2</sub> batteries. Figure 1 summarizes the main content of this review.

## 2. Inorganic Compounds

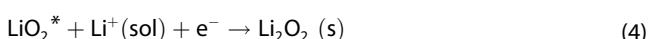
### 2.1. H<sub>2</sub>O

The ultimate goal for Li–O<sub>2</sub> batteries is Li-air ones that can capture O<sub>2</sub> from the surroundings. However, in an open system, other species in air such as water (H<sub>2</sub>O) are also unavoidable to be introduced into the aprotic battery system. Hence, probing the influence of humidity on the properties of Li–O<sub>2</sub> cells is crucial.

The impact of H<sub>2</sub>O on aprotic electrolytes is usually considered to be detrimental; recently, however, research has revealed its duality. H<sub>2</sub>O has a prodigious influence on the discharge capacity, discharge products, and morphology of Li<sub>2</sub>O<sub>2</sub>; this effect is related to the cathode material, electrolyte component, H<sub>2</sub>O content and so on (Table 1). Different groups have shown great interest in H<sub>2</sub>O and its effect on the discharge capacity of the first cycle of a Li–O<sub>2</sub> cell; a certain

amount of H<sub>2</sub>O generally causes an increase in specific capacity.<sup>[5]</sup> However, disputes on the discharge products remain unresolved. Gasteiger's group believes that Li<sub>2</sub>O remains the dominant discharge product in Li–O<sub>2</sub> cells with H<sub>2</sub>O,<sup>[6]</sup> whereas other researchers have found LiOH.<sup>[5c,7]</sup> We speculate that these variations may be due to the introduction of ppm levels of H<sub>2</sub>O through electrolytes, anode/cathode materials, separators, and other battery materials. Permeation of H<sub>2</sub>O into cell bodies during cycling is difficult to avoid and control. Wang et al. attributed the formation of LiOH to the interaction between Li<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O,<sup>[5c]</sup> while Qiao et al. proposed a new two-electron transfer mechanism with HO<sub>2</sub><sup>–</sup> intermediates on Ketjenblack cathodes in the presence of H<sub>2</sub>O, the ultimate product of which was merely Li<sub>2</sub>O<sub>2</sub>.<sup>[8]</sup> It is desirable that the parasitic reactions ascribed to superoxide (O<sub>2</sub><sup>–</sup>) were reduced effectively and the discharge capacity was improved simultaneously.

Scholars consistently agree on the fact that the presence of H<sub>2</sub>O enhances the solution formation of Li<sub>2</sub>O<sub>2</sub> through solvation of the intermediate species O<sub>2</sub><sup>–</sup>. Figure 2 shows that the morphology of Li<sub>2</sub>O<sub>2</sub> discharge products relies on the different amounts of H<sub>2</sub>O added to the electrolyte based on the experimental results from Luntz's group. The size of the Li<sub>2</sub>O<sub>2</sub> toroids and thin platelets increases and the shape changes with the amount of H<sub>2</sub>O added to the electrolyte; similar results were also reported by others.<sup>[5d]</sup> To explain this phenomenon, Luntz et al. proposed a mechanism for the growth of Li<sub>2</sub>O<sub>2</sub> toroids in the presence of H<sub>2</sub>O; these mechanisms include two electrochemical paths: surface mechanism and solution mechanism.



The formation of Li<sub>2</sub>O<sub>2</sub> through surface growth process is carried out by the continuous transfer of solvated Li<sup>+</sup> and an



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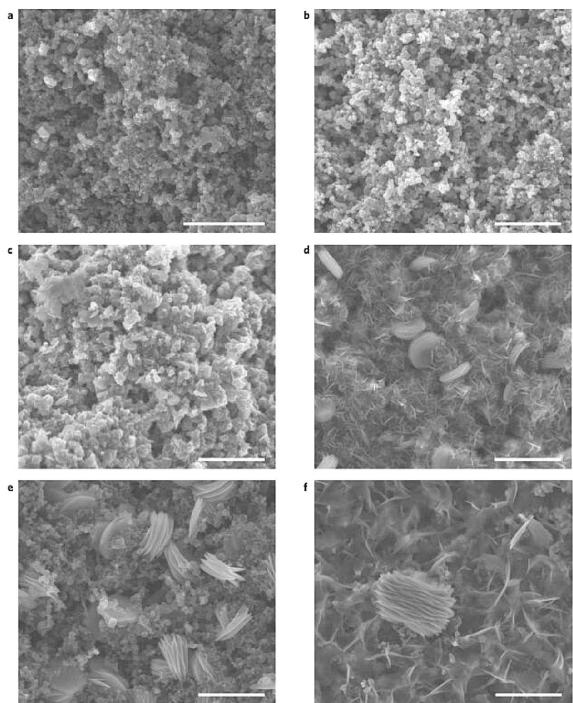
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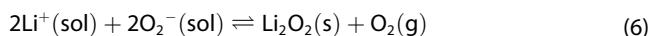
**Table 1.** Representative results about effects of water on Li–O<sub>2</sub> cells. RH stands for relative humidity.

Cathode	Electrolyte	H <sub>2</sub> O content	Cycling life	Discharge product	Ref.
EMD/RuO <sub>2</sub> /SP	0.5 M LiTFSI in Ionic liquids	RH of 51% in O <sub>2</sub>	218 cycles @500 mAh g <sup>-1</sup>	LiOH·H <sub>2</sub> O	[7a]
Ketjenblack	TEGDME-LiTFSI electrolyte	RH of 15% in O <sub>2</sub>	50 cycles @1000 mAh g <sup>-1</sup>	LiOH + Li <sub>2</sub> O <sub>2</sub> + Li <sub>2</sub> CO <sub>3</sub>	[5c]
VulcanXC72 carbon	0.1 M LiClO <sub>4</sub> in PC and DME	H <sub>2</sub> O-saturated O <sub>2</sub>	N/A	N/A	[5a]
Ru/MnO <sub>2</sub> /SP	DMSO	120 ppm H <sub>2</sub> O	200 cycles@500 mAh g <sup>-1</sup>	LiOH + Li <sub>2</sub> O <sub>2</sub>	[7b]



**Figure 2.** The morphology of Li<sub>2</sub>O<sub>2</sub> discharge product. SEM images of a cathode without discharge (a), of similar cathode discharged using nominally anhydrous electrolyte (b), with 500 ppm (c), 1,000 ppm (d), 2,000 ppm (e) and 4,000 ppm (f) water contents in the electrolyte. All scale bars, 1 μm. Reproduced with permission.<sup>[5d]</sup> Copyright 2014, Macmillan Publishers Limited.

electron to the intermediate species LiO<sub>2</sub>\* (Equations 3 and 4). Given the very poor conductivity of Li<sub>2</sub>O<sub>2</sub>(s) when the thickness of deposits reaches a certain extent, the process is forced to stop.



H<sub>2</sub>O can cause LiO<sub>2</sub>\* to solvate into Li<sup>+</sup> (sol) and O<sub>2</sub><sup>-</sup> (sol), thus triggering a solution pathway that promotes the growth of toroids; O<sub>2</sub><sup>-</sup> (sol) ultimately disproportionates to form Li<sub>2</sub>O<sub>2</sub> (Equations 5 and 6). Thereby, the solution growth process staves off the conductivity limitations of surface growth through an electrochemical process, leading to the formation of larger particles. The stability of Li<sup>+</sup> and O<sub>2</sub><sup>-</sup> ions in the electrolyte is highly relevant to the Gutman donor number (DN) and acceptor number (AN). Water has a very high AN of ~55; thus, its presence can solvate O<sub>2</sub><sup>-</sup> efficiently and promote the solution mechanism, which increases the discharge

capacity. However, addition of H<sub>2</sub>O also brings about the parasitic electrochemical reaction of conversion to H<sub>2</sub>O<sub>2</sub> and reaction with the Li anode.

Although mutual agreement that a moderate amount of H<sub>2</sub>O exerts a positive impact on capacity has been reached, the added H<sub>2</sub>O induces parasitic processes during discharge. Owing to the complexity of the reaction, the battery chemistry of H<sub>2</sub>O-contaminated aprotic Li–O<sub>2</sub> cells remains to be further elaborate. In view of the two-sided effect of H<sub>2</sub>O, we should adopt corresponding effective measures to bring its advantages into full play and avoid its disadvantages by protecting the Li anode.

## 2.2. Lithium Halides

### 2.2.1. Lithium Iodide

Lil, as a common RM for Li–O<sub>2</sub> batteries, is insoluble in most organic electrolytes, and the decomposition mechanism of Li<sub>2</sub>O<sub>2</sub> with Lil in the electrolyte is considered to follow the reaction below:



First, I<sup>-</sup> form I<sub>2</sub> molecules directly at the electrode surface, and then I<sub>2</sub> facilitates the chemical dissociation of Li<sub>2</sub>O<sub>2</sub> during charging, yielding Li<sup>+</sup> and O<sub>2</sub> gas while I<sup>-</sup> is generated reversibly. It should be noted that, I<sub>3</sub><sup>-</sup> can be formed at a potential (I<sub>3</sub><sup>-</sup>/I<sup>-</sup> 3.28 V) similar to that of I<sub>2</sub> (I<sub>2</sub>/I<sub>3</sub><sup>-</sup> 3.60 V); thus, the following reactions cannot be neglected.



It has been reported that an additional soluble Lil was introduced to cooperate with solid catalysts, such as Co<sub>3</sub>O<sub>4</sub>,<sup>[9]</sup> carbon,<sup>[10]</sup> and RuO<sub>2</sub>/MnO<sub>2</sub>,<sup>[11]</sup> to form a multi-catalyst system. The combination of the RM Lil with a solid catalyst leads to a lower overpotential and enhanced reversibility. The soluble Lil is accessible to the electrode surface and functions as an electron-hole transfer medium between the electrode materials and the solid discharge products, leading to excellent electrochemical performance. The added Lil can also affect the surface morphology of the cathode and the crystallinity of the discharge products.<sup>[12]</sup>

Zhang et al. found that the electrolyte solvent can greatly affect the rate of the reaction between the oxidized RM and  $\text{Li}_2\text{O}_2$ , simultaneously impacting the efficiency of the  $\text{LiI}$  catalytic performance.<sup>[13]</sup> They carried out research on a variety of solvents and discovered that protic solvents, such as  $\text{H}_2\text{O}$  and alcohols, can greatly accelerate the reaction rate due to the hydrogen-bond-assisted solvation of  $\text{Li}_2\text{O}_2$ . Nevertheless, excessive proton activity can also result in undesirable peroxide disproportionation. Further experiments prove that *n*-butanol exhibits the most adaptive proton activity among a series of alcohols to balance the reaction rate and selectivity, as well as dramatically enhance the efficiency of the redox mediators and reduce the overpotential of  $\text{Li}-\text{O}_2$  cells.

