Current Challenges and Routes Forward for 
Non-aqueous Lithium-Air Batteries

Tao Liu,*,1,2 J. Padmanabhan Vivek,3 Evan Wenbo Zhao,2 Jiang Lei,1 Nuria Garcia-Araez,3 Clare P. Grey*,2

1. Shanghai Key Laboratory of Chemical Assessment and Sustainability, Department of Chemistry, Tongji University, Shanghai 200092, P. R. China.
2. Chemistry Department, Lensfield Road, University of Cambridge, Cambridge, UK CB2 1EW
3. Chemistry Department, University of Southampton, Highfield Campus, Southampton, UK SO17 1BJ

* corresponding authors: tliu@tongji.edu.cn; cpg27@cam.ac.uk

Abstract

Non-aqueous lithium-air batteries have garnered considerable research interests over the past decade due to its extremely high theoretical energy densities and potentially low cost. Great advances have been achieved in both the mechanistic understanding of cell reactions and in the development of effective strategies to help realize a practical energy storage device. By drawing attention to reports published mainly within the past 8 years, this review demonstrates an updated mechanistic picture of the lithium peroxide based cell reaction, and highlights key remaining challenges due to the parasitic processes occurring at the reaction product-electrolyte, product-cathode, electrolyte-cathode and electrolyte-anode interfaces. We introduce the fundamental principles and critically evaluate the effectiveness of the important strategies that have been proposed to mitigate issues of the battery, which include the use of solid catalysts, redox mediators, solvating additives for oxygen reaction intermediates and gas separation membranes, etc. Recently established cell chemistries based on the superoxide, hydroxide and oxide phases are also summarized and discussed.
1. Introduction
2. Fundamentals of Non-aqueous Lithium-Oxygen Electrochemistry
   2.1 Discharge Reaction Mechanisms
      2.1.1 Surface Mechanism versus Solution-Mediated Process
      2.1.2 Evidence for the Superoxide Intermediate
      2.1.3 LiO₂ Formation, Li₂O₂ Precipitation, Growth and Termination
      2.1.4 Factors Governing the Solution-Mediated Mechanism
   2.2 Charge Reaction Mechanisms
      2.2.1 Solid Solution Decomposition and Liquid Phase Mediation
      2.2.2 Reaction Interfaces and Charge Transport Pathways
      2.2.3 The Origins of High Charging Overpotentials
      2.2.4 Parameters Characterizing the Reaction Reversibility
3. Key Remaining Challenges: Parasitic Processes
   3.1 (Electro-)Chemical Instability of Electrolytes
      3.1.1 Mechanisms of Electrolyte Decomposition by Reactive Oxygen Species
      3.1.2 Progress in Solvent Discovery
   3.2 Parasitic Reactions at the Carbon Cathode
      3.2.1 Carbon Corrosion at the Carbon-Electrolyte and Li₂O₂-Carbon Interface
      3.2.2 Influence of N₂, CO₂ and H₂O on the Non-aqueous O₂ Electrochemistry
   3.3 Lithium Metal Anode Instability
      3.3.1 Planar, Mossy versus Dendritic Li Deposition and Low Coulombic Efficiency
      3.3.2 The Effect of O₂, CO₂ and H₂O on Li Metal Instability
4. Potential Solutions
   4.1 Electrocatalysis in Non-aqueous Li₂O₂ Batteries
      4.1.1 A Real Need for Electrocatalysis on Charging?
      4.1.2 Noble Metals, Transition Metal Carbides and Oxides
   4.2 Redox Mediators: Enabling Facile Solution-Phase Charge Transfer
      4.2.1 Fundamental Principles
      4.2.2 Selection Criteria for Redox Mediators
      4.2.3 Progress in RMs Development
   4.3 Functional Additives
      4.3.1 Water
      4.3.2 Alcohols
      4.3.3 Singlet Oxygen Quenchers
      4.3.4 Fluorinated Additives
   4.4 Protection Strategies for Li Metal in Lithium-Air Batteries
      4.4.1 Solid Electrolyte Interface
      4.4.2 Inorganic/Organic Protective Membranes
5. Alternative Battery Chemistries:
   5.1 MO₂ or M₂O₃ as the Potential Discharge Products?
      5.1.1 Reversibility and Stability of Superoxide-Based Electrochemistry
      5.1.2 A Molten-Salt Li₂O₂ Battery Based on Li₂O Formation and Decomposition
   5.2 Cycling Based on LiOH Formation and Decomposition?
      5.2.1 Metal-Catalyzed LiOH Electrochemistry
      5.2.2 Synergistic Effect of LiI and H₂O on Modulating the O₂ Electrochemistry
6. Summary and Outlook
1. Introduction

Currently more than 80% of the global energy demand is supplied by fossil fuels.\(^1-^3\) This worldwide use of fossil energy leads to massive release of carbon dioxide and other greenhouse gases that cause issues of global climate change. The petroleum that is consumed in automobile applications represents around one third of the global primary energy sources and results in a third of greenhouse gases released. There is no doubt that electrification of our current transportation systems from renewable energy sources (such as solar, wind energies) will significantly improve our environment and energy security. This transition from fossil fueled vehicles to hybrid electric vehicles (HEV) and electric vehicles (EV) has already begun. Driven by government policies in many countries as well as technological development in private sectors, rapid growth rates (around 50% per year) in HEV/EV sales are recorded over the past few years. In 2018, the global EV sales reached 2 million where more than half (62.5%) of the cars are sold in China alone.

The core issue facing complete electrification of transportation is the development of a good battery, that is, a long-lived, safe, affordable battery with sufficient power and energy densities to cover most driving range scenarios for a day. Current EVs are predominantly based on lithium ion batteries (LIB) and active R&D efforts are still being devoted to further optimizing the LIB chemistry. Around 5 years ago, one opinion evolved in the battery community that LIBs may not be the energy storage technology that can realize mass EV adoption, because scientists estimate that the scope for energy density improvement in LIBs is at most another 30%. Therefore, the LIB – unless it is large and thus extremely costly – is unlikely to allow a driving range of 500 miles/charge to be achieved, this range being offered by a single refill of a petrol tank.\(^4\) This idea certainly drives more fundamental research activities to the so-called beyond Li-ion battery chemistries (such as Si, S and O\(_2\)-based Li redox chemistries). Nevertheless, in 2017 Tesla Model 3 successfully demonstrated a driving range of more than 300 miles based on current LIB technologies, and a new Tesla model to be released soon is claimed to achieve even 400 miles/charge; these improvements in driving ranges are mainly obtained by loading more batteries on board (478 kg for battery packs of 80.5 kWh accounting for 30% of vehicle weight in Model 3). While Tesla’s performance highlights the importance and necessity of re-engineering car manufacturing in developing EVs, their strategy, however, increases the cost and reduces the effective loading capacity of the car. In the long term, much energy-denser batteries that can significantly reduce battery cost, weight and afford long driving ranges is the research direction forward.

One of the high-energy candidates considered for EV applications is metal-air batteries.\(^5-^8\) Metal-air batteries have garnered considerable research interests over the past decade. In 2009, only 25 papers were published on the subject, this number continuing to rise, reaching over 800 in 2018. Most papers describe lithium-air, sodium-air, potassium-air, zinc-air and aluminum-air batteries, which can involve one, two or four electrons stored per O\(_2\) molecule due to the versatility of the O\(_2\) redox chemistry. Since O\(_2\) from the air acts as the active material storing
electric charge, in principle, the battery should have a denser energy, lower cost, potentially less toxicity and better recyclability, as compared to LIBs that use transition metal oxides as the positive electrode. Among them, the lithium-air battery possesses the highest theoretical energy density and is most intensely studied; this is the focus of this review.

There are two types of lithium-air batteries, one based on aqueous electrolytes and the other using non-aqueous electrolytes. The non-aqueous lithium-air batteries will have varied theoretical specific energies (defined as Wh/kg of the redox active material), depending on the type of lithium-oxygen product formed during discharge. For instance, the formation of \( \text{Li}_2\text{O}_2 \) (2\( \text{Li}^+ + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \)), \( \text{Li}_2\text{O} \) (4\( \text{Li}^+ + \text{O}_2 \leftrightarrow 2\text{Li}_2\text{O} \)), \( \text{LiOH} \) (4\( \text{Li}^+ + 2\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 4\text{LiOH} \)) lead to theoretical capacities of 1165, 1787 and 1117 mAh/g, respectively; hence the corresponding specific energies, assuming a voltage of around 3 V for them, would be 3495, 5361, 3350 Wh/kg, clearly several times higher than those of typical LIBs (500-800 Wh/kg). On the other hand, the aqueous lithium-air cell (e.g., at alkaline conditions) is described by the following reaction: 4\( \text{Li}^+ + 6\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 4\text{LiOH} \cdot \text{H}_2\text{O} \), the forward reaction characterizing discharge and the backward one for charge. During discharge, the generated LiOH is dissolved in the electrolyte until reaching its saturation solubility; LiOH•H\(_2\)O then precipitates and deposits on the positive electrode. Since LiOH•H\(_2\)O rather than LiOH (as in the non-aqueous system) is the product, the specific energy of the aqueous system is much lower, around 2170 Wh/kg. As a result, much less research is done on the aqueous system compared to the aprotic one. Most contents of this review will be dedicated to discussing non-aqueous lithium-air batteries.

Although we do not attempt to give a full history of development for lithium-air batteries, it is important to acknowledge important early work. Originally proposed in the 1970s as a potential power source for electric vehicles, non-aqueous lithium-air batteries started to regain research interests since late 1990s. Jiang and Abraham in 1996 accidently identified the \( \text{Li}_2\text{O}_2 \)-based Li-O\(_2\) electrochemistry when they attempted to intercalate \( \text{Li}^+ \) into graphite via a gel polymer electrolyte in the presence of some air leaks. Later on, more researchers studied the discharge reaction of lithium-air batteries using various electrolytes. In 2006, Bruce and coworkers showed that \( \text{Li}_2\text{O}_2 \) can be decomposed on recharging, an important first step in producing a reversible Li-O\(_2\) battery. Since Bruce et al’s work, and also driven by the advances of materials science and the increased need for renewable energies, research on lithium-air batteries has increased substantially. It is also worth noting that many early studies should be interpreted with caution, because many of the cell electrochemistries reported were mainly based on parasitic reactions (e.g., where a carbonate electrolyte is used, and the major product on charge is CO\(_2\)). A major reason for this mistake is that the non-aqueous Li-O\(_2\) electrochemistry is prone to undergo unwanted degradation side reactions. The situation is further complicated by the multiple interfaces and phases (solid vs. liquid) at which the chemical transformations occur. As a result, simple coulometry and non-quantitative diffraction/microscopy characterization are insufficient to fully evaluate the battery chemistry. Instead, a wide range of \textit{in situ} quantitative gas, chemical titration,
spectroscopy techniques are usually required to assess the true reversibility and unravel the mechanisms of the Li-O₂ electrochemistry.

It is now well-recognized by the community that the development of a practical non-aqueous lithium-air battery faces many technical challenges. The cell suffers from poor rate capability, which results in a low practical specific energy. The voltage hysteresis during cycling is large, giving rise to low energy efficiencies. These high overpotentials in turn cause significant electrode and electrolyte decomposition and consequently, the cell life is quite limited. The use of a lithium metal anode involves safety concerns. In addition, other components in air (such as CO₂, H₂O) can interfere with the Li-O₂ electrochemistry and cause further parasitic reactions. As such, most lab-based lithium-air battery research is simplified and uses pure O₂ rather than air. In this context, it is more accurate to use the term Li-O₂ rather than Li-air batteries.

To put the requirements for lithium air batteries into context, the calculations by Gallagher and coworkers of the figures of merit achievable by Li-air batteries at a system level for electric vehicle applications (Fig. 1a) are worth considering.²⁸ Using the data originally reported in Gallagher and co-workers’ article, we compiled Figure 1b to show the energy densities, specific energy and cost per usable energy, as a function of the electrode areal capacity for a Li-air battery at a system level, where the areal capacity is defined as the capacity normalized by the geometric electrode area. The figure shows that very high energy densities (>380 Wh/l), specific energies (>330 Wh/kg) and very low costs per usable energy (<105 $/kWh) can be achieved with Li-air cells with high areal electrode capacities (>10 mAh cm⁻²). For comparison, when these estimates are performed with Li-ion battery materials such as graphite and NMC111 at a system level, these authors obtained energy densities (ca. 360 Wh/L), specific energies (ca. 180 Wh/kg) and costs per unit density (ca. 200 $/kWh) that are inferior to the values projected in Figure 1b for Li-air batteries. Two points should be stressed however: first, Gallagher and coworkers have pointed out that advanced Li metal anode batteries paired with a high performance layered NMC metal oxide could provide a more competitive performance, but these novel battery chemistries need to overcome a number of fundamental challenges to reach commercialization, as it is the case for metal-air batteries. Second, the energy densities for traditional Li-ion batteries have continued to improve and costs have dropped noticeably since this paper was published largely due to incremental improvements, changes in cathode chemistries and massive increases in production. Nonetheless, the calculations by Gallagher and coworkers illustrate target requirements in terms of areal electrode capacity, rate capability, electrolyte loading, excess of anode capacity and cycle life required for building competitive Li-air batteries for electric vehicles. Recent improvements in Li-air batteries are critically analyzed in view of these challenging target requirements in Section 4 of this review article.
Fig. 1 Figures of merit of Li-air batteries at a system level. (a): Illustration of required components for an open Li-O\textsubscript{2} system. (b): Plot of the energy density, specific energy and cost per usable energy as a function of the areal Li\textsubscript{2}O\textsubscript{2} electrode capacity, as obtained from the data reported by Gallagher and coworkers.\textsuperscript{28} Values of areal Li\textsubscript{2}O\textsubscript{2} electrode capacities (called “loadings” in the original article) relate to the content of Li\textsubscript{2}O\textsubscript{2} per geometrical unit area of the electrode. The calculations were made considering that the wet, discharged electrode contained 60% Li\textsubscript{2}O\textsubscript{2}, 8% carbon, 2% binder, 5% open porosity and 25% of liquid electrolyte (volume percentages). The values shown are for an open Li-air system, but similar results are obtained with a closed Li-O\textsubscript{2} system. Figure 1(a) reprinted with permission from ref 28. Copyright 2014 The Royal Society of Chemistry.

At the fundamental level, great effort has been made to unravel the principles underpinning the irreversibility of lithium-air batteries. Nevertheless, many fundamental questions remain unresolved. For instance, the reactive interfaces of a lithium-oxygen battery during discharge and charge are still under debate: whether are they at the product-electrolyte interface or the product-electrode interface and what are the influential factors determining the operation of different reaction mechanisms? The answer to this question is crucial to guide the design of efficient electrocatalysts for the oxygen reduction and evolution reactions in lithium-air batteries. The true species/processes responsible for the side reactions at the cathode also merit further research; previously, the superoxide and Li\textsubscript{2}O\textsubscript{2-x} species were considered to be the main cause. However, recent studies suggest that singlet oxygen might be playing a more detrimental role. This demands the development of suitable singlet oxygen quenchers, electrolytes and mediators that are stable against singlet oxygen. Furthermore, trace amounts of water, carbon dioxide, and nitrogen are probably inevitable in practical lithium-air cells, their impact on the anode and cathode chemistry and stability needs more attention.

In this article, we review literature published until June 2019, focusing on the fundamental aspects of the key scientific and technical challenges in developing a successful and technologically relevant lithium-air battery. In Section 2, we first discuss the current understanding of the discharge and charge reaction mechanisms – the fundamentals of a basic Li-O\textsubscript{2} reaction based on Li\textsubscript{2}O\textsubscript{2} formation and decomposition. We will show that great advances in improving the cell chemistry have been achieved through fundamental studies. Next in Section 3,
we highlight the outstanding key challenges, which relate to parasitic reactions occurring at the electrode/electrolyte interfaces. In Section 4, we introduce some novel and useful materials and strategies to address the key challenges and discuss improvements in chemistries beyond those used in Gallagher’s original model. In Section 5, we discuss some recent reported new types of Li-O₂ electrochemistry, based on LiO₂, Li₂O and LiOH, which really highlight the tremendous opportunities for research to understand and modulate the versatile O₂ electrochemistry. Finally, in Section 6, we present our own, subjective perspectives and future research directions.

2. Fundamentals of Non-aqueous Lithium-Oxygen Electrochemistry

A basic non-aqueous lithium air battery consists of a lithium metal anode, a non-aqueous electrolyte (including organic solvent and lithium-containing salt) soaked in a separator and a porous carbon-based cathode (Fig. 2). The carbon cathode is not the active material for energy storage, but simply a porous framework to host the active materials. Carbon is a commonly chosen cathode host due to its light weight, low cost, good electrical conductivity and relatively high chemical stability. On discharging, dioxygen molecules from the air react with lithium ions and electrons at the cathode surface (Fig. 2a). As a result, a solid reaction product, typically lithium peroxide (Li₂O₂), is formed and deposits within the porous carbon framework. Upon charging, Li₂O₂ is decomposed and O₂ is released back to the atmosphere (Fig. 2b).

The characteristic electrochemical profile of a cell using a carbon-based cathode is shown in Figure 2c. Based on the standard Gibbs free energy change of reaction (1), the equilibrium voltage is calculated to be 2.96 V versus Li⁺/Li. The discharge profile shows a relatively flat plateau followed by an abrupt polarization region, also known as the ‘sudden death’, marking the end of the discharge process. The charging process exhibits a much larger overpotential (typically ~1 V) than the discharge (~0.2 V): a sloping region in the beginning, then a flatter charge plateau and finally a high voltage tail can usually be identified.

\[ 2Li(s) + O_2(g) \leftrightarrow Li_2O_2(s), \quad E^\circ = 2.96 \text{ V} \]  

\[ (1) \]
Fig. 2 Schematic illustration of the discharge (a) and charge (b) processes of a non-aqueous Li-O₂ battery and its typical electrochemical profile (c). The potential of the O₂/Li₂O₂ vs. Li⁺ (2.96 V) is marked.

2.1 Discharge Reaction Mechanisms

2.1.1 Surface Mechanism versus Solution-Mediated Process

Because of its close link to the practical energy density of Li-O₂ batteries, the discharge reaction has been extensively studied. Through studies using a wide range of experimental techniques, it is suggested that the discharge reaction at the cathode can proceed either via a surface mechanism or a solution mediated pathway. These different scenarios are summarized in reactions (2-6), where ‘ads’ and ‘sol’ subscripts refer to species that adsorb on the surface and that exist in solution, respectively.

In the surface mechanism (reactions 2-3), lithium superoxide (LiO₂) forms via one-electron O₂ reduction, where the electron transfer and association with a Li⁺ cation occur at the electrode surface. The surface bound LiO₂(ads) then undergoes another one-electron electrochemical reduction to form Li₂O₂(ads). In the solution-mediated mechanism (reactions 4-6), the formation of LiO₂(sol) occur via two steps: first one-electron electrochemical reduction of O₂ to form lithium superoxide at the surface, which then diffuses into solution (reaction 4); the LiO₂(sol) species is dissolved in the electrolyte (in equilibrium) with its Li⁺ and O₂⁻ ions solvated by the solvent (reaction 5). The LiO₂(sol) generated in solution can undergo a disproportionation reaction to produce Li₂O₂(sol) and O₂(g) (reaction 6). Due to a low solubility in organic electrolyte, Li₂O₂ quickly precipitates out of the solution (reaction 6), nucleating and growing as Li₂O₂ crystallite. A strong evidence for the solution-mediated Li₂O₂ precipitation is the observation of Li₂O₂ particles forming on the electrically insulating glass fiber separators.

\[
\begin{align*}
O_2(g) + e^- + Li^+(sol) &\rightarrow LiO_2(ads) \quad (2) \\
LiO_2(ads) + e^- + Li^+(sol) &\rightarrow Li_2O_2(ads) \quad (3) \\
\text{or} \quad O_2(g) + e^- + Li^+(sol) &\rightarrow LiO_2(sol) \quad (4) \\
LiO_2(sol) &\leftrightarrow O_2(sol) + Li^+(sol) \quad (5) \\
2LiO_2(sol) &\rightarrow Li_2O_2(sol) + O_2(g) \quad (6)
\end{align*}
\]

A key distinction between these two scenarios is whether significant amounts of reduced oxygen species (superoxide and peroxide) are transported from the surface into the electrolyte solution to promote large Li₂O₂ crystal formation (not necessarily on the current collectors). Next, we introduce existing evidence that supports the proposed elementary steps (reactions 2-6) and discuss factors dictating the discharge mechanism.

2.1.2 Evidence for the Superoxide Intermediate

The existence of a superoxide reaction intermediate either at the surface or in solution has been verified by electrochemical analysis, Raman spectroscopy, chemical analysis,
ultraviolet-visible (UV-vis) spectroscopy,\textsuperscript{38, 41} rotating ring disc electrode (RRDE),\textsuperscript{42-45} electron spin resonance (ESR) spectroscopy\textsuperscript{46} and fluorescence spectroscopy.\textsuperscript{47} While surface-enhanced Raman spectroscopy techniques can be used to probe superoxide species at the electrode surface region,\textsuperscript{30, 37, 39} the other techniques are useful to quantify the superoxide species dissolved in the electrolyte.\textsuperscript{38, 41-47}

Hardwick and coworkers studied the oxygen reduction reaction (ORR) in acetonitrile (ACN) and dimethyl sulfoxide (DMSO)-based electrolytes on glass carbon (GC) electrodes using shell isolated nanoparticle enhanced Raman spectroscopy (SHINERS).\textsuperscript{39} The electric field enhancement (Fig. 3a) between the SiO$_2$-coated gold nanoparticles allowed the detection of reaction species on non-metallic electrode surfaces, whilst removing any potential surface catalytic effect due to gold. Superoxide species ($\nu_{\text{O}-\text{O}}$) with Raman shifts at 1125 and 1128 cm$^{-1}$ were detected in ACN and DMSO electrolytes respectively, which are ascribed to LiO$_2$$_{(\text{ads})}$. While SHINERS enables the detection of reaction products close to the electrode surface (red areas in Figure 3a, note that the SHIN particles are ca. 55 nm), surface-enhanced Raman spectroscopy (SERS) is most sensitive to species directly adsorbed on the electrode surface. SERS was used by Bruce and coworkers to detect the reaction intermediates in the reduction of O$_2$ on roughened gold electrodes (Fig. 3b).\textsuperscript{30} In DMSO, the superoxide peak (1117 cm$^{-1}$) was ascribed to superoxide anions, O$_2$$^-$ (since the same peak position was obtained in solutions with TBA$^+$ cations substituting the Li$^+$ cations), while in ACN, the superoxide peak was at higher frequencies (1128 cm$^{-1}$), consistent with the stronger O-O bond expected in LiO$_2$$_{(\text{ads})}$, due to the lower occupancy of 2$\pi^*$ antibonding orbital of LiO$_2$ compared to O$_2^-$ . These results demonstrate that the main reaction intermediates change with the solvation strength of the solvents: solvents that strongly solvate lithium cations (e.g. DMSO), favor the formation of soluble superoxide anions, O$_2$$_{(\text{sol})}$ (or, strictly speaking, superoxide anions coordinated with highly solvated lithium cations), while poorly solvating solvents favor the formation of poorly-soluble, surface bonded lithium superoxide intermediates, LiO$_2$$_{(\text{ads})}$.

Dissolved superoxide species in highly solvating electrolytes (e.g., DMSO) can also be analyzed by other techniques. In a typical RRDE experiment,\textsuperscript{42-45} the disc electrode is swept negatively (e.g., from 3.0 to 2.0 V), whereas the ring electrode is held at a potential high enough to electrochemically oxidize the soluble oxygen intermediates (e.g., typically set to 3.0-4.0 V). The generation of soluble superoxide species is thus manifested as an oxidation current at the ring electrode, whose magnitude is proportional to the corresponding cathodic peak at the disc electrode. \textit{In-situ} UV-vis absorption spectroscopy provides another means to study the behavior of soluble superoxide species, the superoxide species showing a characteristic absorption band at 252 nm due to the 1$\pi_u$$\rightarrow$$1\pi_g$ transition.\textsuperscript{38, 41} Based on the absorption coefficient,\textsuperscript{48} the signal of superoxide can be quantified and correlated with the electrochemistry, the intensity being observed in these experiments being close to that expected for a one-electron oxygen reduction reaction.
Fig. 3 *In situ* SHINERS (a) and SERS (b) characterization of reduced oxygen species in acetonitrile and dimethyl sulfoxide-based LiClO$_4$ electrolytes. The SHINERS technique (a) uses nanoparticles (~55 nm) composed of an Au core and SiO$_2$ shell (<4 nm) to enhance Raman sensitivity specifically to regions between particles, as indicated by the red-colored areas (some enhancement also occurs between particles and the substrate); multiple Raman spectra are acquired while the electrode potential is being swept negatively from open circuit voltages; as a result, peroxide and superoxide are observed. The SERS technique (b) here uses roughened gold electrode to enhance Raman sensitivity, which is maximal at the electrode surface-electrolyte interface; the Raman spectra are acquired at different times at the specified potentials (as indicated). Note that the appearance of the band associated with LiO$_2$(ads) at ~1125 cm$^{-1}$ in DMSO in (a) is probably a result of low reductive potentials, compared to the case in (b) where at higher potentials O$_2$(sol) (1117 cm$^{-1}$) species form. Reprinted with permission from ref 30 and 39. Copyright 2014 Nature Publishing Group and 2016 ACS.

2.1.3 LiO$_2$ Formation, Li$_2$O$_2$ Precipitation, Growth and Termination

To investigate whether the formation of lithium superoxide is a surface process (reaction (2)) or a solution-based process (reactions (4-5)), cyclic voltammetry measurements were performed by McCloskey, Bruce and coworkers on the O$_2$/O$_2^-$ redox couple in ACN and DMSO electrolytes (Fig. 4a). When TBA$^+$ (tetrabutyl ammonium) is the cation, it is well established that
O₂ undergoes a reversible one-electron redox reaction to form O²⁻ as a highly solvated species. In the presence of a Li⁺ salt, the reduction of O₂ takes place at higher potentials, indicating that the redox potential of the O₂/LiO₂ couple is higher than the O₂/O⁻² couple. This reflects the thermodynamics of the process: the association energy of Li⁺-O⁻² is larger than TBA⁺-O²⁻, this being controlled by the coordination of the corresponding cation by solvent molecules. A more negative ΔG° of the electrochemical reaction implies a higher E°.

The difference in redox potentials of the O₂/O⁻² and O₂/Li₂O₂ couples has been used to obtain an estimate of the solubility product constant of Li₂O₂:

\[ \text{Li}_2\text{O}_2(s) \leftrightarrow 2\text{Li}^+(\text{sol}) + \text{O}_2^{2-}(\text{sol}) \quad K_{\text{Li}_2\text{O}_2} = \frac{a_{\text{Li}^+}^2 a_{\text{O}_2^{2-}}}{a_{\text{Li}_2\text{O}_2}} \quad (7) \]

where \( a_i \) is the activity of species \( i \), and since Li₂O₂ is a solid, \( a_{\text{Li}_2\text{O}_2} = 1 \). Strictly speaking, \( K_{\text{Li}_2\text{O}_2} \) is the dissociation constant of Li₂O₂ into Li⁺ and O₂⁻², but if ion pairing effects are considered minor, \( K_{\text{Li}_2\text{O}_2} \) is also equal to the solubility product. A value of \( K_{\text{Li}_2\text{O}_2} \approx 10^{-51} \) in pyrroldinium-based ionic liquids (IL) was estimated, which was later corroborated by computational studies. Following a similar approach, the difference in redox potential of the O₂/O⁻² and O₂/LiO₂ couples can be used to estimate the LiO₂ dissociation equilibrium constant:

\[ \text{LiO}_2(s) \leftrightarrow \text{Li}^+(\text{sol}) + \text{O}_2^- (\text{sol}) \quad K_{\text{LiO}_2} = \frac{a_{\text{Li}^+} a_{\text{O}_2^-}}{a_{\text{LiO}_2}} \quad (8) \]

The LiO₂ dissociation constant provides a measure of the coordination strength of Li⁺ cations with O⁻² anions. In ACN the onset potential of ORR is 0.25 V higher in the presence of LiTFSI than TBATFSI (Fig. 4a(i)). This value of potential difference of 0.25 V corresponds to a LiO₂ dissociation constant of \( K_{\text{LiO}_2} = \exp(-\text{FAE}/RT) \approx 6 \times 10^{-5} \). This low value suggests that LiO₂ precipitation occurs early in the discharge of Li-O₂ cells in ACN, which agrees with the suggestion that the ORR in ACN proceeds via the formation of a LiO₂ surface-bond intermediate. This leads to a high rate of surface passivation, which results in a much decreased ORR current (Fig. 4a(ii)). In the DMSO electrolyte (Fig. 4a(ii)), on the other hand, the redox peaks show little intensity change and potential shift with increasing Li⁺ concentrations. Using a shift in the ORR onset potential of ca. 60 mV upon Li⁺ addition, a dissociation constant of \( K_{\text{LiO}_2} = \exp(-\text{FAE}/RT) \approx 0.1 \) is obtained. This calculation demonstrates that the energy associated to Li⁺ ion pairing with O⁻² is much smaller in DMSO than in ACN. This is consistent with the stronger solvation of Li⁺ by DMSO than by ACN.

Shao-horn and coworkers performed electron microscopy measurements to follow the nucleation and growth process of Li₂O₂ in a dimethoxyethane (DME)-based electrolyte. They observed that during discharge Li₂O₂ first existed as platelet and continued to grow anisotropically into a toroidal morphology (Fig. 4b), the toroids later being typically taken as a characteristic feature of a liquid-phase mediated process. To understand how fresh Li₂O₂ is
added to the existing toroidal crystal, McCloskey et al., studied Li$_2$O$_2$ precipitation mechanism using differential electrochemical mass spectrometry (DEMS) and time of flight secondary ion mass spectrometry (ToF-SIMS) aided with isotopic labeling. For example, Lu et al. discharged a cell sequentially under $^{16}$O$_2$ and then $^{18}$O$_2$ in a tetraglyme electrolyte. Subsequent SEM and ToF-SIMS measurements of the discharged electrode confirmed that the toroidal Li$_2$O$_2$ products have a Li$_2^{16}$O$_2$ core and Li$_2^{18}$O$_2$ shell, as indicated by the depth-analysis of $^{18}$O ToF-SIMS signals (Fig. 4c), strongly supporting the formation of fresh Li$_2$O$_2$ on the existing product particles at the Li$_2$O$_2$-electrolyte interface (Fig. 4e). Nevertheless, it should be noted that a toroidal Li$_2$O$_2$ morphology does not always necessitate a solution-mediated discharge mechanism. At very high overpotentials (>6 V) toroidal morphologies of Li$_2$O$_2$ has also been observed in an all-solid-state Li-O$_2$ battery; no liquid electrolyte was present in these batteries, suggesting a different mass/charge transport mechanism in this case.

![Image of Fig. 4](image.png)

**Fig. 4** Investigating the processes of LiO$_2$ formation, Li$_2$O$_2$ precipitation, growth and termination. (a): Cyclic voltammograms of the O$_2$/O$_2^-$ couple in CH$_3$CN (i) and DMSO (ii) electrolytes as a function of Li$^+$ concentration; the effect of replacing the TBATFSI (0.5 M) solute by LiTFSI (1 M) in CH$_3$CN results in a positive shift of 0.25 V in the O$_2$ reduction potential, whereas in DMSO replacement of TBAClO$_4$ salt by LiClO$_4$ (total cation concentration is always 0.1 M) leads to positive voltage shift by only 60 mV. Reprinted with permission from ref 30 and 35. Copyright 2014 Nature Publishing Group and 2012 ACS. (b): SEM images show the progressive growth of Li$_2$O$_2$ particles from small nuclei with deeper discharge. Reprinted with permission from ref 53. Copyright 2013 ACS.
(c): three selected layers from a 3D image of $^{18}\text{O}$ signals using ToF-SIMS depth scan of the discharged electrodes and a reproduced structure of a toroidal $\text{Li}_2\text{O}_2$ particle showing a shell region of $\text{Li}_2^{18}\text{O}_2$ and a core region of $\text{Li}_3^{16}\text{O}_2$. Reprinted with permission from ref 54. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d): in situ surface enhanced Raman spectra acquired at open circuit potential (OCP) and at the end of passivation under $^{16}\text{O}_2$ (red) followed by measurements performed at various times of further discharging under $^{16}\text{O}_2$ at 2.0 V versus Li$^+/\text{Li}$. Reprinted with permission from ref 56. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (e): schematic illustration of $\text{Li}_2\text{O}_2$ precipitation and growth process via a solution-mediated pathway or a surface mechanism.

Subsequently, using in situ surface enhanced Raman spectroscopy (SERS), Peng and coworkers$^{56}$ studied the $\text{Li}_2\text{O}_2$ growth process occurring via the surface mechanism, where high discharge currents were applied and $\text{Li}_2\text{O}_2$ films formed. A cell was first fully discharged in $^{18}\text{O}_2$ to form a surface film of $\text{Li}_2^{18}\text{O}_2$ on a gold electrode. Then the cell was forced to discharge further in $^{16}\text{O}_2$ using a large overpotential at 2 V. As a result, the $\text{Li}_2^{18}\text{O}_2$ Raman signal was gradually replaced by $\text{Li}_2^{16}\text{O}_2$ (Fig. 4d). Since SERS is only sensitive to interfacial species close to the gold electrode surface, this replacement suggests fresh $\text{Li}_2^{16}\text{O}_2$ formation occurs at the buried interface between $\text{Li}_2^{18}\text{O}_2$ and the gold electrode,$^{56}$ as schematically depicted in Figure 4e. In this case, clearly $\text{O}_2$ and $\text{Li}^{+}$ can, perhaps in the presence of some defects, be transported through the previously deposited $\text{Li}_2\text{O}_2$ film, and reach the underlying gold surfaces.$^{56}$

The phenomenon of ‘sudden death’ that marks the end of a cell discharge is important due to its close connection to the obtainable energy density. This rapid electrochemical polarization can stem from rising impedance at the anode and at the cathode. Many groups have shown that as $\text{Li}$-O$_2$ cells (using ether electrolytes) continue to discharge, more byproducts including LiOH, Li$_2$CO$_3$, Li$_2$O etc., accumulate at the Li anode surfaces due to electrolyte decomposition.$^{57-59}$ Formation of this SEI can help reduce further electrolyte decomposition, but a poor quality SEI layer (with low lithium ion conductivity) can also significantly increase the charge transfer impedance at the anode. At the cathode, it is thought that the discharge terminates when all active surfaces have been passivated by a thick layer of $\text{Li}_2\text{O}_2$ (a wide band gap insulator)$^{60,61}$ and consequently the tunneling current through $\text{Li}_2\text{O}_2$ can no longer support electrochemical current.$^{62-65}$ Several groups have probed the charge transfer through $\text{Li}_2\text{O}_2$ using reversible redox couples and in situ electrochemical impedance spectroscopy, observing that the rate constants of the reversible redox couples exponentially decreased with thickening $\text{Li}_2\text{O}_2$ films.$^{62,63,65}$ The EIS measurements also revealed that the impedance associated with electronic transport through $\text{Li}_2\text{O}_2$ deposited at the cathode increases abruptly and considerably at the ‘sudden death’ on discharging,$^{66}$ whereas the impedance linked to the anode SEI increases only slightly, indicating that the rapid termination of discharge is predominantly limited by an electronic charge transport through $\text{Li}_2\text{O}_2$ layers covering the cathode surface.

2.1.4 Factors Governing the Solution-mediated Mechanism

From the above discussion, it is clear that promoting the solution-mediated mechanism on discharging is beneficial as it can postpone the ‘sudden death’. In fact, large toroidal $\text{Li}_2\text{O}_2$
crystals up to tens of micron meters in diameter has been reported via a solution-phase reaction pathway (Fig. 5a); this results in both higher specific and volumetric energy densities, because the geometric pore volume can be more efficiently taken up, thereby increasing the active/non-active material ratio. Whether the surface or solution-mediated mechanism dominates in a cell discharge is dependent on a wide range of factors, including the donor number (DN) or acceptor number (AN) of solvents, association strength of salt anion with Li\(^+\), presence of larger cation additives that can stabilize \(\text{O}_2^-\), \(\text{H}_2\text{O}\)/weak acid additives that solubilize \(\text{Li}_2\text{O}_2\), the use of redox mediators, the reduction potential/rate, the temperature and pressure of the cell, and/or a combination of these factors.

The most critical factor is linked to the ability of the electrolyte to promote the formation of soluble \(\text{LiO}_2\) in the form of \(\text{Li}^+(\text{sol})\) and \(\text{O}_2^-\text{(sol)}\) or \(\text{LiO}_2\text{(sol)}\) (Fig. 5a). Bruce and Aetukuri and coworkers found that both solvents with high DN (e.g., DMSO, which better solvates \(\text{Li}^+\)), and additives with high AN (e.g., \(\text{H}_2\text{O}\), which better stabilizes \(\text{O}_2^-\)) can promote \(\text{LiO}_2\) dissolution and thus the formation of large toroidal \(\text{Li}_2\text{O}_2\) via a solution-mediated mechanism (Fig. 5b). They predicted that solvents with both high DN and AN are essential to realize a high capacity \(\text{Li}-\text{O}_2\) batteries. Unfortunately, high DN solvents such as DMSO, dimethylformamide (DMF), N-methyl pyrrolidone (NMP) are known to be less electrochemically stable than low DN solvents such as ACN and ethers. Khetan and coworkers, using thermodynamic analysis, further showed that the chemical stability of a solvent against nucleophilic attack by superoxide and peroxide species is anticorrelated with the solvent ability to promote a solution-mediated mechanism (Fig. 5c). Therefore, alternative strategies to improve energy densities without compromising cell rechargeability are needed.

Many groups subsequently reported that \(\text{LiO}_2\) dissolution can also be promoted by a judicious choice of lithium salt anion (Fig. 5d), e.g., \(\text{NO}_3^-\), even in a low DN solvent, DME: the association strength of \(\text{NO}_3^-\) with \(\text{Li}^+\) is stronger than TFSI, thereby stabilizing \(\text{Li}^+\) in solution. The cell capacity using a \(\text{LiNO}_3\) electrolyte is increased by 5 times compared to the case of LiTFSI. In addition to the salt anion, having larger alkali cations (e.g., \(\text{K}^+\)) as electrolyte additives can also increase the discharge capacity by promoting a solution pathway; this is because according to the Hard and Soft Acid and Base Theory (HSAB), \(\text{K}^+\) as a softer (more polarizable) cation binds less strongly with a soft \(\text{O}_2^-\) anion than the harder \(\text{Li}^+\) cation, thus promoting the formation of a stabilized \(\text{O}_2^-\).

Therefore, by optimizing the electrolyte salt, the constraint of identifying an electrolyte solvent that can both solubilize \(\text{LiO}_2\) well and have good chemical stability can be relaxed, potentially providing a pathway to find an optimized electrolyte system that can afford both good rechargeability and high energy density. Another promising strategy to decouple various stringent requirements for an ideal electrolyte is the use of redox mediators that can chemically reduce \(\text{O}_2\) and effectively drive the reaction zone of \(\text{Li}_2\text{O}_2\) precipitation away from surface; this concept is discussed in detail in Section 4.2.
Besides the factors discussed above, electrochemical cycling parameters and cell operation temperatures and O₂ pressures can also affect the discharge reaction mechanism and capacity. Lower current rates, lower discharge overpotentials, higher cell temperatures and pressures all tend to promote larger Li₂O₂ formation and usually higher discharge capacities (where higher temperatures being an exception in fact lead to lower capacities). It is worth noting that increasing the solubility of LiO₂ or Li₂O₂ in electrolyte is not always a positive strategy for a Li-O₂ battery, because it may also incur serious shuttling of reduced oxygen species towards the separator and Li metal anode. As a result, the Li₂O₂ deposited far away from the cathode becomes difficult to be decomposed on recharge and the anode may also be degraded due to reactions with reduced oxygen species shuttling from the cathode. Optimizing the performance of Li-O₂ batteries requires a holistic approach considering all cell components.

---

**Fig. 5** Influence of electrolyte properties on the discharge reaction mechanism via a surface or a solution mediated pathway. (a): Physicochemical properties of the solvent and salt (such as donor/acceptor numbers (DN/AN), Li⁺ cation-anion association strength) that can help promote a solution-mediated discharge process, which typically leads to larger discharge capacities and Li₂O₂ crystal sizes (up to tens of microns, all scale bars are 5 μm). Reprinted with permission from ref 67. Copyright 2018 ACS. (b): The free energy of dissolution of LiO₂ into Li⁺ and O₂ in various solvents as a function of Gutman acceptor and donor numbers; dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and dimethyl acetamide (DMAc) have high DNs and thus can stabilize Li⁺, whereas solvents (water and methanol) that have high ANs can stabilize O₂⁻. Reprinted with permission from ref 31. Copyright 2015 Nature Publishing Group. (c): Solvent stability against proton/hydrogen abstraction via nucleophilic attack and solvent ability to facilitate the solution mediated discharge; the susceptibility of solvents to parasitic processes is evaluated as the rate of nucleophilic attack normalized against that of acetonitrile, and their solvation capabilities are evaluated in terms of ΔG°, free energy of LiO₂ dissolution; solvents that promote LiO₂ dissolution
can lead to higher discharge capacity, but they are susceptible to nucleophilic attack by O$_2^-$ and suffer from limited cycle life.$^{92}$ Reprinted with permission from ref 92. Copyright 2015 ACS. (d): Contour plot showing the free energy of Li$^+$ solvation for electrolytes with varying DN of the solvent and salt anion, in kcal/mol; the free energy is normalized with respect to that of DME and 1 M LiTFSI. The electrolyte is a 50:50 mixture of LiTFSI and a salt consisting of Li$^+$ and the labelled salt anion in the solvent; red regions correspond to those can trigger solution-mediated discharge, whereas those in blue regions cannot.$^{32}$ Reprinted with permission from ref 32. Copyright 2015 National Academy of Sciences.

2.2 Charge Reaction Mechanisms

2.2.1 Solid Solution Decomposition and Liquid Phase Mediation

The mechanisms by which the charge processes occur are more varied than those seen on discharge and there is less consensus in the literature. The very different electrochemical profile and the much higher overpotentials needed for recharge compared to discharge (Fig. 2c) suggest that charge occurs via a different reaction mechanism rather than simply being a mirror process of the discharge reaction.