Kwak et al. reported that the concentration of  $\text{LiI}$  in the electrolyte is related to the discharge products of  $\text{Li}-\text{O}_2$  batteries.<sup>[12b]</sup> When the concentrations of  $\text{LiI}$  in the ether solutions are high, the existence of the  $\text{LiI}$  facilitates a side reaction generating a primary product  $\text{LiOH}$ .  $\text{Li}_2\text{O}_2$  or the superoxide produced during the ORR process is both a strong alkali and a strong nucleophilic reagent in aprotic solutions, and a competing reaction exists between the nucleophiles with

$\text{Li}^+$  ions and solvent molecules. The high concentration of  $\text{LiI}$  can accelerate the decomposition of  $\text{LiOOH}$  which generates from the E2 elimination reaction with the organic solvent molecules acting as the leaving group, into  $\text{LiOH}$  and  $\text{LiOI}$ . The product can continue to react with additional  $\text{LiOOH}$ , generating  $\text{O}_2$ ,  $\text{LiI}$ , and more  $\text{LiOH}$ , as described in Figure 3. The authors also pointed out that, when the concentration of  $\text{LiI}$  is low, the primary discharge product is  $\text{Li}_2\text{O}_2$  while the content of the by-product  $\text{LiOH}$  is insignificant.

### 2.2.2. Lithium Bromide

$\text{LiBr}$  is similar to  $\text{LiI}$  as a simple Li-halide catalyst. The semblable process can be described as follows: First, the  $\text{X}^-$  ion of the  $\text{LiX}$  salt is converted to  $\text{X}_3^-$ , a polyhalogen anion. Subsequently,  $\text{X}_3^-$  is oxidized to  $\text{X}_2$ , and finally, both  $\text{X}_3^-$  and  $\text{X}_2$  diffuse from the cathode surface to oxidize the discharge product  $\text{Li}_2\text{O}_2$ . As demonstrated in Figure 4 by the cyclic voltammetry test, the  $\text{Br}^-/\text{Br}_3^-$  oxidation runs after the  $\text{I}^-/\text{I}_3^-$  couple. The two oxidation potentials of  $\text{LiBr}$  are 3.48 and 4.02 V, which are higher than those of  $\text{LiI}$  and also slightly higher than the decomposition potentials of both  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$ , which enables investigation of both  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$  oxidation. The redox reactions are as follows:<sup>[11b]</sup>



Kwak et al. demonstrated that the concentration of Li-halide salts and the type of solvents greatly affect cell performance. They also pointed out that although an overdose of the RMs enhances the catalytic effect, side reactions may be induced. After comparing two Li-halide candidates, Kwak et al. concluded that the catalytic effects of  $\text{Li}-\text{O}_2$  cells with  $\text{LiBr}$  are superior to those with  $\text{LiI}$ . Liang's report supported these results, demonstrating that a greater degree of improved

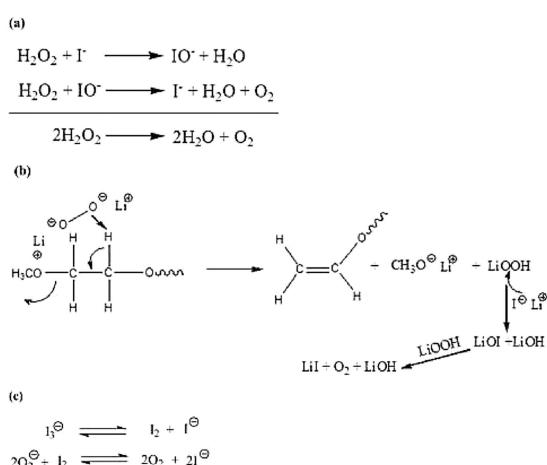


Figure 3. The possible reaction mechanisms of ether solvents in  $\text{Li}-\text{O}_2$  cells containing  $\text{LiI}$ . Reproduced with permission.<sup>[12b]</sup> Copyright 2016, Royal Society of Chemistry.

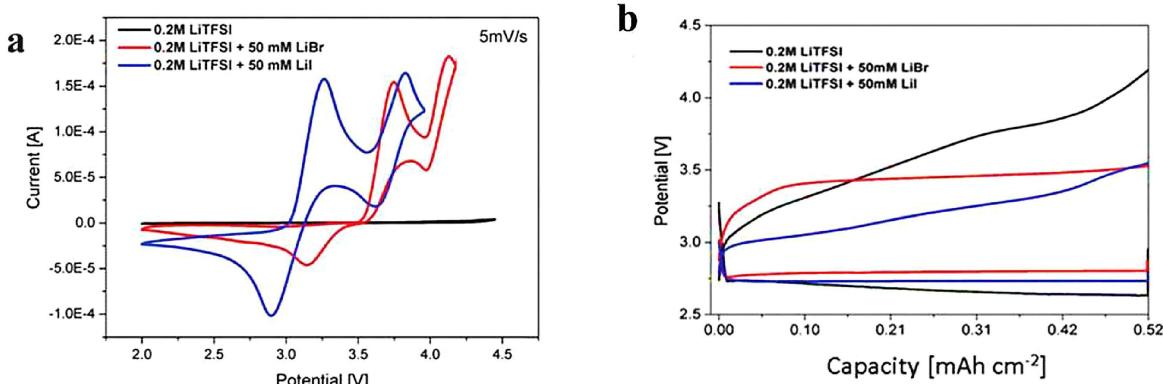
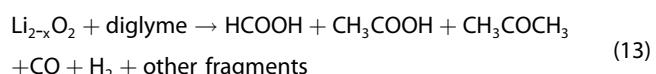


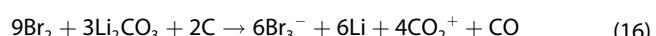
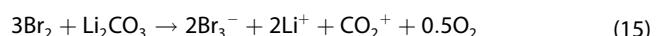
Figure 4. a) Cyclic voltammogram in an argon atmosphere; b) voltage profiles with different diglyme electrolytes. Reproduced with permission.<sup>[14]</sup> Copyright 2016, Royal Society of Chemistry.

stability can be obtained by using LiBr compared than by using LiI.<sup>[14]</sup> The scholars conjectured that this finding could be related to the formation of side products, such as LiOH stemming from the usage of LiI.

Based on the evidence of high temporal resolution online electrochemical mass spectrometry (OEMS) and <sup>1</sup>H NMR, Liang et al. demonstrated that LiBr can improve O<sub>2</sub> recovery efficiency and meanwhile reduce parasitic H<sub>2</sub> and CO evolution. The authors suggested that electrochemical oxidation process generates reactive intermediate species that are aggressive oxidants, yielding H<sub>2</sub> and CO through electrolyte decomposition, and speculated that a plausible expression of the side reaction could be as follows:



In the presence of LiBr, the OER process can convert from electrochemical pathways to chemical ones, which may circumvent the presence of highly reactive Li deficiency species, thereby avoiding electrolyte decomposition in the authors' viewpoint. Liang et al. believed that the by-product Li<sub>2</sub>CO<sub>3</sub> can be oxidized by the dissolved LiBr.<sup>[1b]</sup> First, Br<sub>3</sub><sup>-</sup> is oxidized to Br<sub>2</sub>, followed by the oxidation of Li<sub>2</sub>CO<sub>3</sub> into CO<sub>2</sub> and O<sub>2</sub>; meanwhile, the carbon cathode could be corroded to yield CO:



In summary, LiBr dissolved in electrolyte can decrease the oxidation potential to 3.5 V, and suppress charging side

reactions superior to LiI since its redox potential is higher than that of LiI.

### 2.3. Lithium Nitrate

LiNO<sub>3</sub>, a widely-acknowledged passivation agent for lithium metal has been extensively reported as a capital component in Li–S batteries.<sup>[15]</sup> The nitrate anion forms a protective solid-electrolyte interphase (SEI) on Li metal, mitigating the shuttle effect of the polysulfide in Li–S cells. The passivation process was proposed as follows:<sup>[16]</sup>



In 2013, Wesley et al. first introduced LiNO<sub>3</sub> to Li–O<sub>2</sub> cells and revealed that the stabilization of the Li/electrolyte interface in *N,N*-dimethylacetamide (DMA) is dramatically dependent on the addition of LiNO<sub>3</sub>.<sup>[15a]</sup> A Li–O<sub>2</sub> cell utilizing 1 M LiNO<sub>3</sub>/DMA electrolyte managed to prolong the cycle life to more than 80 cycles without much capacity loss and minimal CO<sub>2</sub> and H<sub>2</sub> gases. After that, the drumbeat of research on the lithium nitrate in other solutions has grown louder. DMSO,<sup>[17]</sup> DME<sup>[18]</sup> and mixed electrolytes<sup>[18b]</sup> were tested, and all demonstrated positive results. Colin et al. investigated the changes in Li<sub>2</sub>O<sub>2</sub> morphology during ORR process by scanning electron microscopy (SEM) with increasing LiNO<sub>3</sub> concentration.<sup>[18c]</sup> When the concentration is 0 M LiNO<sub>3</sub> and 0.01 M LiNO<sub>3</sub>, the morphology of cathodes appeared indistinguishable. With increasing LiNO<sub>3</sub> concentration, the morphology was inclined to form progressively larger toroid structures. These results indicate that LiNO<sub>3</sub> can increase the solubility of the intermediates, which further hastens the solution growth of Li<sub>2</sub>O<sub>2</sub>. Figure 5 demonstrates the discharge voltage profiles of the Li–O<sub>2</sub> cells at different LiNO<sub>3</sub> salt concentrations. The cell capacity was observed to be

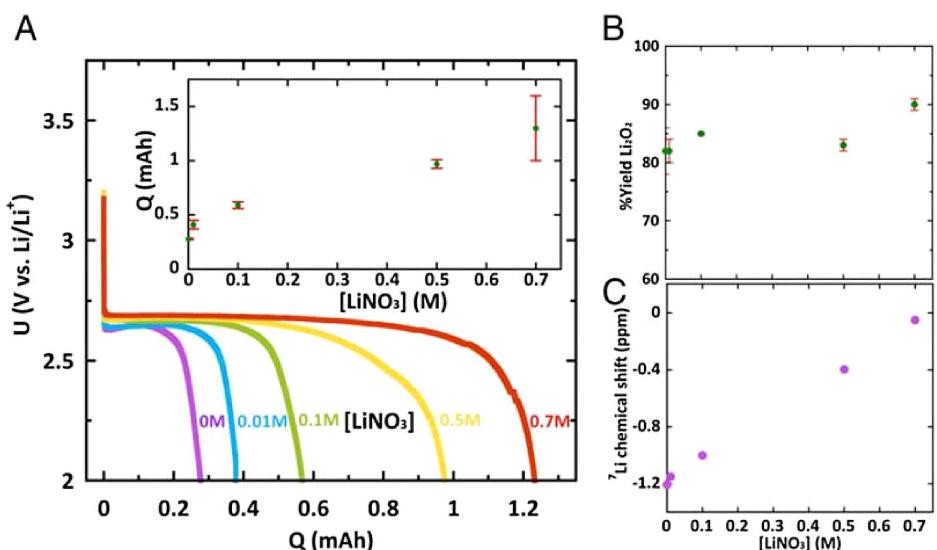


Figure 5. A) Capacity dependence, B) Li<sub>2</sub>O<sub>2</sub> discharge yield, C) <sup>7</sup>Li chemical shift of electrolyte solutions as a function of electrolyte LiNO<sub>3</sub> concentration.<sup>[18c]</sup> Copyright 2015, National Academy of Sciences.

optimized more than fourfold, evidently indicating the significant implication of the  $\text{NO}_3^-$  anion to cell capacity. In addition to the protective effect on the Li anode,  $\text{LiNO}_3$  has also been recently reported by Rosy et al.<sup>[19]</sup> and Kang et al.<sup>[20]</sup> to suppress the oxidative damage of carbon cathode in  $\text{Li}-\text{O}_2$  cells.

Sharon et al. reported in 2015 that  $\text{LiNO}_3$  can act as both an electrolyte and a beneficial RM. They also proposed that  $\text{NO}_2$  formed from  $\text{NO}_2^-$  at approximately 3.6–3.8 V can be an RM that oxidizes the  $\text{Li}_2\text{O}_2$  below 4 V. Hence, the ORR process is performed at relatively low overpotentials after a shuttle interaction of the  $\text{NO}_2/\text{NO}_2^-$  couple.<sup>[18a]</sup>

Although the use of  $\text{LiNO}_3$  as an electrolyte in polyether solutions has numerous benefits, the instability of the polyether solutions for rechargeable  $\text{Li}-\text{O}_2$  batteries remains undeniable. An assortment of side products, including alkoxides and carbonates, derived from solvent decomposition during  $\text{O}_2$  reduction are also inevitable. In order to accelerate the practical  $\text{Li}-\text{O}_2$  battery technology, systematic and careful studies remain a preliminary step.

### 3. Organic Compounds

#### 3.1. Tetrathiafulvalene

In 2013, Bruce and co-workers first proposed tetrathiafulvalene (TTF), which allows battery to recharge at high current densities and low overpotential.<sup>[21]</sup> Figure 6 shows the diminishing charging voltage with the advent of TTF in the system, especially at high rates. The enhanced oxidation kinetics can be elucidated as follows. Solid insulating  $\text{Li}_2\text{O}_2$  particles generated from the ORR process are not in intimate touch with the electrode hence experience the retarded charge transport

during oxidation, resulting in intense polarization without the addition of TTF; whereas, with the presence of TTF, they can be readily oxidized at the surfaces of the electrode, diffused rapidly from the surfaces to  $\text{Li}_2\text{O}_2$  particles, and oxidized. The total result is that the polarization has been greatly reduced due to the fact that the chemical oxidation of the  $\text{Li}_2\text{O}_2$  is faster and easier than the direct electrochemical oxidation.

Pham et al. utilized  $\text{LaNi}_{0.9}\text{Cu}_{0.1}\text{O}_3$  perovskite oxide as the cathode and with TTF in the electrolyte, bringing about remarkable bifunctional catalytic activities in the  $\text{Li}-\text{O}_2$  cells.<sup>[22]</sup> Whittingham et al. explored the electrochemical behavior of TTF in tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte for  $\text{Li}-\text{O}_2$  batteries via synchrotron and lab X-ray diffraction.<sup>[23]</sup> Yang et al. reported straightforward observed results of the formation and decomposition process of  $\text{Li}_2\text{O}_2$  with TTF in the electrolyte for  $\text{Li}-\text{O}_2$  microbattery by means of operando scanning transmission electron microscopy.<sup>[24]</sup> The oxidation reaction of large  $\text{Li}_2\text{O}_2$  particles was found to occur as far as 200–300 nm away from the electrode, rather than at the  $\text{Li}_2\text{O}_2/\text{electrode}$  interfaces. Therefore, the TTF-assisted  $\text{Li}_2\text{O}_2$  oxidation is a diffusion-controlled process. This real-time and real-space study provides an in-depth understanding of the mechanisms of TTF.

In fact, an RM with an equilibrium potential closer to 2.96 V, which is the theoretical redox potential for  $\text{Li}_2\text{O}_2$  oxidation, would further reduce the polarization. The redox potential of TTF is 3.65 V, which can be lowered by modifying TTF with electron-donating groups. As far as we know, this modified research of TTF has not been reported but might be fulfilling.

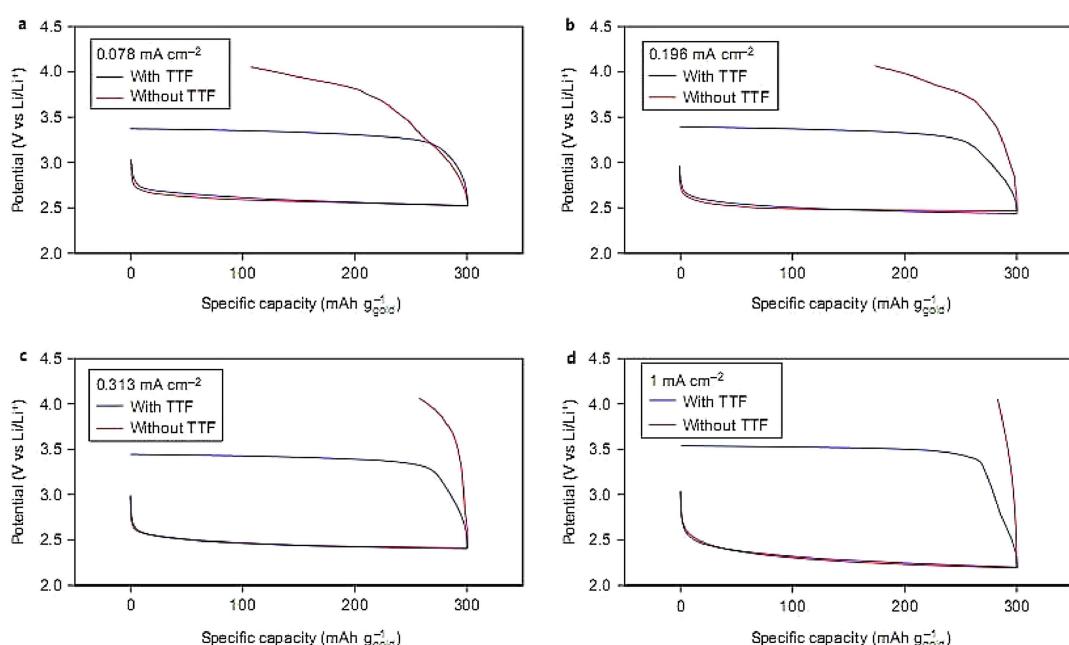
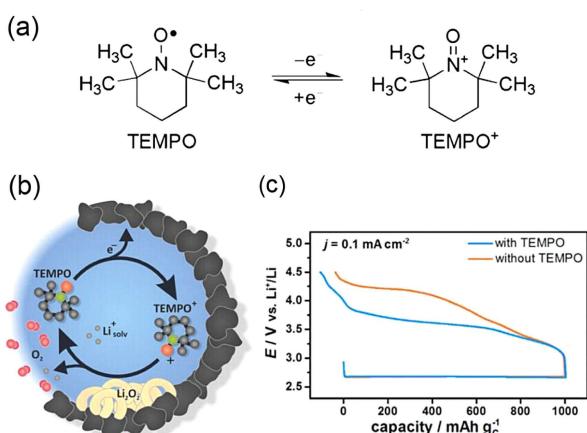


Figure 6. The discharge/charge curves with and without TTF. Reproduced with permission.<sup>[21]</sup> Copyright 2013, Macmillan Publishers Limited.



**Figure 7.** a) Scheme of TEMPO<sup>+</sup>/TEMPO. b) The proposed catalytic cycle mechanism. c) The initial voltage profiles with and without TEMPO. Reproduced with permission.<sup>[25]</sup> Copyright 2013, Macmillan Publishers Limited.