Earlier studies, using electrochemistry methods and in situ Raman spectroscopy, revealed that a high overpotential is required for the oxidation of Li$_2$O$_2$ and that no LiO$_2$ intermediate was observed by Raman in an ACN-based electrolyte on charging.$^{33, 34, 37}$ Consequently, it was proposed that the oxidation of Li$_2$O$_2$ is via a direct two electron electrochemical reaction (reaction (9)).

\[
\text{Li}_2\text{O}_2(s) \rightarrow \text{O}_2(g) + 2e^- + 2\text{Li}^+(\text{sol}) \tag{9}
\]

Later studies suggested that the charging process can involve a mixed solid-solution decomposition and liquid phase-mediated process, depending on the solvating properties of the electrolyte, as summarized in reactions (10-13).$^{36, 45, 93-98}$ Reactions (10-11) are solid-state steps and (12-13) involve the formation of species dissolved in solution. Overall, there are still two electrons per Li$_2$O$_2$ decomposed on charging.

\[
\begin{align*}
\text{Li}_2\text{O}_2(s) & \rightarrow \text{Li}_2\cdot_x\text{O}_2(s) + x\text{e}^- + x\text{Li}^+(\text{sol}) \\ 
\text{Li}_2\cdot_x\text{O}_2(s) & \rightarrow \text{O}_2(g) + (2-x)e^- + (2-x)\text{Li}^+(\text{sol}) \\
\text{Or} & \\
\text{Li}_2\cdot_x\text{O}_2(s) & \rightarrow \text{LiO}_2(\text{sol}) + (1-x)\text{Li}^+(\text{sol}) + (1-x)e^- \\ 
2\text{LiO}_2(\text{sol}) & \rightarrow \text{Li}_2\text{O}_2(s) + \text{O}_2(g) 
\end{align*}
\tag{10-13}
\]

Wagemaker and coworkers$^{93}$ investigated the charging process in a TEGDME-based (DN=16.6) electrolyte using an operando XRD method and observed two distinct stages in the electrochemical profile (Fig. 6a): an initial sloping region (3.0-3.4 V) and then gradual polarization to a flat plateau (at 3.8 V). Interestingly, the (100) and (101) diffraction peak areas of Li$_2$O$_2$ are essentially constant in the sloping region (Fig. 6b,c) but the Li site-occupancy
continues to decrease (Fig. 6d), which suggests that this sloping stage is associated with decomposition of Li$_2$O$_2$ crystal surfaces or amorphous Li$_2$O$_2$. When smaller particles (high Li$_2$O$_2$ surface areas) and more amorphous Li$_2$O$_2$ phases are formed using higher discharge rates (Fig. 6e)$^{36}$, a longer sloping region is observed on the following recharge. Of note, this low voltage sloping region cannot be attributed to decomposition of LiO$_2$ species, due to the observed two electrons per evolved O$_2$ in the corresponding DEMS experiments.$^{99}$ At the second stage, continuous weakening of the diffraction peak intensities and decreases in Li occupancy are observed (Fig. 6c,d), which supports a solid-solution reaction route and this stage is ascribed to the delithiation of bulk crystalline Li$_2$O$_2$ via a Li-deficient intermediate, Li$_{2-x}$O$_2$ (reactions (10-11)). Wagemaker et al. postulated that the Li$_2$O$_2$ particles continue to decompose preferentially at the surface and disappear layer by layer (schematically illustrated in Fig. 6a)$^{93}$ Shao-Horn and coworkers’ PITT (Potentiostatic Intermittent Titration Technique) result$^{96}$ obtained in a DME-based (DN=20) electrolyte further supports this solid-solution view: the observed current in response to potentiostatic steps in the plateau region shows a peak, which is indicative of nucleation and growth of reactive sites (e.g., Li vacancies) in a solid-solution reaction.

Fig. 6 Investigation of the electrochemical decomposition of toroidal Li$_2$O$_2$ crystals in a TEGDME-based electrolyte by operando X-ray diffraction and electrochemical methods. (a): Schematic illustration showing that the charging process undergoes first amorphous Li$_2$O$_2$ decomposition, and then anisotropic delithiation of bulk Li$_2$O$_2$ crystals. (b): three dimensional charge plots of the Li$_2$O$_2$ XRD patterns in the 2θ region of 32-36° recorded in operando during charging. (c): Integrated and normalized areas under the (100) and (101) peaks as a function of charging time; the pink line indicates the linear fit of the points within the shaded or unshaded areas. (d): Evolution of average lithium occupancy as a function of charging time.$^{93}$ (e): Electrochemical charge profiles of Li-O$_2$ cells (at a constant charging rate) following prior discharges with increasing discharge currents.$^{36}$ (f): PITT (which probes the minimum potential needed to drive an electrochemical reaction) charging of a pre-discharged cell in a TEGDME-based electrolyte.$^{98}$ (a-d) Reprinted with permission from ref 93. Copyright 2014 ACS and (e) from ref 36. Copyright 2013 The Royal Society of Chemistry. (f) From ref 98. Copyright 2013 The Royal Society of Chemistry.
Lu and coworkers recently investigated in detail the correlation between the donicity of solvents and the charging mechanism. Unlike the solid-solution charging mechanism that dominates in low donicity solvents (such as TEGDME and DME discussed in Fig. 6), high donicity solvents such as DMSO (DN=30) and Me-Im (1-methylimidazole, DN=47) can lead to charging reactions mediated via the liquid phase (Fig. 7a). By the use of rotating ring disc electrode (RRDE) during charging, for the first time, the oxidation of LiO$_2$ intermediate at the ring electrode was unambiguously observed in a DMSO electrolyte, but no LiO$_2$ was seen in TEGDME (Fig. 7b,c). Similar previous attempts to observe in DMSO was unsuccessful; this was probably due to the low concentration of solvated LiO$_2$ generated by a planar GC disc electrode: Lu et al. used a high surface-area particulate carbon disc electrode. Furthermore, the presence of surface LiO$_2$ species during charging in a high donicity solvent (e.g., Me-Im) was also detected by X-ray absorption near edge structure (XANES) spectroscopy (Fig. 7d,e). Both the RRDE and XANES results thus strongly support the formation of LiO$_2$ reaction intermediate, as solid surface species and dissolved solution species, on charging. Considering that the ring current due to LiO$_2$ oxidation only starts to emerge beyond 3.7 V, Lu and coworkers proposed that in high-donicity solvents the first step on charging is the same as in low-donicity solvents, namely, it occurs via the solid-state reaction (10). The Li-deficient Li$_{2-x}$O$_2$ can be further delithiated to generate LiO$_2$ that dissolves and disproportionates to form Li$_2$O$_2$ in high donicity electrolytes, namely, via reactions (12-13). This redistribution of Li$_2$O$_2$ on charging was also observed by electron microscopy by the same authors.

Although high donicity solvents can promote an additional liquid-phase mass transport pathway on charging, the overpotential in Me-Im is only reduced by 0.2 V compared to diglyme (Fig. 7f), and a large overpotential 0.7 V remains. It thus suggests that reaction (10) is the dominant step determining the charging overpotential. Strategies to facilitate the first delithiation step of Li$_2$O$_2$ need further investigation. In addition, even though the charging voltage is slightly lower, more CO$_2$ evolution due to Me-Im decomposition occurs than in TEGDME, consistent with many earlier conclusions that polar solvents are more susceptible to nucleophilic attack. Therefore, under the mechanism described above, high-donicity solvents are probably not good choices to realize highly rechargeable nonaqueous Li-O$_2$ batteries.
Fig. 7 Solvent dependent oxidation mechanism of Li$_2$O$_2$ in Li-O$_2$ batteries (a). Thin-film RRDE measurements probing the existence of any LiO$_2$(sol) reaction intermediate species during Li$_2$O$_2$ formation and decomposition in 0.2 M LiTFSI TEGDME (b) and DMSO (c) electrolytes; the solid and broken lines correspond to the currents recorded in positive- and negative-direction scans, respectively. O K-edge XANES total-electron yield spectra of various charging stages for Li$_2$O$_2$-prefilled electrodes in LiTFSI/TEGDME (d) and LiTFSI/Me-Im (e) electrolytes. (f): Electrochemical profiles and current responses during PITT charging of Li$_2$O$_2$-prefilled electrodes in four model solvents, namely, tetruglyme (TEG), diglyme (DG), DMSO and Me-Im. Reprinted with permission from ref 45. Copyright 2018 Elsevier.

It is worth noting that some solvents (e.g., hexamethylphosphoramide and water) can significantly increase the solubility of Li$_2$O$_2$ in the electrolyte, thereby enabling a solution-phase mediated mass transport route on charging. Effectively, the charging reaction becomes a three-step process: dissolution of solid Li$_2$O$_2$ in electrolyte, diffusion of solvated peroxide species to the surface, and decomposition of solvated peroxide at the electrode surface. This electrolyte-mediated mechanism is further discussed in Section 4.3.

2.2.2 Reaction Interfaces and Charge Transport Pathways

As can be seen from the above discussion (Figs. 6 and 7), many researchers have pictured, at least at low rates and overpotentials, the solid-solution decomposition and the solvent-mediated steps on charging as starting from Li$_2$O$_2$ surfaces, that is, initiating at the Li$_2$O$_2$-electrolyte interface. This view is broadly consistent with many electron microscopic observations, isotope-assisted DEMS/OEMS and time of flight secondary ion mass spectrometry (ToF-SIMS) results and observations in other alkali-metal oxygen batteries. Figure 8a(i-vi) shows the progressive disappearance of Li$_2$O$_2$ particles with increasing depths of charge. These toroidal particles gradually decrease in diameter with larger gaps being simultaneously developed between individual platelets; an intimate solid-solid contact between Li$_2$O$_2$ and the carbon electrode surface appears to be always maintained. At some point (Fig.
Fig. 7a(iv)), individual platelets of Li$_2$O$_2$ crystals can be identified and they continue to shrink in diameter (v), until complete removal (vi). The constant contact between Li$_2$O$_2$ and carbon electrode suggests that O$_2$ evolution at the Li$_2$O$_2$-carbon interface is unlikely; otherwise, physical detachment will probably occur. If O$_2$ evolution occurs at the Li$_2$O$_2$-electrolyte interface, electronic and ionic charge transport through Li$_2$O$_2$ must occur on charging, even if Li$_2$O$_2$ is a known wide bandgap insulator; feasible charge transport through Li$_2$O$_2$ crystals is further supported by an in situ SEM study of an all solid-state Li-O$_2$ battery where liquid phase mediation can be ruled out.\(^{55}\) Indeed, many theoretical studies identified that Li$^+$ vacancies and hole polarons are the charge carriers in Li$_2$O$_2$.\(^{60, 61, 105-109}\) In the presence of defects, e.g., generation of Li$^+$ vacancies in Li$_2$-xO$_2$ (a Li-deficient intermediate), the ionic and electronic conductivities of Li$_2$O$_2$ can be increased by orders of magnitude,\(^{60, 61, 106, 110, 111}\) especially at the surfaces.\(^{112, 113}\)

The potential charge transport mechanisms during the decomposition of a Li$_2$O$_2$ crystal are schematically illustrated in Figure 8c. When the reaction occurs at the Li$_2$O$_2$-electrolyte interface (Fig. 8c(i-ii)), charge transport can be either dominated by Li$^+$ vacancy diffusion or polaron hopping, or a mixture of both. Charge transport is likely to be predominantly confined to the surface, because of the higher conductivity due to a higher concentration of defects and its proximity to sites where O$_2$ is released. During charging, the constant solid contact between Li$_2$O$_2$ and the electrode surface indicates a strong interaction between them, especially in the presence of high overpotentials; The formation of this chemical bond at the interface has been confirmed by several studies.\(^{54, 114, 115}\) On one hand, the coupling strength of the electrode surface with Li$_2$O$_2$ can be used to mediate the interfacial delithiation of Li$_2$O$_2$, but on the other hand, it also requires the substrate material to be quite resistant to Li$_2$O$_2$ oxidation.

Finally, it should be stressed that the reaction interface on charging is highly dependent on the charge rate and voltages, i.e., high rates/overpotentials tend to cause O$_2$ evolution at the Li$_2$O$_2$-electrolyte interface,\(^{56}\) detaching the remaining Li$_2$O$_2$ from the electrode (Fig. 8b,c(iii)). This disintegration has been reported in both liquid electrolyte\(^{116}\) and all-solid-state Li-O$_2$ setups (Fig. 8b).\(^{117}\) This high dependence of the reaction interface on the charging rate and voltages is in part connected to the intrinsically low conductivity of Li$_2$O$_2$ for both electrons and Li$^+$.\(^{56, 60, 105-109, 118}\) As discussed above, charging reactions occurring at the Li$_2$O$_2$-electrolyte interface necessitate continuous transport of Li$^+$ and/or hole polarons through Li$_2$O$_2$ (Fig. 8c). At low rates, Li$_2$O$_2$ decomposition at the Li$_2$O$_2$/electrolyte interface may be sustained by Li$^+$ and hole polaron diffusion through Li$_2$O$_2$ bulk/surfaces. However, once the transport rate cannot keep up with the current, the reaction interface can switch to the Li$_2$O$_2$/electrode interface. The latter is often observed in CV tests, where voltage sweeps induce high charging rates and as a result, the charge reaction primarily takes place at the Li$_2$O$_2$/electrode interface, thus leading to detachment of Li$_2$O$_2$ from the electrode.\(^{119-121}\) Therefore, to determine where the reaction interface is, one should consider the solvating properties of the electrolyte (Fig. 7), the charging current, overpotentials, and more generally factors that can affect the kinetics of charge transport through
Li$_2$O$_2$ (e.g., temperature). Of note, other charging mechanisms, such as the use of redox mediators and phase transfer catalysts can also alter the reaction interface; this is discussed in detail in Sections 4.2 and 4.3.

Fig. 8 Electron microscopic investigation of Li$_2$O$_2$ oxidation on charging. (a): Morphological evolution of Li$_2$O$_2$ decomposition with progressively deeper charge in a TEGDME-based electrolyte (i-vi). Reprinted with permission from ref 101. Copyright 2013 ACS. (b): *in situ* TEM measurements on the decomposition of toroidal Li$_2$O$_2$ particles deposited on a carbon nanotube (CNT) electrode (highlighted by red broken lines), where a high bias voltage of 10 V against a Si anode is applied to drive the reaction. Reprinted with permission from ref 117. Copyright 2013 ACS. (c): Schematic representation of three mechanistic scenarios for Li$_2$O$_2$ decomposition on charging; in the first two cases (i-ii), the reaction occurs at the Li$_2$O$_2$-electrolyte interface, where charge transfer in Li$_2$O$_2$ is mediated by diffusion of Li$^+$ vacancies (i) and hole polaron hopping (ii); in the third case, the reaction occurs at the Li$_2$O$_2$-electrode interface.
2.2.3 The Origins of High Charging Overpotentials

Unlike the discharge process, the charging is typically characterized by a much larger average overpotential even at low currents: the voltage profile progressively increases with deeper states of charge, from just over 3.0 V to 4.5 V, distinct plateaus being observed in many cases (Fig. 6 and Fig. 9a).36, 66, 96-99 This high charging overpotential can cause considerable parasitic reactions among Li₂O₂, the cathode material and organic electrolytes, posing a significant challenge for achieving a highly rechargeable and energy efficient Li-O₂ battery.91, 99, 122-126 Despite of its importance, the origins of the high overpotential, however, remain somewhat elusive.

Since Li₂O₂ is a wide band-gap insulator,60, 61 many researchers ascribe this high charging overpotential to its low electrical and ionic conductivities. A number of theoretical and experimental studies show that the electrical conductivity is in the range of 10⁻⁹ to 10⁻¹² S/cm and the Li⁺ ionic conductivity is of the order of 10⁻¹⁰ S/cm at room temperature.56, 60, 105-109, 118 These values are considerably lower than those of active materials for high-rate Li-ion battery. Nonetheless, many researchers argue that delithiation of Li₂O₂, especially at its surfaces, is quite facile111,112,118 and that when in the presence of defects, the electronic and ionic conductivities of Li₂O₂ can be increased by orders of magnitude.105,110-113 In situ impedance measurements during charge following a full discharge reveal that the polarization resistance actually decreased from several kΩ (due to the ‘sudden death’ on discharging) to around 500 Ω at the beginning of charge (Fig. 9),66 suggesting that low conductivities of Li₂O₂ is not an major reason for the observed high charging voltage, at least under low charging currents. CV and DEMS measurements show that the onset voltage for an oxidation current in CVs (Fig. 4a) is quite close (<0.2 V) to its equilibrium value,35 where O₂ evolution is indeed detected,99 implying a low reaction kinetic barrier and a small ohmic loss.

Another viewpoint relates the continuously rising overpotential with charging capacity to the gradual detachment of Li₂O₂ from the cathode,127, 128 where the decomposition reaction is considered to occur preferentially at the cathode-Li₂O₂ interface (Fig. 8c(iii)). This mode of charging mechanism, as discussed previously, is typically observed at high charging currents or high overpotentials.56,116,117 If this were indeed the case, an increase of the charge resistance by at least an order of magnitude would be expected; but experimentally the resistance upon charging does not increase,66 so physical detachment cannot explain the high overpotentials seen at low current conditions.
Fig. 9 Electrochemical impedance measurements of Li$_2$O$_2$ formation and decomposition processes at various stages of charge, A-C. Substantial increase in polarization resistance occurs towards the end of the discharge, whereas at the beginning of the charging, this polarization resistance decreases compared to that at the end of the prior discharge. Reprinted with permission from ref 66 and 99. Copyright 2015 ACS and 2012 ACS.

McCloskey, Shao-Horn and coworkers proposed that the rising overpotential with a deeper charge is primarily caused by parasitic reactions. It has been shown by many groups that on charging considerable parasitic reactions occur involving Li$_2$O$_2$, the carbon electrode and the organic electrolyte. As a result, layers of Li$_2$CO$_3$ (and other insulating by-products) accumulate at the Li$_2$O$_2$-cathode and Li$_2$O$_2$-electrolyte interfaces with deeper states of charging and over repeated cycles (Fig. 9). The interfacial Li$_2$CO$_3$ likely plays a decisive role in determining the sluggish oxidation kinetics. It is established that Li$_2$O$_2$ decomposition can readily occur at just over 3 V, whereas Li$_2$CO$_3$ can only be decomposed at beyond 4 V. McCloskey et al. thus proposed that the gradual rising charging profile is a reflection of mixed potentials due to the low oxidizing potential of Li$_2$O$_2$ and the high decomposition potential of Li$_2$CO$_3$, its actual value being critically dependent on the Li$_2$O$_2$/Li$_2$CO$_3$ ratio at the interfaces, and thus depth of charge (Fig. 9). Their hypothesis is consistent with the experimental observation that the average charging voltage increases when more Li$_2$CO$_3$ is present at the Li$_2$O$_2$-electrolyte interface: as the voltage rises on charging, O$_2$ evolution due to Li$_2$O$_2$ progressively reduces while CO$_2$ evolution due to Li$_2$CO$_3$ decomposition continues to increase beyond 4 V. Subsequent modeling shows that just two monolayers of Li$_2$CO$_3$ on top of Li$_2$O$_2$ can reduce the transport current by two orders of magnitude, reiterating the critical challenge due to the interfacial Li$_2$CO$_3$ formation.

In summary, at lower rates, the observed high overpotentials are likely to be a combined result from both byproducts accumulation at the reaction interfaces and the insulating nature of all deposits (Li$_2$O$_2$, Li$_2$CO$_3$ and so on). At high rates, physical detachment of Li$_2$O$_2$ from the electrode and loss of electrical contact may become the dominant reason. In addition to the aforementioned factors, clogging of porous carbon electrode by byproducts and degradation of
Li metal anode due to an unstable solid-electrolyte interface (SEI) are other plausible reasons for the increasing polarization.

Although further investigations are required to fully unravel the origins of high charging voltages, existing evidence highlights the necessity of enabling faster charge/mass transport kinetics and minimizing parasitic byproduct formation and accumulation during charge. Soluble redox mediators that can chemically decompose Li₂O₂ have been considered as a promising strategy to achieve these goals. Facile charge (electron/hole) transfer pathways in electrolytes are realized by shuttling of reduced/oxidized mediator molecules between the electrode surface and Li₂O₂, the latter being decomposed by the oxidized state of the mediator. This approach will be discussed in detail in Section 4.2.

2.2.4 Parameters Characterizing the Reaction Reversibility

The reversibility and performance metrics have been intensively discussed since the early days of lithium-air battery research. It was gradually realized that coulometry alone is insufficient to evaluate the true reversibility of a Li-O₂ battery. Therefore, it is of paramount importance to use multiple quantification methods to investigate the discharge-charge cycles. McCloskey, Bruce and their coworkers designed a series of in situ and ex situ characterization methods, namely mass spectrometry (differential electrochemical mass spectrometry, DEMS and online electrochemical mass spectrometry, OEMS) and chemical titration, to quantify the O₂ consumption/evolution and Li₂O₂ formation/decomposition at different stages of cycling. Parasitic reaction products, such as Li₂CO₃ and Li carboxylates etc., can also be quantified by FTIR, NMR, mass spectrometry and UV-vis methods.

Since gaseous O₂ is converted to a solid on discharging and is expected to be released back to the atmosphere on charging, the ratio of O₂ evolution/consumption or O₂ recovery efficiency (OER/ORR) of a single electrochemical cycle is the most critical parameter to assess the battery reversibility. This parameter can be obtained by DEMS/OEMS measurements. Figure 10(a-c) shows the quantification of O₂ and Li₂O₂ at different states of discharge and charge using DEMS and titration. When O₂ is reduced on discharging, DEMS data show that the oxygen reduction reaction closely follows the expected 2 electrons per O₂ stoichiometry, although Li₂O₂ titration suggests that not all the reduced O₂ ends up as Li₂O₂. During Li₂O₂ decomposition on charging, titration shows that the Li₂O₂ is quantitatively removed as expected from stoichiometry, with small deviations only toward the end of charge. What is more significant on charging, however, is that the actual released O₂ is much less than the expected value from the decomposed Li₂O₂; this discrepancy was later associated with the fact that part of the O₂ evolved is released in the form of singlet O₂, which is consumed in degradation reactions. Overall, O₂ evolution amounts to only ~75% of O₂ consumption (OER/ORR=0.75). The lost oxygen is
primarily converted to parasitic reaction products, such as CO₂, Li₂CO₃, LiOH, LiRCO₃ etc., by corroding the carbon electrode and decomposing the organic electrolyte (Fig. 10a). To achieve a highly reversible Li-O₂ battery, these parasitic reactions must be considerably suppressed.

Fig. 10 A combination of quantitative gas and chemical analysis techniques (such as DEMS, titration, NMR etc.) are needed to quantify the amount of Li₂O₂ and parasitic reaction species formed and decomposed, and the associated O₂ consumption/evolution at the different states of discharge and charge (a). On discharging, the electrochemical O₂ reduction reaction closely follows the 2e⁻/O₂ molar ratio (b), although not all the electrochemical reduced O₂ ends up as Li₂O₂, resulting a slight deviation of the titrated Li₂O₂ from that of e⁻/O₂. On charging (c), Li₂O₂ removal closely follows the 2e⁻/Li₂O₂ trend line until the end of charge, although the detected O₂ evolution considerably deviates from the ideal 2e⁻/O₂ molar ratio. Reprinted with permission from ref 132. Copyright 2013 ACS.