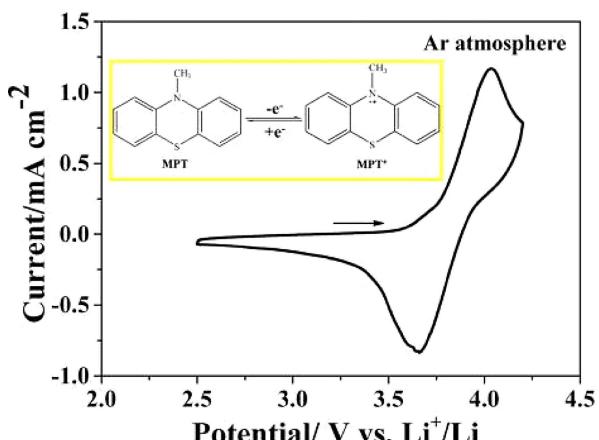
### 3.2. 2,2,6,6-Tetramethylpiperidinyloxy and Its Derivatives

2,2,6,6-Tetramethylpiperidinyloxy (TEMPO) is a persistent radical that belongs to the chemical class of nitroxides. Figure 7a shows its reversible one-electron reaction with TEMPO<sup>+</sup>, the corresponding N-oxoammonium cation. Moreover, TEMPO and its derivatives have been intensively utilized as catalysts in organic reactions and as additives for overcharge protection in Li-ion batteries. Bergner and his coworkers first introduced TEMPO as a homogeneous catalyst for aprotic Li–O<sub>2</sub> cells, providing an unprecedented reduction of the overpotential by 500 mV and leading to doubling of the cycle life.<sup>[25]</sup> In detail, the proposed catalytic cycle of the dissolved RMs TEMPO comprises two parts, as illustrated in Figure 7b. In addition, the same research group reported the joint application of a solid electrolyte to protect the lithium anode from adverse side reactions with TEMPO dissolved in the electrolyte. Combining TEMPO with a solid electrolyte was a highly efficient way for stable charging. In conclusion, more researches should be dedicated to exploring the prolonged stability of Li–O<sub>2</sub> cells with TEMPO as an RM.

### 3.3. N-Methylphenothiazine

Phenothiazine and its derivatives have a robust aromatic core and have been reported for overcharge protection in Li-ion batteries. N-Methylphenothiazine (MPT) is a representative of phenothiazines, and it can be readily oxidized to its cation state, MPT<sup>+</sup> (inset of Figure 8).

Our group reported that a significant decrease in charge overpotential and a better round-trip efficiency close to 76% enabled MPT to be a promising RM in Li–O<sub>2</sub> batteries.<sup>[26]</sup> The redox potential of MPT is tested to be 3.67 V vs Li<sup>+</sup>/Li, which is higher than the formation potential of Li<sub>2</sub>O<sub>2</sub> (2.96 V). The higher voltage of the RMs is an essential prerequisite, indicating that the oxidation state of MPT can oxidize Li<sub>2</sub>O<sub>2</sub>. In general, MPT



**Figure 8.** Cyclic voltammograms containing 0.1 M MPT in TEGDME electrolyte. Inset shows the MPT/MPT<sup>+</sup> couple. Reproduced with permission.<sup>[26a]</sup> Copyright 2017, American Chemical Society.

exerts great influence on the OER process for Li–O<sub>2</sub> batteries,<sup>[27]</sup> it can reduce the polarization upon charging, improve the rechargeability and energy efficiency, as well as suppress the parasitic reactions at high potentials.

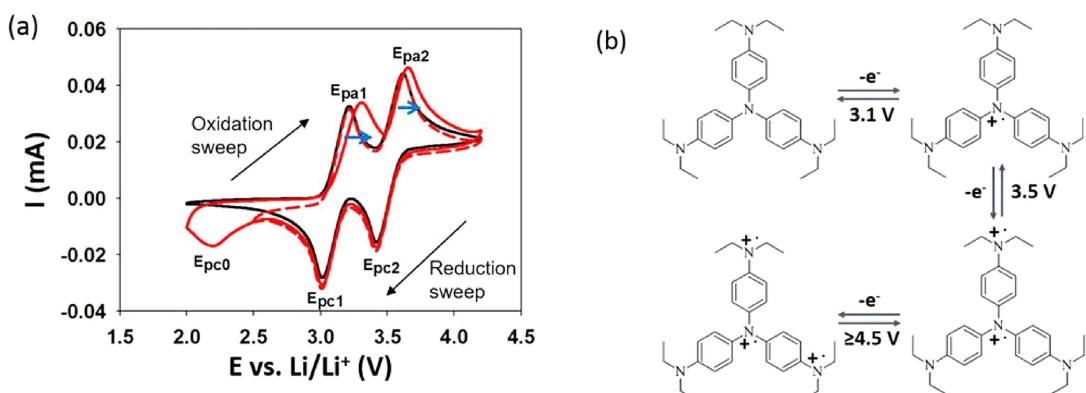
### 3.4. Tris[4-(diethylamino)phenyl]amine

Triphenylamine, which belongs to the triphenylamine class of molecules, is also a redox shuttle additive for preventing overcharging in Li-ion batteries.<sup>[28]</sup> In 2015, Nazar's group reported tris[4-(diethylamino)phenyl]amine (TDPA) as a valid soluble catalyst for a Li–O<sub>2</sub> battery.<sup>[1c]</sup> The diethylamino group, which is an electron-donating group in the molecule of TDPA can lower the redox potential to 3.1 V, which remains the closest to the equilibrium potential of Li<sub>2</sub>O<sub>2</sub> reduction and oxidization among the RMs reported up to now.

Figure 9a displays the cyclic voltammetry plots using the electrolyte of 0.1 M LiTFSI and 5 mM TDPA in TEGDME. The two peaks located at 3.1 and 3.5 V refer to the redox couples of TDPA/TDPA<sup>+</sup> and TDPA<sup>+</sup>/TDPA<sup>2+</sup>, respectively. Notably, the first redox couple of TDPA/TDPA<sup>+</sup> at 3.1 V is the closest to 2.96 V compared with the other RMs in Li–O<sub>2</sub> cells. TTF, which has been recommended in the previous section, analogously has two redox couples, TTF/TTF<sup>+</sup> (at 3.65 V) and TTF<sup>+</sup>/TTF<sup>2+</sup> (at 3.87 V). Using an RM with a relatively lower redox voltage may provide a better energy efficiency, and from this point of view, TDPA has its unique advantage. Research on this unique molecule as an RM is very limited, and we anticipate that further modifying the molecule may lead to fancy and dramatic outcomes for promoting the energy efficiency for Li–O<sub>2</sub> cells.

### 3.5. Iron Phthalocyanine

Iron phthalocyanine (FePc), a kind of quinone, can be dissolved in some organic electrolytes, such as DMSO and TEGDME, rather than in aqueous electrolytes. Sun and his co-workers



**Figure 9.** a) Cyclic voltammograms. b) The TDPA redox couples and the corresponding redox potentials. Reproduced with permission.<sup>[1c]</sup> Copyright 2015, American Chemical Society.

reported the organic-electrolyte-dissolved FePc as an additive in a Li-air cell.<sup>[4]</sup> FePc is tooless to bond with O<sub>2</sub> and LiOOLi because the positive core of the Fe<sup>II</sup> ion can attract the nonbonding 2p orbitals of an O<sub>2</sub> molecule, which was confirmed by UV-Vis absorption spectra. As a consequence, when FePc is performed as the catalyst for Li-O<sub>2</sub> cells, it acts not only as a soluble catalyst, but also as a shuttle of (O<sub>2</sub>)<sup>-</sup> species between the surface of the electrode and the Li<sub>2</sub>O<sub>2</sub> product.

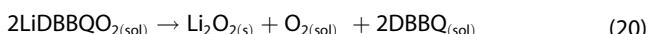
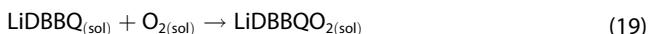
The catalysis mechanism of the FePc is illustrated in Figure 10, and the authors proposed a two-step transformation mechanism of “(FePc-O<sub>2</sub>) $\rightarrow$ (FePc-O<sub>2</sub>)<sup>-</sup> $\rightarrow$ (FePc-LiOOLi)”. In general, the FePc-O<sub>2</sub> molecule acts as a shuttle of electrons. First, it forms (FePc-LiOOLi) near the electrode surface and then moves to Li<sub>2</sub>O<sub>2</sub> sites. Such a catalyzed route is in accordance with the SEM observation results, which showed that the FePc additive altered the morphology of the discharge product Li<sub>2</sub>O<sub>2</sub> (Figure 10c-g). When FePc is not added, the surface of the carbon fibers (CFs) are covered by the Li<sub>2</sub>O<sub>2</sub> formed during discharge, whereas when FePc is added into the solution, Li<sub>2</sub>O<sub>2</sub> may form away from the carbon surface in the electrolyte solution. These morphological changes further confirm that with the presence of FePc, the Li<sub>2</sub>O<sub>2</sub> blocking effect is avoidable to some extent, further enhancing capacity and reversibility.

### 3.6. 2,5-Di-tert-butyl-1,4-benzoquinone

2, 5-Di-tert-butyl-1,4-benzoquinone (DBBQ) is a typical kind of quinone compound that is known to have great solubility in organic electrolytes and can mediate the reduction of O<sub>2</sub> molecules. Bruce's group first reported that DBBQ, as an ORR catalyst for Li-O<sub>2</sub> cells, can promote solution phase nucleation of Li<sub>2</sub>O<sub>2</sub> in aprotic solutions, averting the clogging of the cathode.<sup>[29]</sup>

Figure 11a-d shows the discharge curves of O<sub>2</sub> reduction with and without DBBQ under O<sub>2</sub> at different current densities. In the presence of DBBQ, the discharge capacity of the cells delivered a remarkable increase up to ~80-100 times than

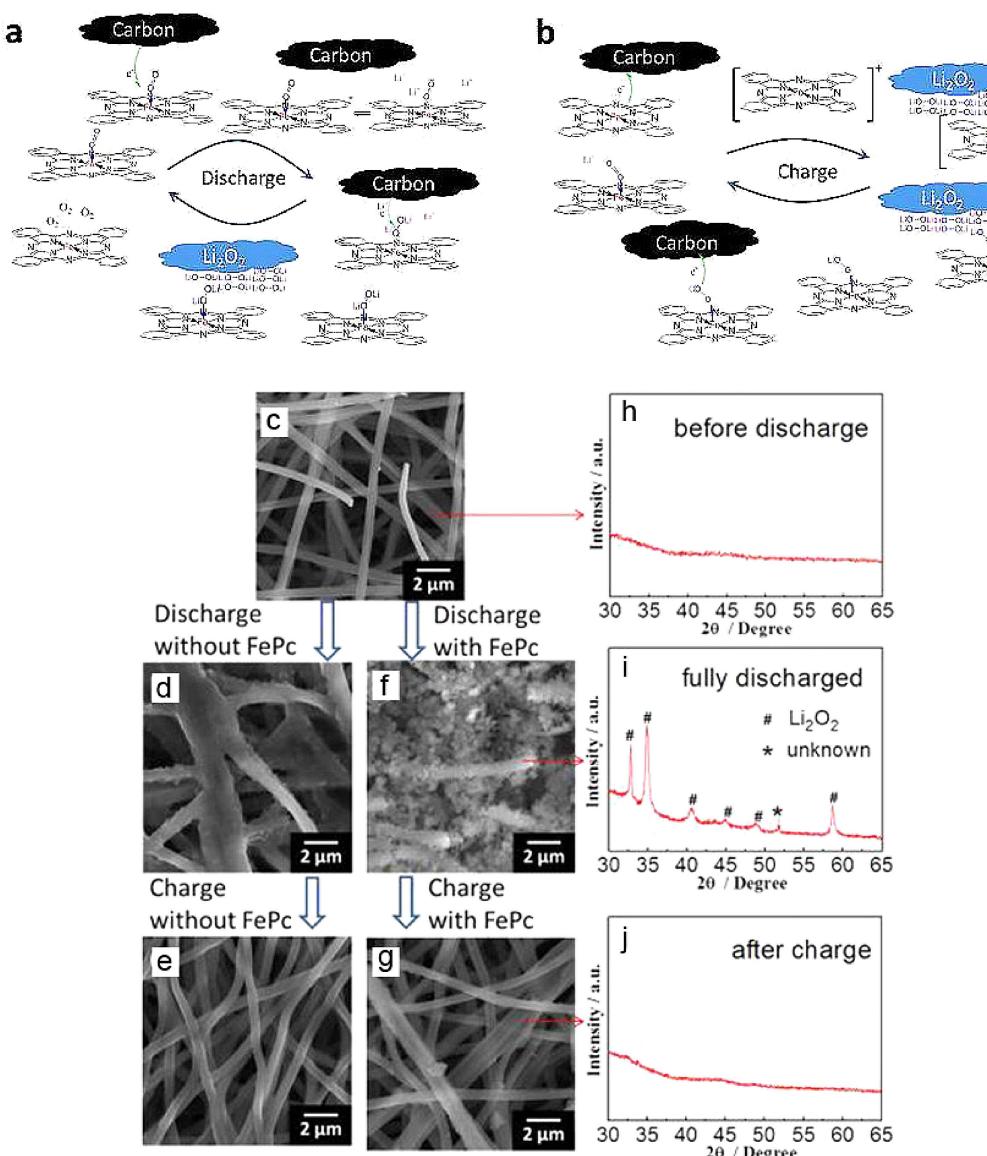
those without DBBQ; meanwhile the discharge overpotential is reduced by half. The mechanism of O<sub>2</sub> reduction in the presence of DBBQ is illustrated in Figure 11e. As shown, given that DBBQ is a kind of quinine, the initial electrochemical reduction step is to form Li-quinone complexes LiDBBQ (Equation 18). In a common Li-O<sub>2</sub> cell without DBBQ, reduction of O<sub>2</sub> to Li<sub>2</sub>O<sub>2</sub> proceeds through the LiO<sub>2</sub> intermediate, while with DBBQ in the electrolyte, it has been circumvented replaced by the complex of LiDBBQO<sub>2</sub> (Equation 19). By forming the new intermediate complex, the reaction pathway is changed; hence, the free energy of the LiDBBQO<sub>2</sub> is lowered. Subsequently, the intermediate LiDBBQO<sub>2</sub> could disproportionate or react with another LiDBBQ, to form Li<sub>2</sub>O<sub>2</sub> that grows in solution (Equations 20 and 21).



As mentioned above, DBBQ works in a new, distinct mechanism that alters the pathway of O<sub>2</sub> reduction while staving off the intermediate of LiO<sub>2</sub>. However, the additive of DBBQ can only take effect on the ORR process, and tries to recharge the cell after discharge turned out unavailing. It is essential to apply a mediator for the OER process simultaneously, which will be discussed in the latter part.

### 3.7. 2,2,2-Trichloroethyl Chloroformate

In 2019, our group for the first time reported the 2,2,2-trichloroethyl chloroformate [ClC(O)OCH<sub>2</sub>CCl<sub>3</sub>, TCCF] as an additive in ether electrolyte. The Li-O<sub>2</sub> cells with this soluble RM have demonstrated a glorious rate capability of 2005 mAh g<sup>-1</sup> at high current densities. Moreover, a stable SEI layer with rich Li salt content formed on the surface of the Li



**Figure 10.** Possible discharge (a) and charge (b) cycles for FePc. c)–g) SEM images of the cathodes before and after discharge and charge with and without FePc catalyst. h)–j) XRD pattern of the cathode before and after discharge, and after charge with FePc in the electrolyte. Reproduced with permission.<sup>[4]</sup> Copyright 2014, American Chemical Society.

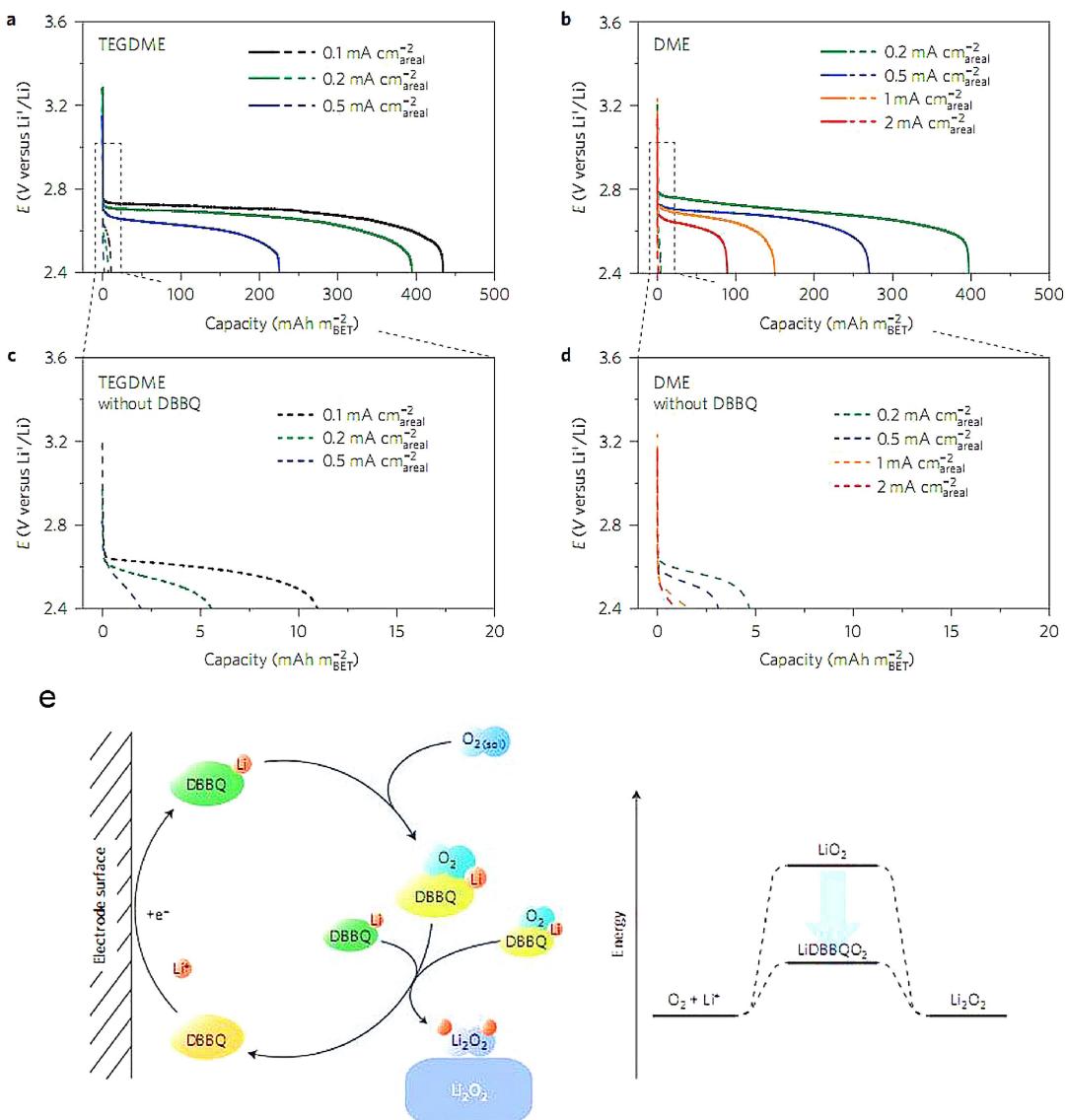
metal electrode, accelerating the electronic transport and restraining the parasitic reactions between Li metal and electrolyte, as displayed in Figure 12.

### 3.8. Other Compounds

Compared with inorganic compounds, there are greater quantities of organic molecules that can act as RMs. Nasybulin et al. reported poly(3,4-ethylenedioxythiophene) (PEDOT), an organic conjugated polymer, as a catalyst for both ORR and OER in Li–O<sub>2</sub> batteries; the charging voltage has been decreased by 0.7~0.8 V for the first cycle.<sup>[30]</sup> In addition to polymer molecules, biomolecules also aroused the interest of scientists. Ryu et al. found that the heme molecule, an usual porphyrin cofactor in blood that has O<sub>2</sub> binding capability, can

serve as an RM and O<sub>2</sub> shuttle for the OER process of Li–O<sub>2</sub> batteries.<sup>[31]</sup> In addition, other organic molecules such as viologen and its derivatives,<sup>[3a,32]</sup> tris(2,4,6-trichlorophenyl)methyl (TTM),<sup>[33]</sup> phenol,<sup>[34]</sup> 5,10-dimethylphenazine (DMPZ),<sup>[3b]</sup> and so on,<sup>[35]</sup> have so far been reported as RMs for Li–O<sub>2</sub> cells. Due to the limited space here, I will not detail them in this article.