3. Key Remaining Challenges: Parasitic Processes

In the early years of research, there were many daunting challenges facing lithium-air batteries, such as low rate capability, low practical capacity, large voltage hysteresis, Li metal anode dendrite formation, and very poor rechargeability due to parasitic reactions. Over the past 8 years, significant progress has been made to address some of these challenges. For example, we now understand that the practical cell capacity can be improved by wisely choosing the salt/solvent/additives for an electrolyte, the rate can be increased by the use of mediators, overpotentials and carbon/electrolyte corrosion can be reduced by using catalysts/redox
mediators.115, 127, 141, 142 As a result, the rechargeability of a lithium-air battery has significantly improved over the past few years.

Nevertheless, many critical challenges still remain concerning the stability of electrodes and electrolytes due to parasitic processes. Reactive oxygen species formed during discharge and charge can seriously degrade the cathode material and the organic electrolyte; the situation is even worse in the presence of high overpotentials. Further reduction of these unwanted side reactions is required to realize practical applications of the battery. In addition, most current lab-scale lithium-air batteries still use pure O2 as the atmosphere. Gas separation and purification technologies have been proposed28 to resolve the air contamination issue to both O2 cathode and Li anode. These air treatment and handling accessories, however, will significantly compromise the specific energy of lithium-air batteries. Simpler and lighter components, such as a single gas separation membrane, currently cannot remove to a low enough level all the unwanted air contaminants (i.e., H2O, CO2 and N2) that can react the lithium metal and the various products and intermediates found in Li2O2 chemistries. This is related to the similarities of gas kinetic diameters and molecular chemical properties as compared to O2, making it very difficult to achieve both high permeance and selectivity of O2 in a single stage separation.143-147 Hence a practical lithium-air battery may eventually have to tolerate hundreds ppm of CO2, H2O, and N2, if it were to be used in electric vehicles, a commonly proposed application. In this section, we review the original causes of parasitic reactions occurring to the organic electrolyte, the carbonaceous electrode and the lithium anode, and discuss the effects of other air components (N2, CO2, H2O) on the electrochemistry at both the O2 cathode and Li anode.

3.1 (Electro-)chemical Instability of Electrolytes

An ideal electrolyte for lithium-air batteries should satisfy the following requirements:8, 91, 122, 148-152 (1) low volatility and nonflammability; (2) high O2 solubility and diffusivity; (3) formation of a stable solid electrolyte interface layer with the Li metal anode; (4) outstanding chemical and electrochemical stability in the presence of reactive oxygen species. Among them, electrolyte stability in the presence of electrode reactions is the most basic and critical requirement; this is the focus of discussion in this section, particularly on the stability issues involving the O2 electrochemistry. The compatibility of Li metal anode and electrolytes will be discussed in Section 3.3. As we will see, to satisfy even just the stability requirement of electrolytes presents a substantial scientific challenge, primarily because many of the desired physicochemical properties of an electrolyte are inversely correlated with each other.

3.1.1 Mechanisms of Electrolyte Decomposition by Reactive Oxygen Species

A nonaqueous electrolyte for a lithium-air battery typically consists of a lithium salt and an organic solvent.91 At the end of Section 2, we mentioned that there is significant electrolyte decomposition at the cathode during battery cycling.40, 91, 99, 122-126, 139, 153 These parasitic
reactions are caused by a number of reactive oxygen species, including superoxides (O$_2^-$, LiO$_2$, HO$_2$), peroxydes (Li$_2$O$_2$, Li$_2$O$_2$) and singlet oxygen ($^1$O$_2$). Since the 1970s, many insightful studies have been performed on the reactivity of these oxygen species, particularly superoxide, towards organic solvents. Their reactivity derives from the fact that they are strong nucleophiles (superoxide and peroxide), strong bases (superoxide and peroxide), good one-electron transfer agent (superoxide), and radicals (superoxide). Because of its high nucleophilicity, O$_2^-$ has the tendency to attack the positively charged components of any organic species in the absence of protons. When acidic groups are present in a solvent molecule, proton abstraction from the solvent by O$_2^-$ due to its basicity may play a significant part in the reaction characteristic. Autoxidation by O$_2^-$ and O$_2$ has also been proposed to be a general mechanism that degrades electrolytes. On the other hand, parasitic processes due to the radical nature of superoxide are much less discussed in literature; but it may become more relevant in the presence of redox mediators, where irreversible reaction of superoxide with redox mediator radicals may occur. Figure 11 summarizes some common side-reaction mechanisms of the reactive oxygen species with organic solvents, namely, nucleophilic attack, acid-base reaction, proton-mediated degradation, and autoxidation. Some of these reactions can also involve the peroxide species, which are nucleophilic and basic as well. Another pivotal factor that must be mentioned is the coordination of solvents with Li$^+$, which being a strong Lewis acid can further polarize solvents, facilitating degradation processes via nucleophilic attack and proton abstraction.

**Fig. 11** Schematic illustration of various decomposition mechanisms of organic electrolytes by reactive oxygen species (O$_2^-$, Li$_2$O$_2$, Li$_2$O$_2$, O$_2$, $^1$O$_2$) in a Li-O$_2$ battery, such as nucleophilic attack, proton mediated decomposition, autoxidation, acid/base reactions, degradation induced by singlet oxygen. Reprinted with permission from ref 167 and 171. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim and 2017 Nature Publishing Group.
Given the above information and experimental observations, considerable effort has been made to find an ideal electrolyte solvent, which is optimized with respect to the electrolyte’s properties against nucleophilic attack, hydrogen/proton abstraction, and on promoting electrochemical stability. Unfortunately, even with large-scale solvent screening methods, this search for an optimal organic electrolyte has largely proven fruitless thus far.\textsuperscript{91, 163, 165, 172-177} For instance, through screening a large number of solvents, a few groups\textsuperscript{175, 177} have identified descriptors that can characterize the stability of a solvent in the lithium air battery context (Fig. 12): bond dissociation energy (relating to H-abstraction), deprotonation free energy/pK\textsubscript{a} (relating to acid-base reaction), nucleophilic substitution free energy (relating to nucleophilic attack) and HOMO level (electrochemical stability against oxidation). As can be seen in Figure 12, the scope for a promising electrolyte is quite constrained.\textsuperscript{91, 175, 177} High chemical stability to nucleophilic attack and H abstraction dictate a solvent with low electron affinity, whereas high electrochemical stability requires a solvent with high ionization potential. These two requirements, unfortunately, are inversely correlated. To alleviate this issue, one needs to find alternative strategies to decouple these requirements for an optimal electrolyte. For instance, the use of redox mediators that significantly reduce the overpotentials is an effective strategy to achieve a more stable electrolyte against reactive oxygen species; this is because the smaller electrochemical window (due to lower overpotentials) permits the use of electrolytes with low electron affinity, thereby less prone to nucleophilic attack or H abstraction by superoxide species. The strategy of redox mediators is discussed in detail in Section 4.2.

Recently, the important role of singlet oxygen (\(^1\text{O}_2\)) in electrolyte decomposition of metal-oxygen batteries has been unraveled.\textsuperscript{139, 140, 153, 178, 179} There is a rich literature on the reactivity of \(^1\text{O}_2\) with organic materials, where peroxide, hydroperoxide species and hydroxyl radicals can be generated by \(^1\text{O}_2\) reactivity and cause further transformation of organic molecules.\textsuperscript{180} By using \(^1\text{O}_2\) trapping molecules such as 2,2,6,6-tetramethyl-4-piperidone\textsuperscript{139} and 9,10-dimethylanthracene (DMAn)\textsuperscript{153}, several groups found that \(^1\text{O}_2\) was formed on both discharge and charge. Two major processes have been suggested for \(^1\text{O}_2\) generation:\textsuperscript{139, 153} 1) chemical disproportionation of superoxide species (LiO\textsubscript{2} or Ho\textsubscript{2}) to form peroxide on either discharge or charge; 2) electrochemical Li\textsubscript{2}O\textsubscript{2} or Li\textsubscript{2}O\textsubscript{2} decomposition occurring at charging voltages higher than 3.26-3.43 V (estimates for the thermodynamic \(^1\text{O}_2\) generation voltage-equilibrium potential of O\textsubscript{2}/LiO\textsubscript{2} + energy difference between \(^1\text{O}_2\) and \(^3\text{O}_2\)).\textsuperscript{153} Electrolyte decomposition products due to \(^1\text{O}_2\), such as Li\textsubscript{2}CO\textsubscript{3} and Li formate, are detected in a DME-based electrolyte, similar to those incurred by reduced oxygen species;\textsuperscript{153} this may be connected to the fact that reactive oxygen species (e.g., peroxides) can be generated via reactions of \(^1\text{O}_2\) with organic solvents.\textsuperscript{180} Further quantitative analysis suggests that \(^1\text{O}_2\) accounts for a major fraction of the side reaction product formed during cycling of aprotic lithium-oxygen batteries.\textsuperscript{153} These results nicely explain the large discrepancy observed between quantities of evolved O\textsubscript{2} actually detected and that expected from the decomposition Li\textsubscript{2}O\textsubscript{2} on charging (Fig. 11),\textsuperscript{171} which amounts to ~20% of O\textsubscript{2} loss per cycle. If reactions of \(^1\text{O}_2\) are indeed the dominant underlying issue hampering reversibility, the current strategies centered around superoxide/peroxide reactivities to minimizing parasitic
reactions must be adjusted. New strategies that can either prevent formation of singlet O$_2$ or quench its reactivity with the electrolyte are urgently needed; this is discussed in Section 4.3.3.

![Diagram](image)

**Fig. 12** Criteria for assessing the electrochemical and chemical stability of an organic electrolyte in a Li-O$_2$ battery, including bond dissociation energies, acidity (deprotonation free energies), nucleophilic substitution free energy, and electrochemical stability. These parameters are used to evaluate the susceptibility of molecules to hydrogen abstraction, deprotonation, nucleophilic substitution and redox reactions. Some of these required properties (e.g., nucleophilic substitution free energy and electrochemical stability) for an ideal organic solvent are inversely correlated, leading to a significant challenge in identifying an optimal electrolyte. Reprinted with permission from ref 175 and 177. Copyright 2014 ACS and 2017 The Royal Society of Chemistry.

### 3.1.2 Progress in Solvent Discovery

A wide range of organic solvents with different functional groups and structures has been explored experimentally and theoretically as electrolytes for lithium-air batteries. These mainly include carbonates, sulfoxides, sulfones, polyethers, nitriles, amides and room temperature ionic liquids. As discussed earlier, all these electrolytes suffer from parasitic reactions due to reactive oxygen species, but to a different extent. Unlike in most other electrolytes where Li$_2$O$_2$ is the main discharge product, carbonate-based electrolytes mainly lead to byproduct formation (such as Li$_2$CO$_3$ and carboxylates) due to the nucleophilic attack of superoxide. Later on, another polar solvent, DMSO, had been considered as a promising electrolyte, encouraged by a few earlier reports. But the subsequent investigations suggest that it is also prone to nucleophilic attack and H abstraction by superoxide, and that the OER/ORR ratio is actually lower than those using less polar electrolytes. Ethers such as glymes are less polar and generally suffer less from side reactions, although H abstraction by superoxide and peroxide species still occur.
More interesting but yet less understood properties have been reported on using nitriles, ionic liquids and amides as solvents for lithium air batteries. In one systematic study, an acetonitrile electrolyte exhibits the highest reversibility of all other 8 solvents, with OER/ORR of 88% (Fig. 13a). On discharging, the e'/O₂ ratio equates to 2.01. On charging, O₂ evolution nicely follows the expected trend line until the end of charging, where CH₃CN decomposition starts to occur above 5 V versus Li⁺/Li. This result suggests that little parasitic reaction due to reactive oxygen species (Li₂O₂, Li₂₋₂O₂, ʻO₂ etc.) occurred during 90% of the recharge, that is, acetonitrile exhibits both high electrochemical stability and chemical stability against nucleophilic attack and H abstraction (clearly an outlier from the theoretical considerations). The origin of these observations is thus worthy of further investigation. Of note, although CH₃CN is not stable in contact with the lithium anode, protection of the lithium anode with a solid electrolyte coating could overcome that issue.

Many room-temperature ionic liquids, such as imidazolium-, pyrrolidinium-, and piperidinium-based ionic liquids, have been explored as solvents for lithium air batteries. Not all the ionic liquids exhibit suitable chemical stability in lithium oxygen cells, but pyrrolidinium-based ILs have been reported to be stable against superoxide attack. It is interesting to note that, under some conditions, the onset charging voltage is just over 3 V and the majority of charging capacity finishes below 3.5 V (Fig. 13b). Online mass spectrometry measurements confirm that the charging process is close to 2e'/O₂. This ability to decompose Li₂O₂ at well below 3.5 V, much lower than in other common organic solvents, is useful and intriguing. Is this lower kinetic barrier linked to a better solvation of O₂⁻ by the soft ionic liquid cation, so that the sluggish 1ˢᵗ step delithiation of Li₂O₂ to Li₂₋₂O₂ (or LiO₂) becomes easier? Or does the ionic liquid better dissolve parasitic reaction products (e.g., Li₂CO₃) and the discharge product (Li₂O₂) by solvating CO₃²⁻ and O₂²⁻, so that the mixed charging potential issue is alleviated; or is a more facile mass transport route for peroxide via the liquid phase enabled by the ionic liquid, which essentially acts as a phase transfer catalyst promoting an electrolyte-mediated charging process? While the reactivity of IL cations with superoxide can be improved via molecular engineering, the significance of understanding the above questions may have a broad impact on how to improve the Li-O₂ electrochemistry. It could help further understand the origin of high charging voltages and develop new mechanisms to improve the energy efficiency. In general, a low cycling voltage hysteresis is always desirable, as it relaxes the other constraints on satisfying the challenging chemical stability requirement in a lithium-air battery.

Another group of solvents that have been intensely studied are amides. Bruce and coworkers investigated common amide solvents, including N,N-dimethyl formamide (DMF), N,N-dimethylacetamide (DMA) and N-methyl-2-pyrrolidone (NMP). Due to high polarity and acidity of amides, considerable parasitic reactions due to nucleophilic attack and acid-base reactions were observed, and the battery’s capacity faded by more than 50% in 10 cycles, even when lithium iron phosphate was used as the counter electrode. Later on, however, Walker, Addison and coworkers reported that by using DMA and N-methylacetamide (NMA) as the electrolyte solvent,
the cell showed no discharge capacity decay after 80 cycles, at 1 mAh/cm² per cycle. O₂ evolution over extended cycles was confirmed and OER/ORR ratio was estimated to be ~85% (based on pressure measurements). More recently, Peng and coworkers reported the use of hexamethylphosphoramide (HMPA) as the electrolyte solvent. An outstanding cycling stability, that is, no discharge capacity decay (~1 mAh/cm² per cycle) up to 180 cycles, was demonstrated. Furthermore, more than 95% of oxygen was recovered on charging (OER/ORR>95%) over the first 100 cycles, suggesting that only very minimal side reactions occur during discharge and charge. The authors ascribed the excellent performance to the increased solubility of Li₂O₂, LiOH and Li₂CO₃ in HMPA that helps reduce the charging overpotential and postpone the complete electrode passivation caused by side reactions. The work by Peng and coworkers indicates that solvents with higher Li₂O₂ solubility can potentially provide a facile solution-phase charging mechanism and significantly lower the charging voltage, consistent with the role of a phase transfer catalyst proposed in literature. Therefore, influential factors that promote Li₂O₂ dissolution in electrolytes and the mechanism of the solvated peroxide decomposition on the electrode surface are worth exploring further.

Fig. 13 A few selected electrolyte systems that exhibit interesting properties for Li-O₂ batteries. (a): Galvanostatic discharge-charge (i) for a cell using 1 M LiBF₄/CH₃CN electrolyte (note: LiFePO₄ is the counter electrode); the cell was discharged under O₂ and charged under Ar, the corresponding O₂ consumption and evolution were quantified (ii-iii). (b): OEMS analysis of the first charge of a Li-O₂ cell using a LiTFSI/Pyr₁₄TFSI ionic liquid electrolyte at 20 and 60°C; O₂ evolution from Li₂O₂ decomposition occurs at as low as 3.0 V in this electrolyte system. (c): Galvanostatic cycling of Li-O₂ cells using hexaphosphoroanamide (HMPA), tetraglyme (TEGDME) and monoglyme (DME) based electrolytes, where HMPA shows a superior performance with much lower charging overpotential and better rechargeability than the other two cases; the corresponding DEMS analysis on O₂ consumption and evolution is presented in (d), where at the 100th cycle the OER/ORR ratio is still close to 100%. (a) Reprinted with
3.2 Parasitic Reactions at the Carbon Cathode

3.2.1 Carbon Corrosion at the Carbon-Electrolyte and Li$_2$O$_2$-Carbon Interface

Carbon is the most extensively explored host material for Li$_2$O$_2$, due to its light weight, low cost, high electrical conductivity, processability into various structures and forms, relative stability etc. The chemical stability of carbon cathode against the reactive oxygen species has a profound impact on the reversibility of the battery. Many fundamental studies have been performed to elucidate the corrosion mechanism of carbon cathode, especially in the presence of high overpotentials.\textsuperscript{99, 123, 124, 126, 213-215} It is now realized that charging overpotentials,\textsuperscript{99, 126} types of electrolyte,\textsuperscript{91, 126} the carbon surface defect and functionalization\textsuperscript{126, 215} can all affect carbon degradation in a Li-O$_2$ battery.

McCloskey and coworkers\textsuperscript{99} first raised the issue that in the presence of the discharge product, Li$_2$O$_2$, and a highly oxidizing environment, carbonaceous cathode may undergo oxidation reaction to form Li$_2$CO$_3$, via reactions (14-15).

\[
\text{Li}_2\text{O}_2 + \text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad (14)
\]

, where $\Delta G^o$ is equal to -542.4 kJ/mol at 300 K.

\[
2\text{Li}_2\text{O}_2 + \text{C} \rightarrow \text{Li}_2\text{O} + \text{Li}_2\text{CO}_3 \quad (15)
\]

, where $\Delta G^o$ is equal to -533.6 kJ/mol at 300 K.

As suggested by the $\Delta G^o$ of these reactions, the formation of Li$_2$CO$_3$ by reacting Li$_2$O$_2$ with carbon cathode is thermodynamically highly favorable. It implies that there should be significant Li$_2$CO$_3$ formation at the Li$_2$O$_2$-carbon interface at the end of discharge. Nonetheless, only very little Li$_2$CO$_3$ byproduct was detected on discharging,\textsuperscript{132} for example, in ether-based electrolytes. To further investigate this source of Li$_2$CO$_3$, Xu and coworkers\textsuperscript{213} performed solid state $^{13}$C nuclear magnetic resonance measurements on a $^{13}$C-enriched (99%) carbon cathode after discharge, which was then compared to that detected on natural abundance carbon cathode. If the formed Li$_2$CO$_3$ was indeed due to a direct reaction with the $^{13}$C cathode, the $^{13}$C NMR signal of Li$_2$CO$_3$ would be higher by around two orders of magnitude than that of a natural abundance sample. However, this was not observed to be the case. In addition, the Li$_2$CO$_3$ species was easily rinsed off by solvents.\textsuperscript{213} Therefore, on discharging the observed Li$_2$CO$_3$ is likely to be due to electrolyte decomposition rather than direct carbon corrosion.\textsuperscript{91, 126, 132, 213} Although thermodynamics permits the Li$_2$O$_2$-carbon reaction (reactions (14-15)), the kinetics of the Li$_2$O$_2$-carbon reactions is slow.
At the carbon-electrolyte interface, carbon corrosion can also be induced by other reactive oxygen species, such as superoxide ($O_2^-$, LiO$_2$), and singlet oxygen (discussed in Section 3.1.1); this process is dependent on the type, crystallinity and surface functionality of the carbon cathode. Bruce, Shao-horn and coworkers found that carbon cathodes (graphitic carbon or reduced graphene oxides) with high density of oxygenated groups (C=O, C-O, C-OH, COOH etc.) exhibit limited stability against the lithium-oxygen electrochemistry: superoxide species formed during discharge can oxidize carbon at the defect site to form Li$_2$CO$_3$. Kang, Itkis and coworkers further pointed out that the crystallinity of the carbon cathode also has an impact on its chemical stability: more ordered carbon structures are preferred for a stoichiometric Li$_2$O$_2$ reaction.

Charging is a completely different case. McCloskey, Bruce and coworkers made cells using $^{13}$C-labeled carbon electrode but naturally abundant ether-based electrolytes, and monitored the CO$_2$ evolution on charging using DEMS. They observed that $^{12}$CO$_2$ evolved at all charging voltages, but significant $^{13}$CO$_2$ only started to evolve beyond 3.8 V (Fig. 14a); this observation suggests that electrolyte decomposition occurs at all charging voltages (due to reactions with Li$_2$O$_2$, Li$_2$O, LiO and O$_2$), whereas direct carbon corrosion happens only at higher charging overpotentials, CO$_2$ being evolved due to electrochemical Li$_2^{13}$CO$_3$ decomposition. Furthermore, they also observed that $^{18}$O-labeled Li$_2^{18}$O$_2$ formed in the prior discharge led to scrambled $^{12}$C$^{16,18}$O$_2$ evolution on charging (Fig. 14a), which indicates that the oxygen in CO$_2$ comes from both Li$_2$O$_2$ and the electrolyte. McCloskey and coworkers thus proposed that as the charge proceeded, parasitic reactions occurred at both the Li$_2$O$_2$-electrolyte and Li$_2$O$_2$-carbon interfaces, with Li$_2$CO$_3$ being accumulated over repeated cycles. The proposed locations of the interfacial Li$_2$CO$_3$ were confirmed later by X-ray absorption near edge structure spectroscopy (total electron yield, TEY mode) and $^{13}$C-$^{13}$C 2D homonuclear correlation NMR spectroscopy (Fig. 14b). The NMR cross peaks (Fig. 14b) between $^{13}$C resonances of Li$_2$CO$_3$ and the carbon electrode (indicated by the arrows) suggest that they are in direct contact (within a few angstroms). These interfacial passivating Li$_2$CO$_3$ films cause significant polarization on charging, which induces further parasitic reactions. Hence, to avoid serious carbon corrosion and minimize the formation of interfacial Li$_2$CO$_3$, it was suggested that the charging voltage in a carbon-based Li-O$_2$ battery should be kept below 3.5 V (Fig. 14c).
Challenges associated with the carbon electrode in Li-O_2 batteries. (a): Linear sweep voltammogram and concomitant CO_2 evolution from a Li-O_2 cell discharged under ^{16}O_2, using a ^{13}C cathode and natural abundance electrolyte (1 M LiTFSI/DME); ^{13}CO_2 is evolved at potentials >3.8 V, and is linked to parasitic reactions occurring at the Li_2O/^{13}C Carbon interface. (b): ^{13}C-^13C 2D homonuclear NMR correlation experiment of a ^{13}C carbon enriched cathode on its 5th discharge to 2 V, the method probing spatial proximity between ^{13}C sites; a homonuclear correlation (a cross peak, indicated by the arrows) was detected between Li_2CO_3 resonance at 168 ppm and the carbon electrode signal at 130 ppm, indicating that at least some of the Li_2CO_3 forms directly (within a few angstroms) on the carbon surface. (c): Schematic illustration showing that on discharging to 2 V and on charging below 3.5 V, CO_2 evolution primarily originates from electrolyte decomposition, whereas above 3.5 V on charging, carbon corrosion also leads to CO_2 evolution. (a) Reprinted with permission from ref 99. Copyright 2012 ACS and (b) from ref 214. Copyright 2013 ACS. (c) From ref 126. Copyright 2013 ACS.