On account of organic compounds serving as a soluble catalyst, it would be effortless to tune the redox performance by molecular design or engineering. Hodgson et al. presented theoretical steps for the determination of the potentials of nitroxides and deliberated the effect of substituents on these systems.<sup>[35]</sup> Their results indicate that, except by common means of trial-and-error, theoretical calculation is also an effective and low-cost route to the discovery and design of new redox shuttles. We believe that a rational and ingenious



**Figure 11.** a-d) Notable effect of DBBQ on discharge. e) Sketch map of reactions on discharge with DBBQ and the effect of DBBQ on the potential determining step. Reproduced with permission.<sup>[29]</sup> Copyright 2016, Macmillan Publishers Limited.

design of an RM will inaugurate a new era of highly efficient catalysts for  $\text{Li}-\text{O}_2$  batteries.

## 4. Dual Mediators

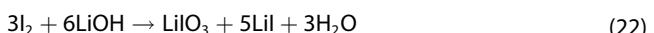
### 4.1. Inorganic Compounds

#### 4.1.1. $\text{H}_2\text{O}$ and $\text{LiI}$

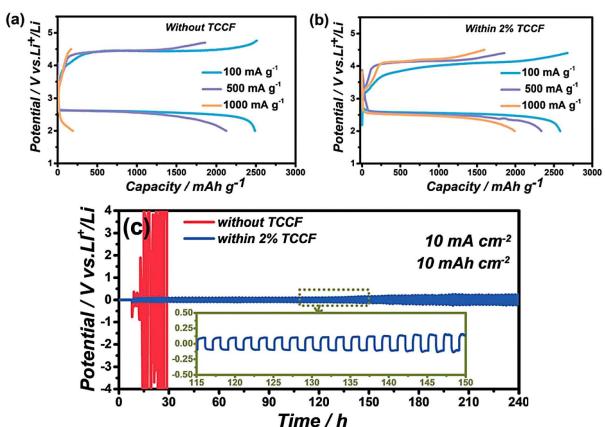
In 2015, Grey's group first reported reversible  $\text{Li}-\text{O}_2$  cells through formation and decomposition of  $\text{LiOH}$ , which is different from the previous reports, in which the discharge product mainly constitutes  $\text{Li}_2\text{O}_2$ .<sup>[36]</sup> With reduced graphene oxide serving as cathode,  $\text{LiI}$  as the additive, and dimethoxyethane as the solvent, high specific capacities and impressive rechargeability with a voltage gap of merely 0.2 V have been

achieved. Moreover, the cells are insensitive to relatively high  $\text{H}_2\text{O}$  content, creating no appreciable change in the electrochemical profile (Figure 13). The discharge and charge reaction mechanisms have also been proposed.

However, Burke et al. reported contrasting results,<sup>[37]</sup> demonstrating that  $\text{LiOH}$  does not decompose at the low potential plateau (~3 V plateau in Liu's report) but can be decomposed at a voltage higher than 3.5 V, with no  $\text{O}_2$  produced. They speculated the feasible reaction as follows:



According to their studies, the reaction between  $\text{LiOH}$  and  $\text{I}_2$  can yield  $\text{LiIO}_3$  without generating  $\text{O}_2$ . Hence, they concluded that  $\text{LiI}$  plus  $\text{H}_2\text{O}$  is not a good additive due to the lack of  $\text{O}_2$  production from the  $\text{Li}_2\text{O}_2/\text{LiOH}$  oxidation process, in spite of the reduced charge overpotential in  $\text{LiI}$ -containing cells.



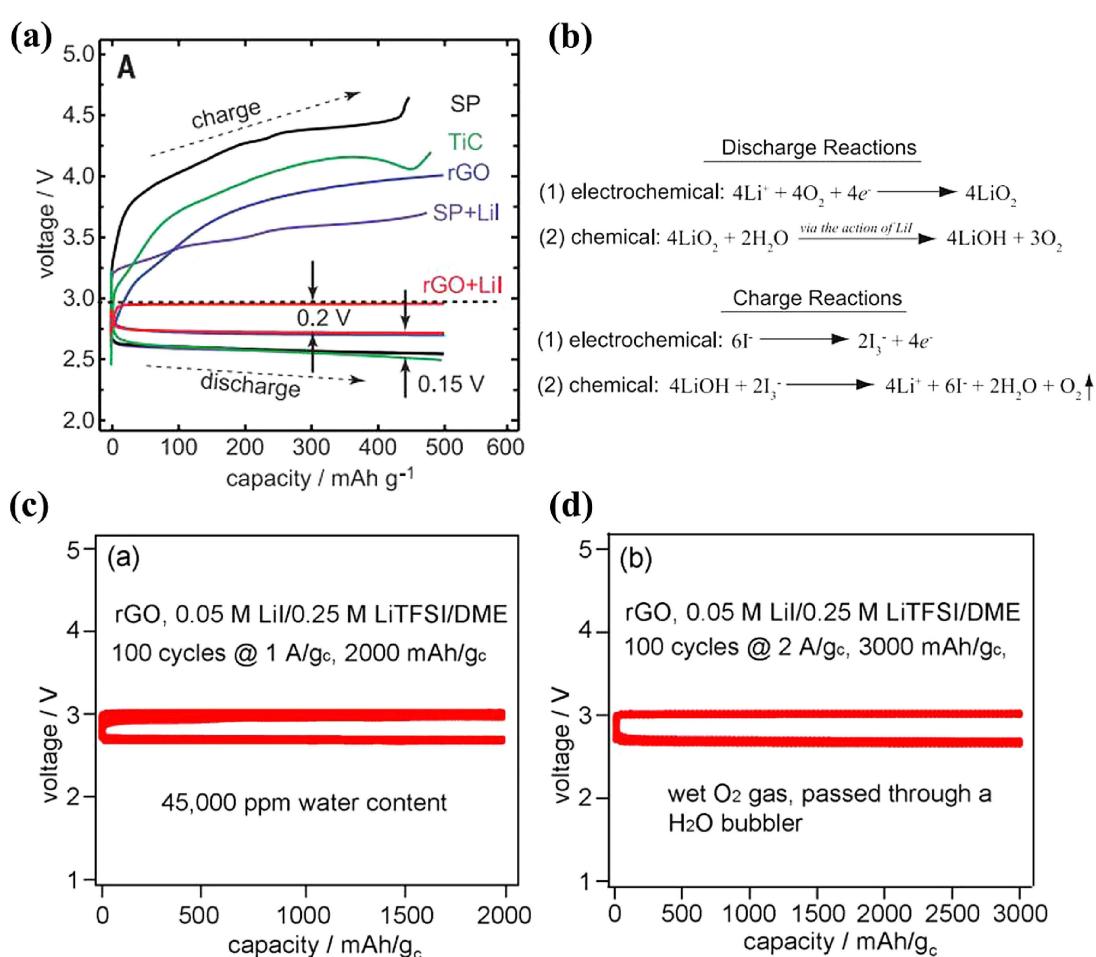
**Figure 12.** Discharge-charge profiles of Li–O<sub>2</sub> cells cycling in electrolyte a) without and b) with TCCF at current densities of 100, 500, and 1000 mA g<sup>-1</sup>; c) voltage profiles of symmetric cells at current densities of 100 mA cm<sup>-2</sup>. Reproduced with permission.<sup>[30]</sup> Copyright 2019, Wiley-VCH.

Yang's group in Massachusetts Institute of Technology reported their studies on the influence of different ratios of H<sub>2</sub>O:Lil for Li–O<sub>2</sub> batteries, and they discovered that at low

H<sub>2</sub>O:Lil ratios (< 5), LiOH was formed without the presence of Li<sub>2</sub>O<sub>2</sub>, coupled with the oxidation of iodide to triiodide; at high H<sub>2</sub>O:Lil ratios (12, 24, and 134), Li<sub>2</sub>O<sub>2</sub>, LiOOH·H<sub>2</sub>O, and LiOH·H<sub>2</sub>O were all detected.<sup>[38]</sup> The strong I–H<sub>2</sub>O interactions at low H<sub>2</sub>O:Lil ratios (< 5) may be accountable for yielding LiOH instead of Li<sub>2</sub>O<sub>2</sub> at the presence of Lil and H<sub>2</sub>O, as further confirmed by <sup>1</sup>H NMR and FT-IR.

Qiao et al. probed into the role of Lil and additional H<sub>2</sub>O by employing various spectroscopic analyses, finding that I<sup>–</sup>/I<sub>3</sub><sup>–</sup> RM can promote the inevitable decomposition of the electrolyte and the formation of byproducts, while H<sub>2</sub>O can relieve the superoxide-related nucleophilic attack and promote the deactivation of iodide, contributing to the survival of hydroperoxide and converting LiOH into Li<sub>2</sub>O<sub>2</sub>, which is novel and interesting.<sup>[39]</sup>

In summary, there are still controversy and inconformity on the complex reaction in the presence of O<sub>2</sub>, H<sub>2</sub>O, and iodine for Li–O<sub>2</sub> system and further mechanistic research is certainly necessary to understand the functions of the additives in the redox process,<sup>[6b,40]</sup> which is critical for the practical applications of Lil in Li–O<sub>2</sub> batteries.



**Figure 13.** a) Discharge-charge plots for Li–O<sub>2</sub> cells using various electrode materials. For SP and rGO, Lil was added to the electrolyte. b) Schematic mechanisms for the iodide mediated Li–O<sub>2</sub> cells in the presence of water. The voltage profiles c) with 45,000 ppm of water; b) purged with wet O<sub>2</sub> gas through a water bubbler. Reproduced with permission.<sup>[37]</sup> Copyright 2015, American Association for the Advancement of Science.

#### 4.1.2. $\text{LiNO}_3$ and $\text{LiBr}$ , $\text{LiNO}_3$ and $\text{CsI}$

Xin et al. reported that by using dual and mixed anions  $\text{Br}^-/\text{NO}_3^-$  in the electrolyte, overcharge potential can be reduced, and Li dendrite formation can also be suppressed, resulting in better cycling life and higher coulombic efficiency.<sup>[41]</sup> The  $\text{Br}^-/\text{Br}_3^-$  redox chemically oxidizes  $\text{Li}_2\text{O}_2$  at the cathode; meanwhile, the  $\text{NO}_3^-$  anion oxidizes the Li at the anode. The formation of  $\text{Li}_2\text{O}$  on the Li anode for the  $\text{Li}-\text{O}_2$  cells with the presence of  $\text{LiNO}_3$  was initially proposed by Uddin et al.,<sup>[42]</sup> and the reaction mechanism has been conjectured as follows:



$\text{NO}_3^-$  anion oxidizes metal Li to produce  $\text{Li}_2\text{O}$  and  $\text{NO}_2^-$ , and the  $\text{NO}_2^-$  can be subsequently oxidized to  $\text{NO}_3^-$  by  $\text{O}_2$  molecules. The presence of  $\text{NO}_3^-$  can result in a stabilized and dense thin layer of  $\text{Li}_2\text{O}$  on the Li anode, which availably hinder the shuttle of  $\text{Br}_3^-$  to the anode. As a result, the surface of the anode was smooth and showed no Li dendrite after cycling. Their results suggest that the mixed  $\text{Br}^-/\text{NO}_3^-$  anions acted synergistically to inhibit both side reactions and dendrite formation at the anode.

Park et al. reported the use of RMs of  $\text{LiI}$ ,  $\text{CsI}$ , as well as  $\text{LiNO}_3$  and  $\text{CsI}$ , in the electrolyte for improved  $\text{Li}-\text{O}_2$  batteries.<sup>[43]</sup> The introduction of RMs availably reduced the overpotential and ameliorated the cyclability of the electrodes. In special, with the presence of both  $\text{CsI}$  and  $\text{LiNO}_3$  added in the electrolyte, the best results have been obtained. The shielding effect of the  $\text{Cs}^+$  and the catalyst of the  $\text{I}^-$  from  $\text{CsI}$  may be responsible for the low overpotential, while  $\text{LiNO}_3$  also suppresses side reactions and stabilizes the Li anode. The synergistic effect of  $\text{CsI}$  and  $\text{LiNO}_3$  as soluble catalysts leads to a remarkable cyclability of more than 250 cycles.

#### 4.2. Organic Compounds

Bruce's group reported in 2017 that dual organic mediators play a good role for  $\text{Li}-\text{O}_2$  cells by utilizing DBBQ on ORR and TEMPO on OER process, leading to the suppressed overpotentials and the stabilized carbon cathode.<sup>[44]</sup> Figure 14 illustrates the electrode reactions in the presence of the dual mediators. The mechanisms of DBBQ-mediated  $\text{O}_2$  reduction and TEMPO-mediated  $\text{Li}_2\text{O}_2$  oxidation process have been described in the preceding text. When the two RMs combine, they can function on both discharge and charge process, resulting in significant enhancement of carbon stability. Moreover, the deposition and growth of  $\text{Li}_2\text{O}_2$  occur in the solution rather than at the electrode surface, which can mitigate the limitations on rate and capacity.

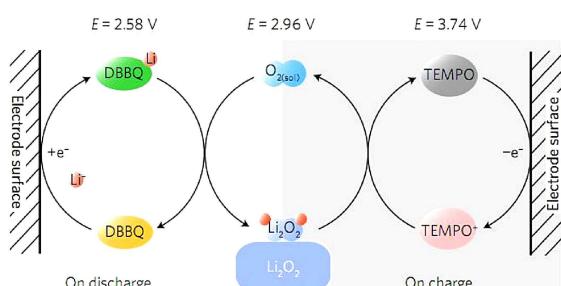


Figure 14. Sketch map of electrode reactions in the presence of DBBQ and TEMPO. Reproduced with permission.<sup>[45]</sup> Copyright 2017, Macmillan Publishers Limited.

#### 4.3. Organic and Inorganic Compounds: TTF and $\text{LiCl}$ , BQ and TPP

Zhang et al. reported that by combining TTF with  $\text{LiCl}$  as dual mediators, an organic conductor of  $\text{TTF}^+\text{Cl}_x^-$  precipitates and deposits on the cathode of a  $\text{Li}-\text{O}_2$  cell.<sup>[45]</sup> The as-formed  $\text{TTF}^+\text{Cl}_x^-$  not only limits the movement of  $\text{TTF}^+$ , eliminating the attacks towards the anode, but also provides an additional electron-transfer pathway from both the precipitates and the electrode to the surface of  $\text{Li}_2\text{O}_2$  (Figure 15). The exquisite design greatly improved the electron transport efficiency of  $\text{Li}_2\text{O}_2$ . Figure 15b evidently shows that the alliance of TTF and  $\text{LiCl}$  immensely improved the cycling stability of  $\text{Li}-\text{O}_2$  batteries. Without  $\text{LiCl}$ , mobile  $\text{TTF}^+$  in the electrolyte suffers severe accumulation problem, thereby explaining the limited cycling performance.

Dong et al. introduced dual RMs to Mg-O<sub>2</sub> batteries: 1,4-benzoquinone on the discharge process and 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) [Co(II)TPP] on the charge process.<sup>[46]</sup> The two mediators are compatible to suppress the overpotential and enhance the energy efficiency of  $\text{Li}-\text{O}_2$  cells.

In summary, research on dual mediators has just started to become popular in the last several years. The two mixed components can work synergistically in the electrolyte to dramatically reduce the charge overpotential, thereby suppressing parasitic reactions and gaining high energy efficiency. The dual-mediator system will serve as an important step toward realizing the  $\text{Li}-\text{O}_2$  batteries.

#### 5. Challenges

The soluble redox mediators have the advantages of their mobility; however, their mobility also brings up the weakness: the RMs may migrate from the cathode side toward the Li metal anode, and degrade the cycle life of the cell, which is the greatest challenge for RMs now. Researchers have found some remedies to solve this problem, and we summarize them into three aspects: modification of the separator, protection on the Li metal anode, and solid electrolyte for  $\text{Li}-\text{O}_2$  cells. Moreover, designing and searching for the electrolyte with absolute

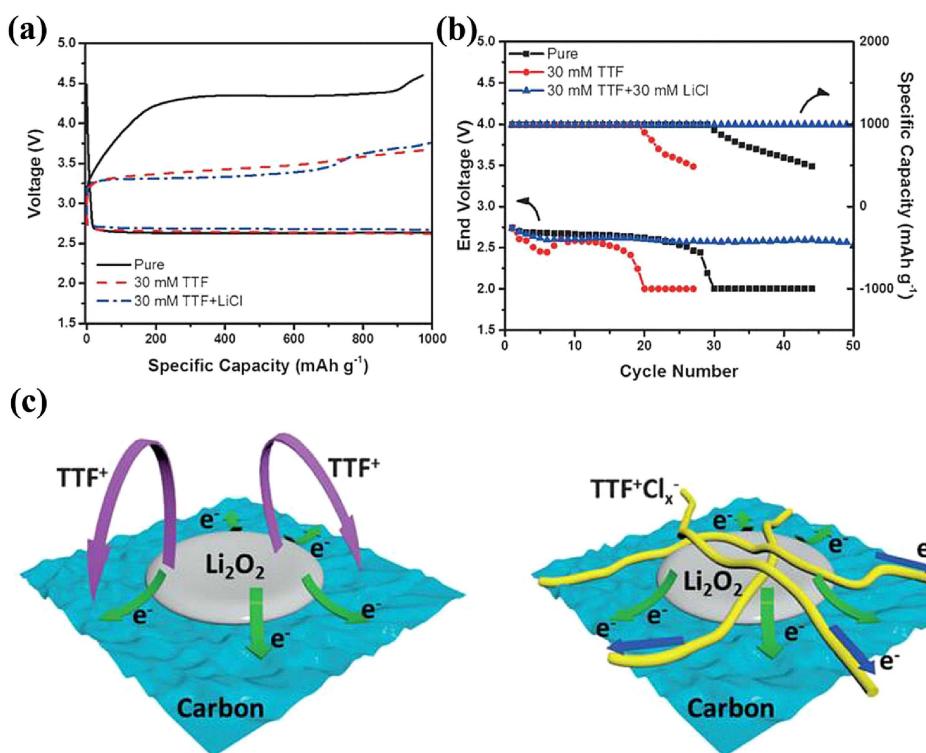


Figure 15. a) The voltage profiles and b) the cycling plots with different electrolytes. c) Schematic diagram of the mechanism of  $\text{TTF}^+\text{Cl}_x^-$ . Reproduced with permission.<sup>[46]</sup> Copyright 2017, Wiley-VCH.

stability is of vital importance as almost all electrolytes suffer from decomposition in this system.

### 5.1. Modification of the Separator

The separators are not only indispensable but also crucial for the batteries. Through the modification of the separators, the migration of the RM molecules towards the anode can be effectively deterred and prevented, thereby prolonging battery life. In the meantime, the electrolyte wettability of the modified separators should also be taken into account. Sun's group reported the modification of the separator with a negatively

charged polymer mixture. When DMPZ is used as an RM, it is found that the modified separator coated by a polymer mixture of PEDOT:PSS [poly(3,4-ethylenedioxythiophene) poly-styrene sulfonate] is able to suppress the migration of DMPZ toward the counter electrode of the Li metal anode.<sup>[47]</sup> SEM, XPS, XRD, visual experiment, and electrochemical test were carried out to confirm whether the polymer-modified separator can suppress Li degradation, as well as improve the cycling performance and energy efficiency. The working mechanism of Li–O<sub>2</sub> batteries with modified separator is illustrated in Figure 16.