3.2.2 Influence of N_2, CO_2 and H_2O on the Non-aqueous O_2 Electrochemistry

Apart from carbon corrosion, the other constituents of the air can also incur undesirable processes at the cathode. In this section, we discuss in sequence the N_2, CO_2 and H_2O effects on the non-aqueous O_2 electrochemistry in lithium-air batteries.

N_2 gas composes 78% of the air. Fortunately it does not seem to affect the oxygen reduction reaction in Li-O_2 batteries. In some studies, Li-O_2 batteries have been cycled in ambient air, but few studies have reported involvement of nitrogen in the oxygen electrochemistry within the typical electrochemical testing window (2-4.5 V), i.e., N_2 seems inactive to any reactions with the reduced oxygen species and it does not undergo any redox reaction itself. Indeed, to electrochemically reduce N_2 and generate Li_3N, one needs to reach to very low potentials, the equilibrium voltage is calculated to be around 0.46 V versus Li^+/Li (formation free energy for
Li$_3$N, $\Delta G^\circ=-129\text{--}135$ kJ/mol.$^{224, 225}$ The absence of any N$_2$ interference with O$_2$ electrochemistry is encouraging, because it avoids increased complexity of cathode reaction and the necessity of complete separation of O$_2$ and N$_2$ from the air.

CO$_2$, by contrast, can react readily with reduced oxygen species (superoxide and peroxide) in a nonaqueous Li-O$_2$ battery.$^{129, 226-233}$ First, CO$_2$ can react with Li$_2$O$_2$ to form Li$_2$CO$_3$ via reaction (16).$^{129, 227, 230}$

$$Li_2O_2 + CO_2 \rightarrow Li_2CO_3 + \frac{1}{2} O_2, \Delta G^\circ=-166.6 \text{ kJ/mol} \quad (16)$$

This reaction has a few consequences: 1) parasitic reactions with aprotic polar electrolyte solvent can be induced by intermediates of this reaction, e.g., peroxycarbonate (Fig. 15a): significant oxidation of DME and DMSO solvents (to methyl methoxyacetate and DMSO) was detected when exposing Li$_2$O$_2$ to CO$_2$ in these solvents;$^{232}$ 2) the conversion of Li$_2$O$_2$ to Li$_2$CO$_3$ causes further polarization on recharging the battery, the high overpotentials in turn accelerating the battery degradation.$^{129, 227, 230}$ The decomposition of Li$_2$CO$_3$ typically involves irreversible reactions (Fig. 15b).

Secondly, O$_2^-$, as a strong nucleophile and a good charge transfer agent,$^{112, 157}$ can react with CO$_2$ to form a series of peroxycarbonate species, namely, COO$_i^-$, CO$_4^{2-}$, C$_2$O$_6^{2-}$ (Fig. 15a).$^{226, 227, 230, 231}$ Some of these species have indeed been confirmed by Qiao and coworkers$^{231}$ using in situ Raman spectroscopy in a Li-free TBACIO$_4$/DMSO electrolyte (Fig. 15(i-iii)). When increasing the CO$_2$/O$_2$ molar ratio in the cell atmosphere, the dominant electrochemistry switches from O$_2$/O$_2^-$ to O$_2$-CO$_2$/C$_2$O$_6^{2-}$ (Fig. 15c(i-iii)).$^{231}$ At O$_2$/CO$_2$ of 4/1 (Fig. 15c(iii)), C$_2$O$_6^{2-}$, CO$_2^{2-}$, and O$_2^-$ appear in sequence on reduction following reactions (17), (18) and (4).$^{231}$ Of note, no carbonate formation (~1095 cm$^{-1}$) occurs in the Li-free electrolyte (Fig. 15c(ii)). In the presence of Li$^+$, however, Li$_2$CO$_3$ forms as the dominant discharge product (Fig. 15c(iv-vi)). Clearly, the soft TBA$^+$ cation can more effectively stabilize the soft peroxycarbonate anion than the harder Li$^+$, hence avoiding further conversion of C$_2$O$_6^{2-}$ to CO$_3^{2-}$. Overall, the discharge reaction has been proposed to occur via reaction (19),$^{227, 230}$ whereby 1.33 electrons are consumed per gas molecule; this has been confirmed by operando electrochemical pressure measurements.$^{230}$

$$O_2 + CO_2 + 2e^- \leftrightarrow COO_i^{2-}, E^o = 2.89 \text{ V} \quad (17)$$

$$O_2 + 2CO_2 + 2e^- \leftrightarrow C_2O_6^{2-}, E^o = 3.27 \text{ V} \quad (18)$$

$$O_2 + 2CO_2 + 4e^- + 4Li^+ \leftrightarrow 2Li_2CO_3, E^o = 3.82 \text{ V} \quad (19)$$

On charging, many groups$^{129, 227-231, 233, 234}$ have reported that the discharge product Li$_2$CO$_3$ is removed at voltages typically higher than 4 V (Fig. 15c(iv)); however, this should not be taken as the evidence for a reversible reaction. In fact, the change in pressure deviates significantly from the predicted 1.33 e$/\text{gas molecule}$ (Fig. 15b)$^{230}$ and no O$_2$ evolution was observed,$^{129, 229-231}$ resulting in a continuously dropping cell pressure over many cycles (Fig. 15b). The missing
oxygen may remain in the cell, either as a component of passivating solid byproducts at the cathode or soluble species in the residual electrolyte (e.g., cumulative DMSO₂ formation seen over cycles in Fig. 15c(vi)²³¹). Freunberger and coworkers¹⁷⁹ recently reported that the electrochemical decomposition of Li₂CO₃ involves stoichiometric generation of singlet oxygen (as in the reversal of reaction (19)), and that the absence of O₂ evolution on charging can be attributed to the parasitic reactions of ¹O₂ with cell components. These authors¹⁷⁹ further showed that with singlet oxygen quencher additives in the electrolyte, a small fraction of the formed ¹O₂ can be released as ³O₂; this observation suggests that electrochemical Li₂CO₃ decomposition in aprotic media involves O-O reformation and that with a suitable singlet oxygen quencher, the reversibility of reaction (19) could be improved.

Fig. 15 The impact of CO₂ on the O₂ electrochemistry in non-aqueous media. (a): Possible reaction intermediates involved in the reaction between CO₂ and reduced O₂ species (O₂⁻, O₂²⁻).²³² (b): Operando pressure measurements during cycling of a Li-O₂/CO₂ cell (O₂:CO₂=7:3) in a LiClO₄/DMSO electrolyte; the discharge process (pressure drop) shows an e⁻/gas ratio of 1.3 (close to the expected 1.33 value), but the charge process exhibits an e⁻/gas ratio of
2.26 indicating an irreversible electrochemistry in the Li-O₂/CO₂ cell.²³⁰ (c): in situ surface enhanced Raman (roughened gold electrode surfaces) investigation on the O₂/CO₂ electrochemical reaction mechanism in the absence (i-iii) and presence (iv-vi) of Li⁺; in the absence of Li⁺, the electrochemistry can be modulated from O₂/CO₂ to O₂- CO₂/C₂O₆²⁻ by increasing the CO₂/O₂ molar ratio in the cell atmosphere; in the presence of Li⁺, the cell electrochemistry is dominated by Li₂CO₃ formation and decomposition, the latter involves DMSO electrolyte oxidation to DMSO₂.²³¹ (a) Reprinted with permission from ref 232. Copyright 2017 The Royal Society of Chemistry and (b) from ref 230. Copyright 2017 ACS. (c) From ref 231. Copyright 2018 The Royal Society of Chemistry.

In summary, contamination of CO₂ in Li-O₂ batteries can cause significant degradation of the electrolyte during its reactions with reduced oxygen species to form Li₂CO₃; Li₂CO₃ cannot be oxidized reversibly via reaction (19), and its removal is actually associated with the degradation of the electrode/electrolyte, likely due to the generation of ¹O₂ on charging. Besides, it significantly raises the charging overpotential, imposing stringent requirements on the cell components (cathode and electrolyte) to achieve a reversible Li₂O₂ chemistry. At the current stage, Li₂CO₃ formation should therefore be avoided in a Li-O₂ battery.

Inspired by the potential stabilization of C₂O₆²⁻ by the softer TBA⁺ ion (vs. Li⁺), Qiao and coworkers²³¹ explored the effect of a complexed Li⁺(DMSO)₃ in concentrated LiTFSI/DMSO electrolyte to stabilize C₂O₆²⁻, where the coordinating DMSO molecules effectively screen the charge of Li⁺, thereby decreasing the interactions of Li⁺ with C₂O₆²⁻. As a result, they found that the dominant charging reaction gradually changes from solid-state Li₂CO₃ decomposition at 4.2 V to decomposition of soluble Li₂C₂O₆ species at 3.5 V (Fig. 16a), via reaction (18). This reaction is further confirmed by chemical titration of Li₂C₂O₆ and DEMS measurements during cycling (Fig. 16b,c). Little electrolyte decomposition product DMSO₂ was detected and the cell rechargeability was improved considerably.²³¹ The generally fatal issues associated with high charging overpotentials and electrolyte decomposition due to Li₂CO₃ formation and decomposition seem to be circumvented altogether, even at high concentrations of CO₂ (CO₂:O₂=1). Although further efforts are required to improve the solubility of Li₂C₂O₆ (thus energy densities) and minimize its shuttling to the Li anode, this work exemplifies how a judicious design of electrolytes can modulate the reaction mechanism of CO₂ contaminated Li-O₂ batteries.
Fig. 16 Modulating the reaction mechanism of CO$_2$ contaminated Li$_2$O$_2$ battery by tuning the solvation condition of Li$^+$ in the DMSO electrolyte. (a): By increasing the LiTFSI/DMSO molar ratio from 1:20 to 1:3, the cell electrochemistry changes from Li$_2$CO$_3$ formation to Li$_2$C$_2$O$_6$ formation, the latter is characterized by a much lower charging voltage than that of Li$_2$CO$_3$. Chemical titration of Li$_2$C$_2$O$_6$ (b) and DEMS measurements (c) confirm the reversibility of the Li$_2$C$_2$O$_6$ formation and decomposition reactions. Reprinted with permission from ref 231. Copyright 2018 The Royal Society of Chemistry.

It is worth mentioning that the possibility of a Li-CO$_2$ battery based on pure CO$_2$ electrochemistry has also been investigated. Contradicting observations were reported by various groups. McCloskey$^{129}$, Grimaud$^{230}$ and coworkers showed that almost no current in the CV and no capacity in galvanostatic discharging experiments were detected in the electrochemical reduction of CO$_2$ in DME/DMSO-based lithium or sodium electrolytes using various carbon-based electrodes (Super P, XC-72 and gas diffusion layer). These authors$^{129,230}$ thus concluded that CO$_2$ is not electrochemically active within the typical testing window of 2.0-4.5 V versus Li$^+$/Li. By contrast, Zhou and coworkers$^{235,236}$ provided a wealth of evidence supporting the electroreduction of CO$_2$ using a DMSO-based electrolyte on Ketjen carbon and on porous gold electrodes. By using a porous gold electrode, they showed that in addition to Li$_2$CO$_3$ formation, amorphous carbon deposits also simultaneously form on discharge, the process being proposed as reaction (20). Furthermore, they discovered that the metal catalyst can play a critical role in improving the reversibility of the cell reaction$^{235,236}$ when carbon or gold electrodes were used, only Li$_2$CO$_3$ was removed on charge, whereas with a ruthenium catalyst concomitant removal of Li$_2$CO$_3$ and C on charging was achieved at a lower potential of 3.6-3.8 V. Quantitative gas analysis is required to further verify the battery reversibility, because the continuing polarization (>3.6 V) due to the solid-state Li$_2$CO$_3$ decomposition on charging may incur unwanted side reactions.$^{179}$ Nevertheless, the mechanism whereby a solid catalyst can simultaneously decompose two solid products is fundamentally intriguing and warrants further studies.
\[ 4\text{Li}^+ + 3\text{CO}_2 + 4\text{e}^- \leftrightarrow 2\text{Li}_2\text{CO}_3 + C \quad (20) \]

where \( E^\circ \) is equal to 2.8 V, versus Li+/Li.

**H₂O** Finally, we discuss the impact of water on the non-aqueous O₂ electrochemistry. For the operation of Li-O₂ cells open to the air, in which O₂ is taken from air, the tolerance of the battery to the presence of water is critical, since water removal would require an additional water trap that would increase the weight and volume of the battery system considerably, thus making it less competitive compared to other types of batteries. Water can also be present as a contaminant in Li-O₂ cells from leaks in imperfect cells or from residual water present in the oxygen supply tubing/electrolyte/cell components. Early studies by Gasteiger and coworkers\(^7\) showed that hundreds to thousands ppm levels of water, present either as electrolyte additive or in leaky cells, produced a marked increase in the capacity of Li-O₂ cells. Surprisingly, water did not change the nature of the discharge product, which remained \( \text{Li}_2\text{O}_2 \).\(^{31,74,75,237-239} \) Interestingly, \( \text{Li}_2\text{O}_2 \) is also the main discharge product in water-in-salt Li-O₂ batteries, which contain no organic solvent and thus have no issues of solvent decomposition during cycling.\(^{240} \) The reaction of water with \( \text{Li}_2\text{O}_2 \) to form \( \text{LiOH} \) is thermodynamically favorable:\(^{241,242} \)

\[ 2\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} + \text{O}_2, \Delta G^\circ = -152 \text{ kJ/mol} \quad (21) \]

Nevertheless, the fact that, for some of the reported water-containing Li-O₂ cells (at or lower than thousands of ppm H₂O), \( \text{Li}_2\text{O}_2 \) is not converted into \( \text{LiOH} \) in the presence of water suggests the above reaction (21) is kinetically slow. If \( \text{LiOH} \) precipitates and forms a surface coating on \( \text{Li}_2\text{O}_2 \), then for the reaction to proceed and convert the \( \text{Li}_2\text{O}_2 \) core of the particles to \( \text{LiOH} \), it would require proton transport from water through the \( \text{LiOH} \) layer to the \( \text{Li}_2\text{O}_2 \) core, coupled to \( \text{O}_2 \) evolution from the \( \text{Li}_2\text{O}_2 \) core. At higher water concentrations, however, the \( \text{LiOH} \) passivation effect may be attenuated by a much increased \( \text{LiOH} \) solubility, where evident conversion of \( \text{Li}_2\text{O}_2 \) to \( \text{LiOH} \) may be observed. Xia and coworkers\(^{243} \) investigated the effect of moisture in O₂ (15% relative humidity) on the battery chemistry using a Ketjen black cathode and a LiTFSI/TEGDME electrolyte. As a result, \( \text{LiOH} \) and \( \text{Li}_2\text{O}_2 \) coexist as the discharge product. The carbon-based cathode does not decompose \( \text{LiOH} \) effectively, leading to large polarization on recharging.\(^{243} \) These studies show that the sluggish kinetics of \( \text{Li}_2\text{O}_2 \) conversion to \( \text{LiOH} \) can only alleviate, but does not radically mitigate the \( \text{LiOH} \)-induced rechargeability issue for Li-O₂ cells exposed to moisture in air. From a scientific point of view, many of the water-induced effects such as higher capacities and suppressed degradation reactions are fundamentally intriguing. The detailed mechanism of water effect on the O₂ electrochemistry in organic media will be discussed in Section 4.3.1.

### 3.3 Lithium Metal Anode Instability

Lithium metal is a promising anode material due to its exceptionally high specific capacity, 3860
mAh g⁻¹ (where this number is calculated based on the mass of lithium, i.e., the battery in the charged state). Its use is implicit in the high energy density quoted for lithium-air batteries. In contrast to the extensive investigation of the cathode (electro)chemistry, in-depth studies of lithium metal anode in non-aqueous lithium air battery are relatively scarce. In many fundamental studies that focus on the cathode, LiFePO₄ (LFP) is used as a replacement to Li metal anode to avoid complication induced by the anode degradation. Nonetheless, to realize the high specific energy of lithium-air batteries, challenges associated with Li metal anode warrant future endeavors.

3.3.1 Planar, Mossy versus Dendritic Li Deposition and Low Coulombic Efficiency

One of the biggest challenges associated with Li metal anode is the adverse morphological change during repeated stripping and plating. In particular, mossy (compact porous microstructures on the Li metal surface) and, at higher current densities, dendritic growth (spiny projections grow outward from the Li metal surface) (Fig. 17a), rather than smooth plating on the Li metal surface, occurs. Dendrite formation can potentially result in electrical shorting of the battery, if the dendrites penetrate the separator and reach the oxygen electrode, thus causing severe safety concerns. In addition, formation of mossy structures results in poor Coulombic efficiency: this is due to the loss of capacity involved in the formation of a new SEI on the increasing lithium surface area, and also due to formation of electrically isolated lithium metal structures that are, thus, electrochemically inactive.

The formation of Li dendrites is associated to depletion of Li⁺ ions in the vicinity of the Li metal surface in Li plating experiments. When the Li⁺ salt concentration drops to zero at the Li metal-electrolyte interface (which happens at a time known as the Sand’s time), the scarcity of Li⁺ ions supply promotes the deposition onto surface protrusions (tip growth mode), over the growth of mossy deposits that grow from their roots (Fig. 17a). A clear demonstration of the correlation between Li⁺-ion depletion at the Li metal surface and Li dendrite growth was achieved via in-situ Magnetic Resonance Imaging (MRI). Because of the sensitivity of Li NMR shift to the local chemical environment and morphology, the changes of both Li salt concentration profile and the growth of different types of Li microstructure can be tracked (Fig. 17b(i)), and indeed a clear transition from mossy to dendritic growth was observed during the in situ MRI experiments. This growth occurs from the tip of the dendrites towards the positively charged electrode, as later verified by Bai et al. using optical measurements. As shown in Fig. 17c(i), in a capillary cell, the growth of Li mossy and later dendritic microstructures was visualized, and the abrupt voltage increase (Fig. 17c(ii)) can be correlated to the onset of dendritic growth. The MRI study shows that at high charge rates, there is a strong correlation between the onset of dendrite growth and the local depletion of the electrolyte at the surface of Li metal anode (Fig. 17b(ii)). Unfortunately, the formation of dead Li and mossy structures slows down the transport of Li⁺ ions due to the increased tortuosity of the Li⁺ ion pathway and, as a result, also accelerates the formation of Li dendrites.
The low Coulombic efficiency of lithium plating/stripping is the other major challenge involved in the development of any batteries using a lithium metal anode. The requirement of >1000 cycles of charge and discharge for electric vehicle applications requires a Coulombic efficiency of 99.98% in order to conserve >80% of the initial lithium material after the 1000 cycles. Therefore, improving the Coulombic efficiency of lithium metal electrodes is a key requirement. Significant improvements in electrolyte formulations have achieved high values of Coulombic efficiency of lithium electrodes approaching 99%. Studies with LiPON thin-film cells in which all of the Li originates from the cathode demonstrated hundreds of cycles, thus implying high Li Coulombic efficiency above 99.9%. The significant progress achieved on Li metal anode development gives reasons for optimism, although much further work is still required. The requirements for commercial Li metal anodes have been recently summarized in excellent review articles, demonstrating that further work is needed in fundamental studies using thinner Li foils (e.g., <30 μm) and lean electrolyte, which are required to produce results representative of commercial conditions.
Fig. 17 Inactive Li formation mechanisms, origins and current state of reversible Li metal development. (a) schemes (i-iii) for various inactive Li plating mechanisms and a general correlation (iv) between morphologies of plated Li with the Coulombic efficiency and the ratio of SEI Li$^+$ versus unreactive metallic Li$^0$. Whisker Li morphology (i) is more likely to lead to electronic disconnects and more Li$^0$ trapped in SEI; granular (ii) Li morphology tends to maintain good electronic contact and only small amounts of Li are trapped; an ideal Li deposit (iii) should have a columnar microstructure with large granular size. Reprinted with permission from ref 247. Copyright 2019 Nature Publishing Group. (b) Electrolyte depletion and dendrite growth revealed by MRI and optical measurements: (i) $^7$Li chemical shift image of the metal (left) and the $^7$Li electrolyte concentration profile (right); (ii) Plot of the theoretical
Sand’s time and the initiation time of dendrite growth measured experimentally from $^7\text{Li}$ NMR spectra.\textsuperscript{252} Reprinted with permission from ref 252. Copyright 2015 ACS. (c) Illustration of the capillary cell (i) and in situ snapshots of the growth of lithium microstructures during the electrodeposition.; The corresponding voltage profile of the cell in (i) is shown in (ii) where the red dash line separates the different morphologies before and after the Sand’s time.; (iii) schematic illustrations of the growth mechanism of mossy and dendritic microstructures based on the electromigration-limited model.\textsuperscript{246} Reprinted with permission from ref 246. Copyright 2016 The Royal Society of Chemistry. (d) Status of efforts in the literature on the cycling of Li metal.\textsuperscript{263} Four parameters are included in this analysis: cumulative areal capacity plated, per-cycle areal capacity (represented by the size of each point), plating current density, and the fraction of the initial lithium metal present that is plated per cycle (indicated by the color). Points 1 and 2 are goals, 3-6 are for LiPON thin-film cells, 7-9 are PEO-based solid polymer electrolytes, 10-12 are solid inorganic separators, 13 and 14 are custom nanostructures and 15-26 are liquid electrolytes. Reprinted with permission from ref 263. Copyright 2018 Nature Publishing Group.

### 3.3.2 The Effects of O$_2$, CO$_2$ and H$_2$O on Li Metal Instability

Extensive research endeavors to investigate the reversibility of Li metal anode in the context of Li-ion batteries have been described in recent review articles and references therein.\textsuperscript{265, 266} In the lithium-air battery systems, while lessons can be learnt from Li-ion rechargeable batteries, Li anode stability needs to be reassessed under different gaseous environments, solvents, salts and electrolyte additives. Next, we review the (electro)chemical reactions among Li metal, different air constituents, typical solvents used in lithium-air batteries. The resulting SEI and its effect on the anode stability will be discussed.

O$_2$ is a key component in lithium-air battery systems. The effects of O$_2$ crossover to the Li metal anode on the anode stability remain a topic under debate. Some researchers\textsuperscript{267} reported that O$_2$ causes continual electrolyte (e.g., DMSO and TEGDME) decomposition over repeated cycles at the Li anode surface (Fig. 18a-c),\textsuperscript{58} resulting in formation of less stable SEI layers, and a much worse electrochemistry. Other groups,\textsuperscript{57, 268} however, propose that O$_2$ can stabilize the SEI. Zhou and coworkers\textsuperscript{57} demonstrated a beneficial effect of O$_2$ using a TEGDME-based electrolyte. SEM (Fig. 18e-h) shows that during charge, the O$_2$-rich electrolyte allows uniform Li deposition generating a columnar structure with a higher Coulombic efficiency, compared to a filamentary structure without O$_2$. In-situ Raman experiments (Fig. 18i-l) revealed relatively constant signals of Li$_2$O, Li$_2$O$_2$ and LiOH layers on the Li surface that seems to stabilize Li, whereas in the absence of O$_2$, the electrolyte decomposition products Li$_2$SO$_3$ and CH$_3$OLi, together with Li$_2$O and LiOH, continually accumulate through the first two discharge/charge cycles. Zhou and coworkers\textsuperscript{57} further pointed out that a high O$_2$ concentration (e.g., direct O$_2$ exposure and diffusion of O$_2$ through macroporous Cu mesh) is required to form a stable SEI and prevent further reaction between Li and the electrolyte; this may help explain the opposite opinions, because in the former study\textsuperscript{58} O$_2$ supply can be limited by diffusion through the microporous cathode. Nonetheless, clarifying the influence of O$_2$ crossover on Li metal stability requires further investigation.
Fig. 18 Effect of O₂ crossover on the morphology and composition of the anode surface. SEM images of Li metal foil immersed in (a) 1.15 M LiTFSI-DMSO and (b) 1.15 M LiTFSI-DMSO-O₂ solution for 30 days. (c) Proposed degradation mechanism of Li metal surface in 1.15 M LiTFSI-DMSO-O₂ solution. Step i: adsorption of TFSI⁻ anions and oxygen molecules on the Li metal surface; step ii: formation of LiO₂ and nucleophilic attack on surrounding DMSO solvent and TFSI⁻ anions; step iii: precipitation of decomposed compounds of mossy structures and continuous Li⁺ dissolution via oxidative reactions.¹²⁶ (d) Illustration of Li anode reduction in ether-based electrolyte when O₂ crossover occurs.°⁵ SEM images of the plated Li metal foil in TEGDME/LiCF₃SO₃ without (e) and with O₂ (f), and the stripped Li metal foil without (g) and with (h) O₂. In situ Raman spectra and voltage profiles of Li plating/stripping without (i, k) and with (j, l) O₂.°⁵⁷ (a–c) Reprinted with permission from ref 126. Copyright
\( \text{CO}_2 \) constitutes 0.04% of dry air, which is much less than \( \text{N}_2 \) and \( \text{Ar} \), however, \( \text{CO}_2 \) is known to be generally more active than \( \text{N}_2 \) and \( \text{Ar} \), and it can undergo chemical reactions with \( \text{Li} \) (some involving \( \text{O}_2 \)), e.g., \( 2\text{Li} + \frac{1}{2}\text{O}_2 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \). In the 1990s, Osaka and coworkers demonstrated that \( \text{Li} \) metal electrodes showed a prolonged cycling life in a \( \text{CO}_2 \) saturated \( \text{LiClO}_4 \)/propylene carbonate electrolyte, and the formation of \( \text{Li}_2\text{CO}_3 \) in the subsurface layer was found to suppress dendritic deposition.\(^{269, 270}\) The authors concluded: “To improve cycle life, carbon dioxide must be present when lithium is initially electrodeposited onto the nickel substrate”. An example recently demonstrates that a pre-coated \( \text{Li}_2\text{CO}_3/\text{C} \) layer can indeed protect the lithium metal anode; when this anode is used together with a molybdenum disulfide cathode and an ionic liquid/DMSO electrolytes, the resulting \( \text{Li}-\text{O}_2 \) cell could be operated in an air-like atmosphere.\(^{220}\) The \( \text{Li}_2\text{CO}_3/\text{C} \) protective layer was pre-synthesized electrochemically in pure \( \text{CO}_2 \) atmosphere, following the net reaction \( 4\text{Li}(s) + 3\text{CO}_2(g) \rightarrow 2\text{Li}_2\text{CO}_3 + \text{C}(s) \). As shown in \textbf{Fig. 19a}, after ten discharge-charge cycles, a dense network of rod-shape structures was formed on the surface. The composition of the surface is \( \text{Li}_2\text{CO}_3/\text{C} \), confirmed by Raman (\textbf{Fig. 19b}), XPS (\textbf{Fig. 19c}) and electron energy loss spectroscopy. The authors argued based on DFT calculations that migration of \( \text{N}_2 \) and \( \text{O}_2 \) through the \( \text{Li}_2\text{CO}_3/\text{C} \) layer has a high energy barrier (1.2 – 3.2 eV) while diffusion of lithium should be facile. This study did not report in-depth studies aimed at understanding the protecting role of \( \text{Li}_2\text{CO}_3 \). It will be interesting to study the morphology and composition of the \( \text{Li} \) metal buried beneath the \( \text{Li}_2\text{CO}_3/\text{C} \) layer, to see whether there is any evidence of gas and electrolyte penetration and associated SEI formation.

The combined effect of \( \text{N}_2 \), \( \text{O}_2 \), and \( \text{CO}_2 \) on \( \text{Li} \) metal anodes has been investigated in few studies. Momma \textit{et al.} studied the SEI layers formed on \( \text{Li} \) metal by XPS (in \( \text{LiPF}_6 \)/ethylene carbonate (EC)-diethyl carbonate (DEC) electrolyte) when cells were assembled in different atmospheres, \textit{i.e.} dry air versus dry argon.\(^ {271}\) They found that the topmost surface of \( \text{Li} \) metal deposited in dry air and dry argon were similar, whereas the underlying SEI layers (revealed after \( \text{Ar}^+ \) milling) contained concentrated \( \text{Li}_3\text{N}, \text{Li}_2\text{CO}_3 \) and \( \text{LiOH} \) in the former case. The cell assembled in dry air exhibited a better cycling performance, \textit{i.e.} higher Coulombic efficiency than the one in dry \( \text{Ar} \), especially in the presence of ionic liquid. These studies underscore the need for fundamental understandings of the interaction between \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{N}_2 \) and \( \text{Li} \) metal anode surface in different electrolytes/salts, and the role of associated SEI layers in protecting the metal anode.
$\text{H}_2\text{O}$ is present in air to varying degrees. It readily reacts with Li metal to form LiOH. Zaghib and coworkers studied the effect of moisture contamination on Li metal anodes in Li-O$_2$ cells.$^{272}$ Using the setup shown in figure 20a, the authors observed different extents of increases in discharge capacity and weight gains from the 1$^{\text{st}}$ to the 6$^{\text{th}}$ cell, following the order of O$_2$ flow through the cells (Fig. 20b). The additional capacity was explained by the following electrochemical reactions at the cathode:

$$2\text{H}_2\text{O} + \text{Li}_2\text{O}_2 + 2\text{Li}^+ + 2e^- \rightarrow 4\text{LiOH} \quad (22)$$

The excessive weight gain of cell 2$^{\text{nd}}$ to 6$^{\text{th}}$ was attributed to the following chemical reaction as moisture penetrates through the battery systems:

$$2\text{H}_2\text{O} + 2\text{Li} \rightarrow 2\text{LiOH} + \text{H}_2 \quad (23)$$

The morphology revealed by SEM and composition by XRD agree with the formation of LiOH, supporting the proposed reaction (23). In a separate study, the formation of LiOH on Li metal anode was also recorded when cycling a Li-O$_2$ battery in ambient air.$^{273}$ How the presence of
water affects the composition and morphology of the SEI in different combinations of electrolytes/salts will be invaluable information to the lithium-air battery community.

![Fig. 20](image_url) Effect of moisture contamination on Li metal anode. (a) Schematic diagram of O2 flow and cell connections. The 1st to the 6th cells were connected in series by a single gas line of O2, while the cells were independently controlled by cyclers. (b) A table shows the discharge capacities and weight gains of the six cells in (a). Reprinted with permission from ref 272. Copyright 2014 Elsevier.

4. Potential Solutions

From the discussion in Sections 2 and 3, we can see that the technological challenges of non-aqueous Li-O2 batteries are closely linked to relevant scientific hurdles, a critical one being the parasitic reactions occurring at the interfaces, namely, the Li anode-electrolyte, Li2O2-cathode (current collector), cathode-electrolyte and Li2O2-electrolyte interfaces. The situation is aggravated in the presence of large overpotentials on charging, because carbon cathode corrosion, electrochemical electrolyte decomposition, 1O2 generation are all sensitive to the high charging voltages. The first major issue to tackle is thus to decrease the charging overpotential, preferably well below 3.5 V. As such, a range of strategies have been developed, including the use of solid catalysts, redox mediators, photo-assisted charging, phase-transfer catalysts and so on. Furthermore, 1O2 trapping/quenching molecules as electrolyte additives, protective thin films on the Li anode and gas-separation membranes have also been used to reduce damages due to singlet oxygen, to enable a more reversible Li plating and stripping, and to minimize unwanted air contamination, respectively. These strategies will be reviewed in the following sections.

4.1 Electro catalysis in Non-aqueous Li-O2 Batteries

The use of solid electrocatalysts for Li-O2 batteries is an intensely studied subject. Numerous studies report that with catalysts, e.g., metal/metal oxides, lower charging voltages and much improved battery rechargeability are often observed compared to the case without catalysts. Nevertheless, many reports also stress that the apparent improved rechargeability by coulometry does not reflect the true reversibility of Li-O2 electrochemistry. In fact,
similar or even worse O$_2$ recovery efficiency (OER/ORR) occurs with these catalysts, compared to a carbon cathode. This seemingly improved rechargeability can be connected to at least three other factors in addition to the desirable effect on Li$_2$O$_2$ decomposition: 1) insulating byproducts (Li$_2$CO$_3$, LiOH, carboxylates) can be removed by catalysts at a lower voltage so that they do not accumulate and rapidly passivate the cathode; 2) organic electrolyte decomposition is promoted in the presence of catalysts, so that the repeated cycling is in fact primarily at expense of electrolyte; 3) some electrolytes tend to more effectively dissolve the common byproducts (Li$_2$CO$_3$, LiOH) or form very soluble decomposition products, thus postponing cell failure. Therefore, efficient catalysts and stable electrolytes should be considered collectively when seeking to develop a truly reversible Li-O$_2$ battery.

Due to the lack of quantitative analysis, it is very difficult to judge in the many reported studies whether the improved battery performance is genuinely a result of electrocatalytic effects on the O$_2$ electrochemistry. Herein, we thus focus on reviewing studies that have quantified the O$_2$ consumption and evolution during battery cycling. We acknowledge the many reviews existing already on the subject, which provide a more exhaustive list of electrocatalysts studied for Li-O$_2$ batteries.

4.1.1 A Real Need for Electrocatalysis on Charging?

The overpotential on charging is typically observed to be several times (> 1 V) larger than that of discharge (0.2 V). Hence, there is a greater need to further improve the kinetics during charge. To investigate whether there is a true role of electrocatalysis, McCloskey and coworkers studied the charging process of Li-O$_2$ batteries using XC72 carbon, Au-XC72 and MnO$_2$-XC72 based cathodes (Fig. 21a). The authors observed overlapping charging voltage profiles starting from the equilibrium voltage of ~3.0 V, where O$_2$ begins to evolve in the corresponding DEMS tests; this observation thus indicates there is hardly any kinetic barrier for the onset of Li$_2$O$_2$ decomposition for all three cathode materials. Furthermore, analysis of cathodic and anodic Tafel plots of Li-O$_2$ electrochemistry on a flat glassy carbon electrode (Fig. 21b) leads to an exchange current density of 1 mA/cm$^2$, consistent with a fast reaction. McCloskey, Luntz and coworkers thus argued that there is no need for electrocatalysis in the Li-O$_2$ electrochemistry. In addition, in conventional catalysis, reaction intermediates are sufficiently mobile so that reactants and products can access and escape from the active site, the site thereby being regenerated. By contrast, the catalyst particles are covered by solid Li$_2$O$_2$ products in lithium-oxygen batteries, and thus catalyst surfaces would be quickly deactivated for further reaction. Clearly, the conventional catalysis concept is not applicable.

Nevertheless, many other groups indeed observed that cells using solid catalysts exhibit different onset charge voltages, the overpotentials throughout the whole charge capacity being decreased compared to that observed using just a carbon-based cathode (Fig. 21c); these observations thus support the existence of catalytic effects on charging (that is, through the use
of a catalyst, the overpotential of a battery reaction is reduced. The next question is how does a solid catalyst facilitate Li$_2$O$_2$ decomposition? Several hypotheses have been put forward to account for the solid-solid effect involved in Li$_2$O$_2$-catalyst interactions. Nazar and coworkers$^{300}$ proposed that solid catalysts (e.g., Co$_3$O$_4$) promote mass transport of Li$_x$O$_2$ species on electrode surfaces by reducing their binding energies with the surface, which in turn facilitates both further oxidation and reduction of Li$_x$O$_2$. Shao-horn and coworkers suggest that solid-state Li$_2$O$_2$ oxidation is mediated by chemical conversion of Li$_2$O$_2$ to a lithium metal oxide at the Li$_2$O$_2$-metal catalyst interface, where Li$_2$O$_2$-catalyst interaction at the interface clearly matters.$^{114}$ Others have suggested an electrolyte-mediated charging process,$^{96, 197, 302}$ which is later confirmed to be dependent on the donicity of electrolyte solvents.$^{45}$ To provide more clear-cut evidence that there is solid-state promotion of Li$_2$O$_2$ decomposition by solid catalysts, Lu and coworker$^{115}$ studied the electrochemical behavior of all solid-state Li-O$_2$ batteries using Vulcan Carbon (Fig. 21d) and Ru-Vulcan Carbon electrodes (Fig. 21e). Compared to the case using carbon electrode, the authors observed more O$_2$ evolution at a lower overpotential using Ru catalysts;$^{115}$ this result thus verifies that some solid catalysts can indeed reduce the kinetic barrier for Li$_2$O$_2$ oxidation and increase O$_2$ recovery efficiency. The authors$^{115}$ then propose that solid catalysts operate by stabilizing reaction intermediates such as Li$_{2-x}$O$_2$ via formation of surface-Li$_{2-x}$O$_2$ species, which then facilitates delithiation of the bound Li$_{2-x}$O$_2$ species (Fig. 21f). This delithiation occurs via Li$^+$ vacancy transport through the Li$_2$O$_2$ particle bulk or surfaces and triggers O$_2$ evolution from the particle surface (Fig. 21f). This mechanistic picture proposed by Lu et al.$^{115}$ for the all solid-state battery is consistent with the general understanding on solid-state Li$_2$O$_2$ decomposition on carbon electrodes (discussed in Section 2.2.1) and is supported by the observation that O$_2$ evolution typically occurs at the Li$_2$O$_2$-electrolyte interface (as discussed in Section 2.2.2). As a result, by modulating the interaction between the catalyst surface and reaction intermediates, the charging voltages can be reduced, providing a guideline for catalyst design.
4.1.2 Noble Metals, Transition Metal Carbides and Oxides

Among noble metals, nanoporous gold (NPG\textsuperscript{204}) and ruthenium-based\textsuperscript{141, 295, 303-306} catalysts have been reported to show the best electrochemical performance. For example, a Li-O\textsubscript{2} cell using NPG electrode and DMSO-based electrolyte shows an onset charging voltage from 3.0 V and O\textsubscript{2} recovery efficiency higher than 98\% for 100 cycles.\textsuperscript{204} The stability of DMSO for Li\textsubscript{2}O\textsubscript{2} electrochemistry, however, was later questioned.\textsuperscript{87, 88, 132, 205} It is now known that solvents with
higher DN (high polarity) are more prone to nucleophilic attack and electrochemical decomposition, compared to low DN solvents (low polarity). Higher O₂ recovery ratios are typically obtained using the same catalyst with low donicity solvents (e.g., TEGDME) than high donicity solvents (e.g., DMSO). Nevertheless, a subsequent study using Ru catalysts and DMSO-based electrolytes provided further evidence that Li-O₂ batteries using a DMSO electrolyte can achieve high O₂ recovery ratios. The reversibility of cells using ruthenium catalysts seems to be dependent on the electrolyte in use. In ether-based electrolytes, ruthenium cathodes exhibit an O₂ recovery of only ~64%, similar to that using a carbon electrode, although the Ru-catalyzed cell is still highly rechargeable for many cycles (probably due to some parasitic processes, discussed in the beginning of Section 4.1). In a more polar DMSO-based electrolyte, however, Ru was reported to effectively catalyze O₂ reduction and evolution reactions, with 92% of O₂ recovered on charging. Other noble metals such as Pt and Pd have been consistently reported to cause significant electrolyte decomposition in ether-based electrolytes.

Transition metal carbides have been considered as a promising class of cathode materials due to the high electrical conductivity and high oxidation resistance. Bruce and co-workers reported that cells using a TiC cathode and a LiClO₄/DMSO electrolyte can be cycled with ~99% O₂ recovery for 100 cycles. Nazar et al. later pointed out that Li-O₂ electrochemistry is very sensitive to the TiC surface condition – a surface TiO₂ film as thin as 3 nm can completely shut down interfacial electron transfer, whereas pristine TiC surfaces with a sub-nanometer TiO₂/TiOC passivation film can effective catalyze Li₂O₂ decomposition. Given the need to passivate the TiC surface by a thin oxide layer in the Li-O₂ cell environment, Nazar and co-workers further exploited titanium oxide phases with high electrical conductivity for Li-O₂ battery applications. The authors found that cells using Ti₄O₇-based cathodes exhibit an ultralow onset voltage from 3.0 V and e⁻/O₂ ratio of 2.42 on charging.

Although many solid catalysts enable a very low onset charging voltage at 3.0 V (such as Ru, NPG, Ti₄O₇, TiCrOₓ), a common issue is that cells all gradually polarize toward 4.0 V or higher with deeper states of charging, which is usually connected to parasitic products accumulating at the reaction interfaces. Above 3.5 V, additional carbon corrosion and electrochemical/chemical electrolyte decomposition occurs to a greater extent, becoming a grave issue for the battery reversibility. Again, minimizing parasitic reactions occurring at the interfaces and constantly keeping the charging voltage below 3.5 V is required to improve the reversibility of catalyzed Li-O₂ batteries.

A desirable solid catalyst should satisfy at least the following criteria: (1) the catalyst needs to be stable against the oxidizing environment (reactive oxygen species and high overpotentials especially on charging) in a lithium-oxygen battery; (2) the catalyst should not promote significant electrolyte decomposition within the battery discharge-charge window (where 2.5-3.5 V is typically the operating window to aim for in order to minimize degradation reactions); (3) a
high binding energy between OER reaction intermediates (e.g., Li$_{2-x}$O$_2$) and the catalyst surface is preferred, as this property is linked to critical steps of Li$_2$O$_2$ delithiation on recharging; (4) it is also desirable that the catalyst can readily decompose LiOH and Li$_2$CO$_3$, because the continued formation of these typical byproducts (if formed) will rapidly clog the porous cathode and cause early cell failure.

4.2 Redox Mediators: Enabling Facile Solution-Phase Charge Transfer

4.2.1 Fundamental Principles

Redox mediators (RM) are electrochemically active species that are used to facilitate electrochemical reactions. The operational mechanism of RMs in Li-O$_2$ batteries is illustrated in Figure 22a. During discharge, RMs transfer electrons from the electrode to an O$_2$ molecule forming Li$_2$O$_2$, and during charge, RMs transfer electrons from Li$_2$O$_2$ to the electrode, evolving O$_2$. In the following, the oxidized and reduced forms of the RM will be termed RM$^{\text{OX}}$ and RM$^{\text{RED}}$, respectively. These reactions involve the following steps:

\[
\text{Discharge:} \quad \text{RM}^{\text{OX}}_{\text{solution}} \rightarrow \text{RM}^{\text{OX}}_{\text{electrode surface}} \quad (24)
\]

eq. 24: mass transport of RM$^{\text{OX}}$ from solution to the electrode surface.
\[
\text{RM}^\text{OX}_{\text{electrode surface}} + e^- \rightarrow \text{RM}^\text{RED}_{\text{electrode surface}} \tag{25}
\]

eq 25: electron transfer to RM\textsuperscript{OX} to form RM\textsuperscript{RED} at the electrode surface.

\[
\text{RM}^\text{RED}_{\text{electrode surface}} \rightarrow \text{RM}^\text{RED}_{\text{solution}} \tag{26}
\]

eq 26: mass transport of RM\textsuperscript{RED} from the electrode surface to the solution.

\[
2\text{RM}^\text{RED}_{\text{solution}} + O_2 + 2Li^+ \rightarrow 2\text{RM}^\text{OX}_{\text{solution}} + Li_2O_2 \tag{27}
\]

eq 27: electron transfer from RM\textsuperscript{RED} to O\textsubscript{2} forming Li\textsubscript{2}O\textsubscript{2} suspended in solution.