Some researchers from Choi's group advocated a cheap but feasible polyurethane (PU) separator to curb the crossover of H<sub>2</sub>O and O<sub>2</sub> from the air-cathode side and achieve the

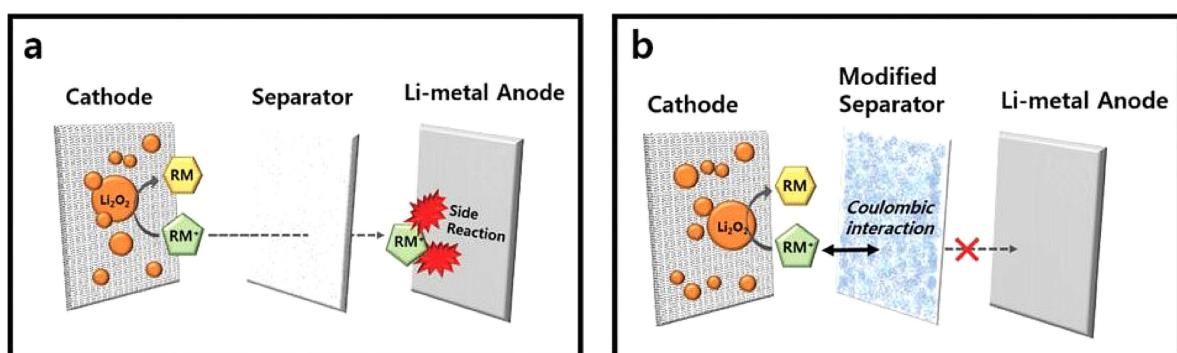


Figure 16. Sketch maps of the operating mechanisms of Li–O<sub>2</sub> batteries using the a) ordinary separator and b) modified separator. Reproduced with permission.<sup>[48]</sup> Copyright 2017, Wiley-VCH.

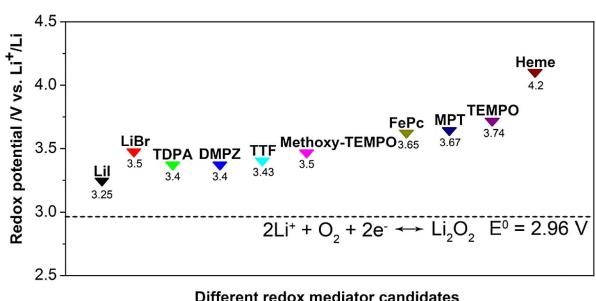


Figure 17. Redox potentials of soluble catalyst candidates.

prolonged cycle life of the Li–O<sub>2</sub> cells.<sup>[48]</sup> SEM and FT-IR were also utilized to prove the enhanced cyclability of the cells (reaching 110 cycles, which is considerably more than that of the Li–O<sub>2</sub> cell with porous polyethylene separator). In fact, the poreless property of the PU separator bears staves off the unexpected and fatal collapse of Li metal interface and promotes decent Li<sup>+</sup> ion diffusion through the system. In addition, the nonporosity of this separator was verified for the Li metal protection from an RM, optimizing the cycling performance (over 200 cycles). In conclusion, scientific researchers must conduct more studies on the modification of separators, which can effectively improve the degradation of the cycle life.

## 5.2. Protection of the Lithium-Metal Anode

In order to prevent the attack from the oxidized RM molecules, in situ protection of the Li anode by forming a protective film was confirmed to be one of the efficient paths. In 2015, Jung-Ki Park and Hee-Tak Kim demonstrated a well-performed Li–O<sub>2</sub> battery by synergistically combining an RM and a protected lithium (Li) metal electrode coated with a composite protective layer (CPL).<sup>[49]</sup> They suggested that the redox reaction between the RM and Li metal can be greatly inhibited due to the existence of the CPL, thereby maintaining the function of RM without serious self-discharge and receiving an extended cycle life. In order to verify the feasibility, the researchers designed a Li–O<sub>2</sub> battery with TEMPO as an RM and Al<sub>2</sub>O<sub>3</sub>/PVdF-HFP composite as CPL.

Our group devised a self-defense RM (SDRM) of InI<sub>3</sub> to alleviate the shuttle phenomenon in DMSO with a Lil RM, where soluble I<sub>3</sub><sup>-</sup> was observed to be migrating towards a Li anode. A partially-dissolved Lil was obtained, contributing to the loss of the RM and energy efficiency.<sup>[50]</sup> In fact, the introduction of InI<sub>3</sub> to form a protective indium layer on a Li anode was originally used to mitigate the serious attack of I<sub>3</sub><sup>-</sup>. However, surprisingly, the results also indicated that the SDRM even inhibited the growth of Li dendrite and the formation of Li alloying, which consequently leads to more favorable electrical energy efficiency and better cycling performance.

## 5.3. Solid Electrolytes for Lithium-Oxygen Cells

The application of solid electrolytes (SE) to separate the anode and the cathode for Li–O<sub>2</sub> cells prevents the oxidation of the anode and other unfavorable side reactions. Benjamin et al. reported a promising aprotic Li–O<sub>2</sub> cell by introducing a solid electrolyte in conjunction with high RM concentrations.<sup>[51]</sup> The improved cyclability of this battery can be attributed to the protection of the Li anode from the SE membrane, which greatly impedes the deactivation of the oxidized species. The application of the SE also includes eradication of any detrimental side reactions occurring at the carbon electrode and stabilizing the charging process. Besides, the high concentrations of RM can enlarge the discharge capacity for making RM as part of the storage energy. In the research of N-methylphenothiazine (MPT) by Feng et.al, a solid electrolyte, Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub>, was used to eradicate the shuttle of MPT molecules to the anode.<sup>[26a]</sup> In conclusion, the use of a Li<sup>+</sup> selective solid electrolyte to protect the Li anode is a crucial and promising route towards practical Li–O<sub>2</sub> batteries.

A good number of reports used partially charged LiFePO<sub>4</sub> instead of Li metal to evade the side reactions caused by the RMs and due to the invariable potential during charging process, as well as the insensitivity of LFP to the electrolyte.<sup>[21,25–26,52]</sup> However, LFP is definitely not suitable for the practical Li–O<sub>2</sub> batteries on account of the high potential and expropriation of the mass density.

## 6. Summary and Outlook

Redox mediators have been considered as an effective pathway to increase the discharge capacity as well as improve the cell rechargeability and rate capability of Li–O<sub>2</sub> batteries. Notably, an eligible RM must have the following properties: (i) a higher redox potential than the equilibrium potential of Li<sub>2</sub>O<sub>2</sub> formation (2.96 V vs. Li<sup>+</sup>/Li). The redox potential is a critical indicator of RM and the voltage distribution of the majority of the RMs are summarized in Figure 17; (ii) adequate solubility in electrolytes; (iii) chemical and electrochemical stability. The RM molecules should endure the attack from the oxidizing species, such as O<sub>2</sub>, O<sub>2</sub><sup>-</sup> and Li<sub>2</sub>O<sub>2</sub> and maintain stability in the voltage window of the Li–O<sub>2</sub> batteries; and (iv) fast diffusion kinetics.

Although a number of RMs has been discovered, the general principles for finding and designing a new type of RM molecules remain unclear. Lim et al. suggested that the ionization energy (I.E.) can be a descriptor for the RM, and the organics with the I.E. value in the range of 5.8–6.8 eV are capable to be soluble catalysts.<sup>[3b]</sup> The inquiry of the key factors for predicting and designing of a RM is of great concern for the development of the future Li–O<sub>2</sub> cells; however, the research on this aspect is scarce.

According to the literature, most of the concentrations of the RMs employed in the research were chosen to be in the range of 10~50 × 10<sup>-3</sup> M, whether inorganic or organic species. The optimal concentration of RMs is related to the cathode structure, electrolyte composition, current density, and phys-

icochemical properties of RM molecules. However, the relevant studies and reports are not sufficient. Bergner et al. used the electrolyte containing different concentrations of 4-methoxy-TEMPO from 10 mM to 200 mM and discovered that the advantage of high concentration is multifold; for instance, expansion of capacity, enhanced cycling stability and so on.<sup>[51]</sup> The optimization of the concentration must be studied further.

Solid-state electrolytes (SSEs) have been one of the research hotspots in recent years. When applied in the Li–O<sub>2</sub> systems instead of using the organic liquid electrolytes, the SSE can circumvent the hazards of toxicity, inflammability, and decomposition during discharging caused by the liquid electrolyte.<sup>[52]</sup> Benjamin et al. successfully used inorganic ceramic Li<sub>1+x+y</sub>Al<sub>x</sub>(Ti, Ge)<sub>2-x</sub>Si<sub>y</sub>P<sub>3-y</sub>O<sub>12</sub> (LATGP) to prevent the shuttle of RM molecules towards the anode Li,<sup>[51]</sup> leading to stable and prolonged cycling. The popularization of the solid electrolyte is fundamental for the future development of Li–O<sub>2</sub> batteries, but it did not receive enough attention by the academicians in the past.

A battery functions as a whole system. We noticed that the solvent in which the RMs dissolved has a significant influence on the catalytic effect. An electrolyte with low viscosity may be beneficial to the diffusion of the soluble molecules. Integration of the electrolyte, electrode materials, and RM molecules exerts a marked influence on the final performance. Hence, a parallel and over-all study is essential for harmonic and uniform development of future Li–O<sub>2</sub> batteries with a stable and prolonged life.

The establishment of new type of devices stimulates the development of Li–O<sub>2</sub> batteries. Wang Qing and his co-workers put forward the new concept of rechargeable redox flow Li–O<sub>2</sub> battery (RFLOB).<sup>[54]</sup> In a typical RFLOB, a pair of RMs enables the formation and decomposition of Li<sub>2</sub>O<sub>2</sub> in a detached gas diffusion tank (GDT), which is different from the conventional battery devices. The advantages of this design circumvent the surface passivation and clogging of the cathode materials, thereby leading to better cell performance.

Recently, a number of metal–O<sub>2</sub> (Na–O<sub>2</sub>, K–O<sub>2</sub> and Mg–O<sub>2</sub> et al.) batteries with RMs have been reported.<sup>[55]</sup> After being used in Li–O<sub>2</sub> batteries, the RM molecules seem to shine in other battery systems and helps in significantly boosting the cell performance. Predictably, the RMs have promise and are worth pursuing further.

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## Conflict of Interest

The authors declare no conflict of interest.

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