Charge:

\[
\text{RM}^\text{RED}_{\text{solution}} \rightarrow \text{RM}^\text{RED}_{\text{electrode surface}} \tag{28}
\]

eq 28: mass transport of RM\textsuperscript{RED} from solution to the electrode surface.

\[
\text{RM}^\text{RED}_{\text{electrode surface}} \rightarrow \text{RM}^\text{OX}_{\text{electrode surface}} + e^- \tag{29}
\]

eq 29: electron transfer from RM\textsuperscript{RED} to form RM\textsuperscript{OX} at the electrode surface.

\[
\text{RM}^\text{OX}_{\text{electrode surface}} \rightarrow \text{RM}^\text{OX}_{\text{solution}} \tag{30}
\]

eq 30: mass transport of RM\textsuperscript{OX} from the electrode surface to the solution.

\[
2\text{RM}^\text{OX}_{\text{solution}} + Li_2O_2 \rightarrow 2\text{RM}^\text{RED}_{\text{solution}} + O_2 + 2Li^+ \tag{31}
\]

eq 31: electron transfer from Li\textsubscript{2}O\textsubscript{2} to RM\textsuperscript{OX} evolving O\textsubscript{2}.

The reduction and oxidation of RMs (reactions (25) and (29)) involve, in some cases, lithium cations, and the reactions of RMs with O\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2} (reactions (27) and (31)) are not elementary reactions.

The reaction steps shown above illustrate that RMs do not change the net ORR or OER reactions, but they alter the reaction pathway in such a way that the kinetics of the reaction are improved. RMs act as electron/hole “carriers” and facilitate Li-O\textsubscript{2} cell reactions by shuttling electrons between O\textsubscript{2} or Li\textsubscript{2}O\textsubscript{2} and the electrode. Thus, RMs not only alter the reaction mechanism, but they also enlarge the region where reactions can take place. This is key to the development of high-capacity Li-O\textsubscript{2} batteries, for the following two reasons: 1) RMs tend to circumvent rapid electrode passivation due to the surface mechanism during discharge, and lead to larger discharge capacities via solution-mediated processes; 2) RMs can help realize a facile charge transfer pathway via the electrolyte, so that the high charging overpotentials incurred by the insulating nature of Li\textsubscript{2}O\textsubscript{2} can be circumvented. An alternative mechanism pathway involving the dissolution of solid Li\textsubscript{2}O\textsubscript{2} forming soluble Li\textsubscript{2}O\textsubscript{2}, which could then diffuse to the electrode
surface and get oxidized, is unlikely to proceed at significant rates due to the poor solubility of \( \text{Li}_2\text{O}_2 \) in most electrolytes.\(^5\) The mediated reaction of \( \text{Li}_2\text{O}_2 \) oxidation via RMs thus appears very promising.

The reactions of RMs with \( \text{O}_2 \) and \( \text{Li}_2\text{O}_2 \) (reactions (27) and (31)) involve a net transfer of two electrons; thus they require at least two, one-electron transfer reactions (reactions (32) and (33)). Figure 22b illustrates a suggested simplified reaction mechanism involving the formation of superoxide species \( \text{LiO}_2 \) as reaction intermediates:\(^4\)

\[
\text{Li}^+ + \text{R} \text{M}_{\text{RED}} + \text{O}_2 \leftrightarrow \text{LiO}_2 + \text{R} \text{M}_{\text{OX}} \quad (32)
\]

\[
\text{Li}^+ + \text{R} \text{M}_{\text{RED}} + \text{LiO}_2 \leftrightarrow \text{Li}_2\text{O}_2 + \text{R} \text{M}_{\text{OX}} \quad (33)
\]

Due to the reactivity of superoxide species, the development of mediators that can quickly reduce superoxide to peroxide on discharge (reaction (33)) would be highly advantageous.\(^4\) However, the actual reaction mechanism might be much more complex than the simplified reaction mechanism with reactions (32-33), and it may involve interaction between the different species or the formation of different reaction intermediates. Indeed, Bruce and coworkers\(^8\) ascribed the excellent catalytic activity of the DBBQ (2,5-di-tert-butyl-1,4-benzoquinone) RM to the formation of a DBBQ-superoxide reaction intermediate (reactions (34-37)) that bypassed the formation of superoxide (Fig. 22c).

\[
\text{DBBQ} + e^- + \text{Li}^+ \rightarrow \text{LiDBBQ} \quad (34)
\]

\[
\text{LiDBBQ} + \text{O}_2 \rightarrow \text{LiDBBQO}_2 \quad (35)
\]

\[
2\text{LiDBBQO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 + 2\text{DBBQ} \quad (36)
\]

\[
\text{LiDBBQO}_2 + \text{LiDBBQ} \rightarrow \text{Li}_2\text{O}_2 + 2\text{DBBQ} \quad (37)
\]

Unfortunately, the direct detection of the proposed \( \text{LiDBBQO}_2 \) reaction intermediate is difficult, but it was found that the discharge potentials of mediated \( \text{Li-O}_2 \) cells containing DBBQ was significantly higher than those without DBBQ, which supports the hypothesis that an alternative reaction pathway, involving intermediate species more stable than \( \text{LiO}_2 \), is promoted by DBBQ.\(^3\) Similar conclusions were reached in the study of coenzyme Q10,\(^3\) vitamin \( \text{K}_2 \)\(^3\) and anthraquinone\(^3\) RMs. Furthermore, in the case of anthraquinone, additional support for the formation of alternative reaction intermediate was obtained from the characterization of the complex formed with anthraquinone and lithium superoxide by UV-vis, NMR and computational studies.\(^3\) In situ FTIR measurements of \( \text{Li-O}_2 \) cells containing DBBQ also supported the formation of a reduced DBBQ – \( \text{O}_2 \) complex.\(^3\)

It should be noted that electrochemical measurements alone cannot be used to determine whether a mechanism occurs via reactions (32-33) or reactions (34-37), i.e., whether the reaction occurs via a reduced RM-\( \text{O}_2 \) complex. Since, in most cases, mediators exhibit fast electron transfer kinetics, the electrode potential will depend on the surface concentrations of the oxidized and
reduced forms of the mediator via the Nernst equation. Thus, the consumption of the reduced form of the mediator via reactions (32-33) will produce an increase in electrode potential; and the higher the reaction rate, the higher the associated increase in electrode potential. Thus, an increase in discharge potential of cells incorporating discharge RMs upon addition of O₂ could also be explained via the mechanism involving reactions (25,32-33).

In conclusion, the identification of the reaction mechanism and detection of reaction intermediates is not possible based on electrochemical data alone. Additional analytical techniques are required. The possibility of altering the reaction mechanism by exploiting the interaction of RMs with O₂ or O₂-reduced species, to form reaction intermediates more stable and less prone to induced degradation reactions than superoxide is, without a doubt, a promising approach worth exploring further.

4.2.2 Selection Criteria for Redox Mediators

RMs should fulfil a number of requirements in order to effectively promote Li-O₂ cell reactions. First of all, RMs should exhibit a high catalytic activity towards the Li-O₂ cells reactions, as well as high chemical stability against degradation reactions. Experimental data suggest that those two requirements can be achieved simultaneously. But further work is still required to identify the fundamental descriptors leading to high mediation activity and chemical stability of RMs.

The mass transport rate of RMs (that is their diffusion coefficients) can also be an important factor. Fast diffusion enables the RM to access more regions of the cathode promoting a more homogeneous reaction. Ideally, RMs should also exhibit a high solubility. The kinetics of mediated reactions is, in principle, proportional to the mediator concentration, thus high RM concentrations can increase the cell rate performance. Therefore, the concentration and diffusion coefficient of RMs should be as high as possible. Specifically, for discharge, the product of the diffusion coefficient and concentration of the discharge RM should be higher than that of O₂, since in this way, the electrochemical reactions at the cathode are those of the RM, and the reduction of O₂ to Li₂O₂ via RMs only happens further away from the electrode surface, thus preventing Li₂O₂ deposition on the cathode (Fig. 23a). Similarly, for charge, the product of the diffusion coefficient and concentration of the charge RM should be high enough in order to be able to sustain the charging current; the maximum current associated with the mediated O₂ evolution reaction, j^{\text{oa}} has been calculated with a simple model and validated with experimental data, see Figure 23b. In addition, RMs should also be stable in contact with the lithium anode. If that is not the case, lithium protective membranes need to be incorporated, and the mediator should not react in contact with the membrane. Most of the fundamental work on redox mediators for Li-O₂ batteries has been done using solid lithium ion conductors (e.g. the glass-ceramic membrane from Ohara-GmbH) to prevent the reaction of the redox mediators with the Li metal anode, but future work should address the development of suitable membranes compatible with both Li and redox mediators. In the next section, we present a further discussion
of the two most important selection criteria (redox potential and chemical stability) that should be considered for the successful mediation of Li-O_2 cell reactions.

Fig. 23 Mass transport effects on mediation of Li-O_2 reactions. (a): Schematics of the working principle of the protected dual-mediator Li–O_2 battery, where the cathode surface is protected from passivation and corrosion by deposition of discharge products (Li_2O_2) or degradation by reaction with Li–O_2 reaction intermediates by means of a dynamic O_2 shield made of reduced discharge redox mediator. oDM and rDM correspond to the discharge mediator in its oxidized and reduced forms, respectively. (b): Comparison of calculation and experimental results of the limiting current density (j^\infty) that can be held by a charge redox mediator whose reaction with Li_2O_2 is limited by mass transport. Experiments were performed in a cell with a glassy carbon working electrode, a LFP counter electrode and Li reference electrode, containing 100 mM TEMPO redox mediator in 1M LiTFSI/diglyme, with a distance between the working and counter electrodes of 200 μm. Reprinted with permission from ref 316 and 317. Copyright 2018 The Royal Society of Chemistry and 2015 The Royal Society of Chemistry.

1. Redox Potentials

In general, the selection of redox mediations usually starts by considering the redox potential. Ideally, both redox potentials will be close to E^0(O_2/Li_2O_2)=2.96 V vs. Li^+/Li, while still keeping high mediation activity. Very low redox potentials (e.g. <2.4 V vs. Li^+/Li) are unsuitable, because then the unmediated discharge reaction would compete with the mediated one, the former resulting in the passivation of the electrode and, thus, low capacities. A high discharge RM potential is also advantageous because then the formation of LiO_2 intermediates, which can induce degradation reactions, would be minimal. A low charge RM potential is advantageous because it prevents degradation reactions induced by application of high potentials (electrochemical electrolyte degradation, carbon corrosion, etc.), and also, because it improves the energy efficiency of the battery.

More work is required in order to elucidate the effect of the RM potential on the kinetics of mediated Li-O_2 cell reactions, with standardized testing conditions and involving systematic studies comparing different RMs under the same conditions. Studies of different RMs are often
performed under different conditions of electrolyte composition, cathode material, current
density, etc., thus hampering a quantitative comparison of RM activities.

Tables 1-3 summarizes key properties reported in studies of discharge, charge, bifunctional and
dual RMs for Li-O₂ batteries. In the following, we will discuss some recent studies in which a
comparison of several RMs has been performed under the same conditions.

The discharge mediation activity of a few quinone compounds has been compared, and
DBBBQ was found to produce the highest increase in current (in cyclic voltammograms) or
capacity (in galvanostatic discharge), followed in mediator activity by vitamin K2. Since other
quinones with similar redox potentials did not produce such dramatic effect on the Li-O₂ cell
discharge reaction, it can be concluded that the RM potential is not the only determining factor in
the enhancement of the rate of the ORR. Since DBBBQ and vitamin K2 are both sterically
hindered benzoquinones, it can be tentatively proposed that the enhanced stability of the reduced
quinone, facilitated by the bulky substituent groups in DBBBQ and vitamin K2, might promote a
higher stability of the reduced quinone-oxygen complex, thus facilitating the oxygen
reduction via reactions of type (34-37). Coenzyme Q10 is another sterically hindered quinone
that showed great improvements of discharge capacity of Li-O₂ cells with Super P electrodes and
tetraglyme electrolytes; surprisingly, with gas diffusion electrodes and DME electrolytes, the
mediation action of co-enzyme Q10 was only minor. In another study, an anthraquinone,
which has a lower redox potential than DBBBQ (see Table 1) was found to lead to higher or lower
capacities in Li-O₂ than DBBBQ, depending on the cathode material used.

Bruce and coworkers have compared the activity of a number of charge RMs by quantifying the
kinetics of Li₂O₂ oxidation by RMs with scanning electrochemical microscopy experiments. The
oxidized form of RM was generated at a microelectrode that acted as the tip of the scanning
electrochemical microscope. When the tip approached a Li₂O₂ pellet, an increase in the rate of
oxidation of the RM was observed, the so-called positive feedback effect, as the reduced form of
the RM is regenerated upon reaction of the oxidized form of the RM with the Li₂O₂ substrate
(Fig. 24a). The analysis of the current detected at the microelectrode as a function of the distance
of approach to the Li₂O₂ substrate has been used to quantify the apparent rate constant of the
reaction of the RM with Li₂O₂, k_{app}. The results are shown in Figure 24b, for different RMs, as a
function of the standard potential of the RM. It is observed that the highest values of rate
constant are obtained with nitroxy radical compounds (AZO, MAZO and TEMPO: pink data
points). These values are comparable to those reported for the mediation of Li⁺
insertion/extraction from LiFePO₄. Moderate values of rate constant are obtained with thiazine
compounds (MPT, PPT and BPPT: green data points), while the other compounds studied,
amines (TMPD, DPAB and TDPA: purple data points) and other-class compounds (DMPZ, TTF
and FC: black data points) show much lower rate constants. There is not a clear correlation of the
magnitude of the rate constant with the redox potential of the mediator; this indicates that the rate
determining step of the reaction is not an electron transfer process, and it appears that the
kinetics of Li$_2$O$_2$ oxidation are more affected by the type of chemical functionality of the RM than by its redox potential.$^{318}$

Differences in the rate of Li$_2$O$_2$ oxidation by different RMs have also been evaluated by means of rotating disc electrode experiments in which the change in the diffusion-limiting current of RMs with and without Li$_2$O$_2$ particles suspended in solution was measured (Fig. 24c).$^{320}$ The results of the increase in the limiting current upon addition of Li$_2$O$_2$ in solution are shown as a function of the standard redox potential of the RMs in Figure 24d. To facilitate comparison with the results by Bruce and coworkers$^{318}$ (Fig. 24b), the mediators that are common to both studies have been circled, and only the first electron-transfer process of the mediator has been considered. It is seen that the differences in mediation activity in Figure 24d agree well with the differences in the apparent rate constant of Li$_2$O$_2$ obtained in scanning electrochemical microscopy experiments shown in Figure 24b. This corroborates that the mediation activity is not a simple function of the mediator redox potential, as discussed by Bruce and coworkers.$^{318}$
<table>
<thead>
<tr>
<th>Mediator</th>
<th>c</th>
<th>Redox potential</th>
<th>Discharge voltage</th>
<th>Discharge capacity</th>
<th>Current density</th>
<th>C_m/C</th>
<th>Electrodes (cathode/anode)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tris(2,4,6-trichlorophenyl)methyl radical (TTM)</td>
<td>1</td>
<td>2.6</td>
<td>~2.65&lt;sup&gt;e&lt;/sup&gt;-2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~3.5 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~7.5 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.1</td>
<td>2.1</td>
<td>Super P/Li</td>
<td>1 M LiOTf / TGDME</td>
</tr>
<tr>
<td>Ethyl viologen (EtV)</td>
<td>2</td>
<td>2.4</td>
<td>~2.45&lt;sup&gt;e&lt;/sup&gt;-2.1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~2 µAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~4.7 µAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.02</td>
<td>2.4</td>
<td>GC/Li</td>
<td>0.1 M LiTFSI / Py, LiTFSI</td>
</tr>
<tr>
<td>2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)</td>
<td>10</td>
<td>2.6</td>
<td>~2.7&lt;sup&gt;e&lt;/sup&gt;-2.4&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~11 mAh m&lt;sub&gt;net&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~440 mAh m&lt;sub&gt;net&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.1</td>
<td>40</td>
<td>GDL/LFP</td>
<td>1 M LiTFSI / TGDME</td>
</tr>
<tr>
<td>2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)</td>
<td>10</td>
<td>2.6</td>
<td>~2.65&lt;sup&gt;e&lt;/sup&gt;-2.25&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~1.5 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~4.5 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.1</td>
<td>3</td>
<td>Super P/LFP</td>
<td>0.25 M LiTFSI / DME</td>
</tr>
<tr>
<td>2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)</td>
<td>10</td>
<td>2.6</td>
<td>~2.6&lt;sup&gt;e&lt;/sup&gt;-2.25&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~1 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~4 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.1</td>
<td>4</td>
<td>RGO/LFP</td>
<td>0.25 M LiTFSI / DME</td>
</tr>
<tr>
<td>2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)</td>
<td>10</td>
<td>2.6</td>
<td>~2.65&lt;sup&gt;e&lt;/sup&gt;-2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.3 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>4.5 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.07</td>
<td>1.9</td>
<td>Ketjen Black/Li</td>
<td>1 M LiTFSI / TEGDME</td>
</tr>
<tr>
<td>Anthraquinone (AQ)</td>
<td>2</td>
<td>~2.35&lt;sup&gt;*&lt;/sup&gt;</td>
<td>~2.58&lt;sup&gt;e&lt;/sup&gt;-2.1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>~7.5 mAh m&lt;sub&gt;net&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>~340 mAh m&lt;sub&gt;net&lt;/sub&gt;&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.1</td>
<td>45</td>
<td>GDL/Li&lt;sub&gt;LIPON&lt;/sub&gt; &lt;br&gt; control</td>
<td>0.1 M LiClO&lt;sub&gt;4&lt;/sub&gt; / MeCN</td>
</tr>
<tr>
<td>Anthraquinone (AQ)</td>
<td>10</td>
<td>~2.35</td>
<td>~2.65&lt;sup&gt;e&lt;/sup&gt;-2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.3 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>7.7 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.07</td>
<td>3.3</td>
<td>Ketjen Black/Li</td>
<td>1 M LiTFSI / TEGDME</td>
</tr>
<tr>
<td>Naphthoquinone (NQ)</td>
<td>10</td>
<td>~2.6</td>
<td>~2.6&lt;sup&gt;e&lt;/sup&gt;-2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.3 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>3.1 mAh cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>0.07</td>
<td>1.3</td>
<td>Ketjen Black/Li</td>
<td>1 M LiTFSI / TEGDME</td>
</tr>
</tbody>
</table>
Superscript P indicates that a voltage plateau was observed around this potential and the superscript T indicates the voltage at which the discharge curve terminates.

# If the capacity or current density provided in the article were in mAh g\(^{-1}\), the corresponding capacity normalized to area was estimated from the mass loading.

* For surface-immobilized redox mediator (estimated from CV).

Unless otherwise specified, the normalized areas correspond to geometrical area.

### Table 2. Charge mediators

<table>
<thead>
<tr>
<th>Mediator</th>
<th>[c]</th>
<th>Redox potential</th>
<th>Discharge capacity</th>
<th>Charge capacity</th>
<th>Current density</th>
<th>Charging voltage</th>
<th>OER/ORR (O(_2) ratio)</th>
<th>Electrodes (cathode/anode)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrathiafulvalene (TTF)</td>
<td>10</td>
<td>~3.5</td>
<td>300(^0) mAh g(^{-1})</td>
<td>300 mAh g(^{-1})</td>
<td>0.078</td>
<td>3.4(^{\tau})</td>
<td>~1 (reaction of mediator with Li(_2)O(_2))</td>
<td>Au(nanoporous)/LFP</td>
<td>1 M LiClO(_4)/DMSO</td>
<td>127</td>
</tr>
<tr>
<td>TTF</td>
<td>50</td>
<td>3.38, 3.69</td>
<td>~2.4(^2) mAh cm(^{-2}) (1500(^2) mAh g(^{-1}))</td>
<td>~2.4(^{2}) mAh cm(^{-2}) (1500(^2) mAh g(^{-1}))</td>
<td>0.15</td>
<td>3.2-4.7(^{\tau})</td>
<td>Super C65/Li</td>
<td>1 M LiTFSI/TEGDME</td>
<td>322</td>
<td></td>
</tr>
<tr>
<td>TTF</td>
<td>10</td>
<td>3.75, 3.95</td>
<td>0.2(^2) mAh cm(^{-2})</td>
<td>0.2(^{2}) mAh cm(^{-2})</td>
<td>0.1</td>
<td>3.4-3.7(^{\tau})</td>
<td>Ketjen Black/LFP</td>
<td>0.5 M LiClO(_4)/DMSO</td>
<td>323</td>
<td></td>
</tr>
<tr>
<td>TTF</td>
<td>50</td>
<td>3.38</td>
<td>~0.8(^4) mAh cm(^{-2}) (1000(^4) mAh g(^{-1}))</td>
<td>~0.6 mAh cm(^{-2}) (~800 mAh g(^{-1}))</td>
<td>~0.16</td>
<td>3.6(^{4}) - 4.5(^{\tau})</td>
<td>0.33</td>
<td>CNT/Li</td>
<td>1 M LiTFSI/DME</td>
<td>324</td>
</tr>
<tr>
<td>Material</td>
<td>CVD</td>
<td>~3.35</td>
<td>1 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>1 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>0.2</td>
<td>–3.4°</td>
<td>RGO/Li</td>
<td>0.5M LiTFSI/TEGDME</td>
<td>325</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----</td>
<td>--------</td>
<td>---------------------------------</td>
<td>---------------------------------</td>
<td>-----</td>
<td>-------</td>
<td>--------</td>
<td>----------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)</td>
<td>10</td>
<td>3.74</td>
<td>~7600 mAh g(^{-1})</td>
<td>~7500 mAh g(^{-1})</td>
<td>0.1</td>
<td>–3.25-4.25°</td>
<td>0.77 (assuming ideal ORR)</td>
<td>Ketjen Black/Li</td>
<td>0.1 M LiTFSI/DME</td>
<td>278</td>
</tr>
<tr>
<td>TEMPO</td>
<td>10</td>
<td>3.73</td>
<td>2.1 mAh cm(^{-2}) (~3500 mAh g(^{-1}))</td>
<td>2.1 mAh cm(^{-2}) (~3500 mAh g(^{-1}))</td>
<td>0.1</td>
<td>3.2-4.2°</td>
<td>Ketjen Black/LFP</td>
<td>1M LiTFSI/DME</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>4-methoxy-TEMPO (4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)</td>
<td>10</td>
<td>3.76</td>
<td>2.2 mAh cm(^{-2}) (~3500 mAh g(^{-1}))</td>
<td>1.9 mAh cm(^{-2}) (~3200 mAh g(^{-1}))</td>
<td>0.1</td>
<td>3.2-4.2°</td>
<td>Ketjen Black/LFP</td>
<td>1M LiTFSI/DME</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>1-methoxy-AZADO (1-methyl-2-azaadamantane-N-oxyl)</td>
<td>10</td>
<td>3.6</td>
<td>2.9 mAh cm(^{-2}) (~4900 mAh g(^{-1}))</td>
<td>2.8 mAh cm(^{-2}) (~4700 mAh g(^{-1}))</td>
<td>0.1</td>
<td>3.2-4.2°</td>
<td>Ketjen Black/LFP</td>
<td>1M LiTFSI/DME</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>TMAO (1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene-2-ylxyloxy)</td>
<td>10</td>
<td>3.89</td>
<td>2.5 mAh cm(^{-2}) (~4200 mAh g(^{-1}))</td>
<td>2.4 mAh cm(^{-2}) (~3500 mAh g(^{-1}))</td>
<td>0.1</td>
<td>3.2-4.2°</td>
<td>Ketjen Black/LFP</td>
<td>1M LiTFSI/DME</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>10-methylphenothiazine (MPT)</td>
<td>50</td>
<td>–3.8</td>
<td>0.4 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>0.4 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>0.12</td>
<td>–3.5°-3.7°</td>
<td>Ketjen Black/LFP</td>
<td>1M LiOTf/TEGDME</td>
<td>326</td>
<td></td>
</tr>
<tr>
<td>10-methylphenothiazine (MPT)</td>
<td>100</td>
<td>3.67</td>
<td>533 mAh g(^{-1}) load</td>
<td>533 mAh g(^{-1}) load</td>
<td>0.1</td>
<td>3.2-3.6°-4.2°</td>
<td>Super P/LFP</td>
<td>1M LiOTf/TEGDME</td>
<td>327</td>
<td></td>
</tr>
<tr>
<td>10-methylphenothiazine (MPT)</td>
<td>100</td>
<td>–3.8</td>
<td>21.4 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>21.4 mAh cm(^{-2}) (1000 mAh g(^{-1}))</td>
<td>3.2</td>
<td>3.6°</td>
<td>Super P/LFP</td>
<td>1M LiOTf/TEGDME</td>
<td>328</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Charge</td>
<td>Discharge</td>
<td>Current Density</td>
<td>Potential</td>
<td>Yield</td>
<td>Mass Loading</td>
<td>Current Density</td>
<td>Potential</td>
<td>Yield</td>
<td>Compound</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------</td>
<td>-----------</td>
<td>----------------</td>
<td>------------</td>
<td>-------</td>
<td>--------------</td>
<td>----------------</td>
<td>------------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>Iodide</td>
<td>50</td>
<td>3.41</td>
<td>0.8 mAh cm⁻² (1000 mAh g⁻¹)</td>
<td>0.8 mAh cm⁻² (1000 mAh g⁻¹)</td>
<td>0.16</td>
<td>3.3⁻⁴.5⁷</td>
<td>0.23</td>
<td>CNT/Li</td>
<td>1 M LiTFSI / DME</td>
<td>324</td>
</tr>
<tr>
<td>Bromide</td>
<td>10</td>
<td>3.48</td>
<td>0.2 mAh cm⁻² (500 mAh g⁻¹)</td>
<td>0.2 mAh cm⁻² (~500 mAh g⁻¹)</td>
<td>0.2</td>
<td>3.1⁻⁴.2⁷</td>
<td>0.86</td>
<td>Ketjen Black/Li</td>
<td>1 M LiTFSI / DME</td>
<td>315</td>
</tr>
<tr>
<td>Cobalt bis(terpyridine)</td>
<td>50</td>
<td>3.41</td>
<td>0.8 mAh cm⁻² (1000 mAh g⁻¹)</td>
<td>0.8 mAh cm⁻² (1000 mAh g⁻¹)</td>
<td>0.16</td>
<td>3.3⁻⁴.5⁷</td>
<td>0.23</td>
<td>CNT/Li</td>
<td>1 M LiTFSI / DME</td>
<td>324</td>
</tr>
<tr>
<td>Heme (biomolecular)</td>
<td>2.3</td>
<td>3.4</td>
<td>~2800 mAh g⁻¹ load</td>
<td>~2800 mAh g⁻¹ (100 mAh g⁻¹)</td>
<td>0.05</td>
<td>3.0⁻⁴.25⁷</td>
<td>0.74</td>
<td>CNT/Li</td>
<td>1 M LiClO₄ / TGDME</td>
<td>329</td>
</tr>
<tr>
<td>TDPA (tris[4-(diethylamino)phenyl]amine)</td>
<td>3.6</td>
<td>3.4</td>
<td>~4.1 mAh cm⁻² (~8200 mAh g⁻¹)</td>
<td>~4.1 mAh cm⁻² (~8200 mAh g⁻¹)</td>
<td>0.1</td>
<td>3.2⁻³.75⁷</td>
<td>0.74</td>
<td>Ketjen Black/Li</td>
<td>0.5 M LiTFSI / TEGDME</td>
<td>206</td>
</tr>
</tbody>
</table>

Superscript L indicates that the capacity was limited to the corresponding value rather than limiting the potential.

Superscript P indicates that a voltage plateau was observed around this potential and the superscript T indicates the voltage at which the discharge curve terminates.

# If the capacity or current density provided in the article were in mAh g⁻¹, the corresponding capacity normalized to area was estimated from the mass loading.

Unless otherwise specified, the normalized areas correspond to geometrical area.
Table 3. Bifunctional and dual redox mediators.

<table>
<thead>
<tr>
<th>Mediator</th>
<th>[c]</th>
<th>Redox potential</th>
<th>Discharge capacity</th>
<th>Charge capacity</th>
<th>Current density</th>
<th>Voltage Discharge / Charge</th>
<th>Electrodes</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron phthalocyanine (FePC)</td>
<td>2</td>
<td>2.5, 3.65</td>
<td>1.8 mAh cm⁻² (1800 mAh g⁻¹)</td>
<td>1.7 mAh cm⁻² (1750 mAh g⁻¹)</td>
<td>0.1</td>
<td>2.6-2.9 / 3.1-4.4</td>
<td>C-Fiber /Li</td>
<td>0.1M LiTFSI /TEGDME</td>
<td>78</td>
</tr>
<tr>
<td>2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxy-3-oxide (PTIO)</td>
<td>50</td>
<td>2.3, 3.8</td>
<td>1.5 mAh cm⁻² (6900 mAh g⁻¹)</td>
<td>1.5 mAh cm⁻² (6900 mAh g⁻¹)</td>
<td>0.1</td>
<td>2.75 / 3.5-4.2</td>
<td>CNT/Li</td>
<td>1M LiTFSI /DMSO</td>
<td>330</td>
</tr>
<tr>
<td>cobalt-based polyoxometalate (Co-POM)</td>
<td>0.33</td>
<td>2.6</td>
<td>−1.82 mAh cm⁻² (4050 mAh g⁻¹)</td>
<td>−1.85 mAh cm⁻² (4100 mAh g⁻¹)</td>
<td>−0.05</td>
<td>2.7 / 3.3-4.5</td>
<td>CNT/Li</td>
<td>1M LiTFSI /TEGDME</td>
<td>331</td>
</tr>
<tr>
<td>2,5-di-tert- butyl-p-benzoquinone (DTBBQ / tris(4-[2-(2-methoxyethoxy)ethoxy]phenyl)amine (TMPPA)</td>
<td>10/10</td>
<td>2.63, 3.63</td>
<td>1.5 mAh cm⁻²</td>
<td>1.5 mAh cm⁻²</td>
<td>0.5</td>
<td>2.7 / 3.75, 3.9</td>
<td>C-Felt/Li (redox flow battery)</td>
<td>1M LiTFSI /TEGDME</td>
<td>332</td>
</tr>
<tr>
<td>DBBQ / TEMPO</td>
<td>25/25</td>
<td>2.58, 3.74</td>
<td>2 mAh cm⁻²</td>
<td>2 mAh cm⁻²</td>
<td>1</td>
<td>−2.7 / 3.7</td>
<td>GDL/LFP</td>
<td>0.3 M LiClO₄ /DME</td>
<td>333</td>
</tr>
<tr>
<td>Ethyl viologen / LiI</td>
<td>10/10</td>
<td>2.65, 3.1/3.7</td>
<td>1.5 mAh cm⁻²</td>
<td>1.5 mAh cm⁻²</td>
<td>0.05</td>
<td>2.75 / 3.5-3.75</td>
<td>C-Felt/Li (redox flow battery)</td>
<td>1M LiTFSI /TEGDME</td>
<td>334</td>
</tr>
</tbody>
</table>

# If the capacity or current density provided in the article were in mAh g⁻¹, the corresponding capacity normalized to area was estimated from the mass loading.

Superscript P indicates that a voltage plateau was observed around this potential and the superscript T indicates the voltage at which the discharge curve terminates.

Unless otherwise specified, the normalized areas correspond to geometrical area.
While scanning electrochemistry microscopy and rotating disc experiments are very powerful approaches to compare the rate of Li$_2$O$_2$ oxidation by different RMs, these techniques only provide information about the rate of regeneration of the oxidized RM upon reaction with Li$_2$O$_2$. Unfortunately, the detection and quantification of the O$_2$ evolved in these experiments is very challenging; therefore, additional techniques are needed in order to validate the trends obtained, since the complexity of Li-O$_2$ reactions and proneness to degradation have shown in the past that interpretation of electrochemical data without the support of gas analysis can lead to incorrect conclusions. The evolution of O$_2$ from the reaction of RM with Li$_2$O$_2$ powder has been monitored with an oxygen sensor, which shows that a solution containing a mixture of I$_2$ + I$_3^-$ (equilibrium potential: 3.60 V vs. Li$^+/\text{Li}$)
exhibited the fastest rate of $O_2$ evolution, followed by a mixture of TEMPO$^+ +$ TEMPO (equilibrium potential; 3.74 V vs. Li$^+/Li$) while Fe$^+ +$ Fe mixtures (equilibrium potentials: 3.28-3.36 V vs. Li$^+/Li$) had very low reaction rate and $I_3^- + \Gamma$ mixtures did not produced any detectable $O_2$. Interestingly, addition of a proton donor (BuOH) significantly increased the $O_2$ evolution rate by the $I_3^-$ mediator (in the $I_3^- + \Gamma$ mixture). As discussed in Section 4.3 proton donor additives enable the formation of a more soluble intermediate (LiOOH) in Li-O$_2$ cell reactions, which can explain the enhanced kinetics (since higher solubilities afford a higher concentration, which then promotes a higher reaction rate). While much more work is necessary to elucidate the mechanism of these reactions and the fundamental descriptors affecting reactivity, all these studies show that the redox potential of the mediator is not the only factor determining the activity towards $O_2$ evolution from Li$_2$O$_2$.

2. Chemical Stability

Degradation of RMs in Li-O$_2$ batteries would be even more detrimental than the degradation of the electrolyte, since mediators are present in a much lower concentration than the solvent and their role in Li-O$_2$ cell reactions is critical. However, one advantage of RMs is that they facilitate electron transfer reactions that can deactivate the reactivity of degradation triggers (such as superoxide anion and singlet oxygen).

For example, Sawyer and coworkers showed that reduced methyl viologen (MV$^+$) reacts with superoxide ($O_2^-$) via radical-radical coupling producing various degradation products:$^{166}$

$$MV^+ + O_2^- \rightarrow [MV - O_2] \rightarrow \text{degradation products} \quad (38)$$

However, an analogous viologen, ethyl viologen (EtV$^{2+}$), has been shown to be a suitable discharge mediator for Li-O$_2$ batteries.$^{41}$ By undergoing fast electron transfer reactions, in Li$^+$ containing electrolytes, ethyl viologen promotes the reduction of oxygen to lithium superoxide:$^{41}$

$$EtV^+ + O_2 + Li^+ \rightarrow EtV^{2+} + LiO_2 \quad (39)$$

and also the reduction of lithium superoxide to lithium peroxide:

$$EtV^+ + LiO_2 + Li^+ \rightarrow EtV^{2+} + Li_2O_2 \quad (40)$$

The absence of degradation of ethyl viologen in Li$^+$ containing electrolytes was explained by the fact that the electron transfer reaction from EtV$^+$ to LiO$_2$, forming Li$_2$O$_2$ (reaction (40)), was much faster than degradation reactions such as radical-radical coupling (reaction(38)).$^{41}$

In the search for efficient RMs for Li-O$_2$ batteries, the characterization of the reaction of RMs with LiO$_2$ can be used to evaluate the absence of degradation of the RM, but also, a quantitative evaluation of the reaction rate can be used to rank the mediator activity of different RMs. But LiO$_2$ is not the only degradation trigger present in Li-O$_2$ cells. A recent
study has shown that some RMs (5,10-dimethyl phenazine and tetrathiafuvalene) that are resistant against the attack by superoxide, degrade in the presence of singlet oxygen.\textsuperscript{337} Although there are methods to decrease the presence of singlet oxygen using quenchers,\textsuperscript{153} and the generation of superoxide using RMs\textsuperscript{41,81} in Li-O\textsubscript{2} cells, the long term stability of the battery would require the RM to be reasonably stable in contact with these two potential degradation triggers. Therefore, testing the stability against superoxide and singlet oxygen would be an important part of the protocol for screening new RMs, and the test should be performed for all the oxidation states of the mediator relevant for the operation of the battery. In addition to experiments, \textit{ab-initio} calculations can be very helpful for the rational screening of sufficiently stable RMs, which can provide an estimation of the redox potential and also of the chemical stability of the RMs in different oxidation states.\textsuperscript{338}

In the search for more stable RMs, polyoxometalates have been recently proposed as a new type of RMs for Li-O\textsubscript{2} cells.\textsuperscript{314,331} Polyoxometalates are metal-oxygen clusters with multiple oxidation states exhibiting high stability in oxidizing environments. Although substantial improvements in the polyoxometalates mediation activity in Li-O\textsubscript{2} cells are required, they promise improved resistance against degradation reactions, compared to organic RMs, which warrants further investigation. 

\textbf{4.2.3 Progress in RMs Development}

Many promising RMs have been proposed for Li-O\textsubscript{2} batteries applications (Tables 1-3). As discussed above, different RMs have been tested under different conditions, and therefore, ranking in terms of RM activity is currently not possible and the use of analytical techniques to quantify the oxygen recovery efficiency (OER/ORR) during cell reactions is essential in order to evaluate the true mediation activity.

To put the requirements of RM activity into context, we return to the calculations by Gallagher and coworkers (Fig. 1) performed at a system level to take into account the requirements for electric vehicle applications. It was demonstrated that high values of areal electrode capacities (normalized by the geometric electrode area) are required to reach competitive values of specific energy, energy density and cost per usable energy that would make Li-air batteries superior to the current state-of-the-art Li-ion batteries. To fulfill the requirements for electric vehicle applications, cells should also be able to deliver 90\% of the capacity at C/5 (where C/5 corresponds to a current of 2 mA cm\textsuperscript{-2} for a capacity of 10 mAh cm\textsuperscript{-2}). The authors also mentioned a target of >1000 cycles of cycle life.\textsuperscript{28} This requires an oxygen recovery efficiency (OER/ORR) and Coulombic efficiency >99.9\% per cycle.

While the cell parameters considered by Gallagher and coworkers were very optimistic at the time of the publication, recent studies of Li-O\textsubscript{2} cells incorporating RMs have achieved comparable performance. Bruce and coworkers reported that addition of DBBQ to Li-O\textsubscript{2} cells produced areal capacities (normalized to the geometric area of the electrode) of ca. 11 mAh cm\textsuperscript{-2} at an areal current density of 0.2 mA cm\textsuperscript{-2} (Fig. 25a).\textsuperscript{81} Grey and coworkers later reported that the synergistic combination of DBBQ and water produced Li-O\textsubscript{2} cells capacities of up to 18 mA h cm\textsuperscript{-2} at 0.1 mA cm\textsuperscript{-2} (Fig. 25b).\textsuperscript{67} Interestingly, in that latter study, reduced
graphene oxide electrodes with very low carbon content (of ca. 0.2 mg cm$^{-2}$) were employed; normalization of capacities by the mass of carbon would produce an impressive (but potentially misleading) value of ca. 180000 mAh/g, i.e., both high specific and areal capacities were obtained; these capacity values also remind us that caution should be taken when evaluating the energy density of a lithium-air battery only based on specific capacities normalized by the carbon mass.\textsuperscript{133} Low carbon content in the electrodes is essential to achieve high figures of merit of energy density, specific energy and cost per usable energy, since carbon adds to the volume, weight and cost of the battery. The carbon content considered in the calculations by Gallagher and coworkers\textsuperscript{28} was 9\% in mass of the dry, discharged electrode. The carbon content in the work by Grey and coworkers\textsuperscript{67} corresponded to only 1\% in mass of the dried, discharge electrode; the remaining 99\% was Li$_2$O$_2$ (as confirmed by NMR and quantification of the O$_2$ consumed by mass spectrometry). The next challenge is to significantly improve the reversibility of these systems, i.e., high oxygen recovery efficiencies and Coulombic efficiencies.

![Graph showing discharge curves](image1)

Fig. 25 Selected examples of high-capacity, mediated Li-O$_2$ batteries. (a): Discharge curves of Li-O$_2$ cells with a gas diffusion electrode discharged in 1M LiTFSI in DME with 10mM DBBQ (solid lines) and without DBBQ (dashed lines) at various areal current densities from 0.1 mAc$^{-2}$ to 2mAcm$^{-2}$\textsuperscript{81} (b): Discharge curves of Li-O$_2$ cells made of reduced graphene oxide electrodes either with neat 0.25 M LiTFSI/DME electrolyte, with only DBBQ added (10 mM), or with both DBBQ and H$_2$O added to the neat electrolyte (as labeled in the figures).\textsuperscript{67} (c) Discharge curves of Li–O$_2$ batteries with (green) pristine, (blue) soluble anthraquinone (AQ)-, and (black) polyanthraquinone (PAQ)-catalyzed GDL cathodes in 0.1 M LiClO$_4$ MeCN at various current densities.\textsuperscript{308} (a) Reprinted with permission from ref 81. Copyright 2016 Macmillan Publishers Limited and (b) from ref 67. Copyright 2018 ACS. (c) From ref 308. Copyright 2018 ACS.
Other RMs have also produced high values of areal discharge capacity at reasonably high areal current densities (see Tables 1-3). It is also worth mentioning that immobilization of the anthraquinone (AQ) RM forming a thin conductive polymer film of polyanthraquinone produced the same areal capacities as with the freely diffusing anthraquinone (Fig. 25c). This is a highly promising approach since it overcomes the problem of RM shuttling to the anode, which would degrade the RM, decrease the battery capacity and hamper rechargeability.

While major improvements have been made in the discharge reaction of Li-O₂ cells via the incorporation of RMs, efficient recharging is still one of the most important bottlenecks in Li-O₂ cell development. A key figure of merit is the production, during charge, of the same amount of O₂ that has been consumed during discharge. This is quantified by the oxygen recovery efficiency (OER/ORR), which is defined as the ratio of the amounts of O₂ evolved and consumed in Li-O₂ cell cycling (see Section 2.2.4). As shown in Table 2, oxygen recovery efficiencies approaching 100% OER/ORR have not been found yet, but some promising values have been reported.

High oxygen recovery efficiencies of 98% to 61% OER/ORR have been reported for LiBr-containing Li-O₂ cells, which vary with the applied current (Fig. 26). Although the experiments were performed by limiting the discharge capacity to 500 mAh/g (corresponding to only 0.2 mAh/cm²), the results are certainly encouraging, as typical O₂ recovery ratios are lower than 75% in non-mediated Li-O₂ cells. A very high oxygen recovery efficiency of 92% OER/ORR has been reported for charging Li₂O₂-prefilled electrodes in LiI-containing solutions. A 78% OER/ORR has been reported for a LiI-containing Li-O₂ cell containing a flexible Li-ion conducting membrane to protect the lithium anode, as estimated from operando pressure measurements. With the aid of redox mediators, the electrochemical decomposition of Li₂O₂ is switched to chemical Li₂O₂ decomposition, Li₂O₂ reacting with the oxidized form of the mediators. Lu and coworkers have proposed that accounts for the increase in oxygen recovery, as it minimizes the formation of reactive oxygen species during direct electrochemical recharging. It is interesting to further verify which reactive oxygen species are avoided and by how much, and in particular, whether the generation of singlet oxygen is circumvented with the use of LiBr/LiI. Recent studies indicate that organic redox mediators, such as tetrathiafuvalene and dimethylphenazene, are prone to degradation when exposed to singlet oxygen. Whether these inorganic mediators are more resistant to singlet oxygen attack is another interesting question.

Taken together, the promotion of O₂ evolution from Li₂O₂ by both LiI and LiBr deserves further investigation. Of note, LiI also has the potential to promote LiOH formation via a nominal four-electron ORR in the presence of proton donor molecules (e.g., H₂O); this will be discussed in Section 5.2.
Fig. 26 Examples of mediated Li-O_2 cells with high oxygen recovery efficiency. Voltage and gas evolution profiles during charging with 10 mM LiBr at (a) 500, (b) 1000, and (c) 2000 mA/g after discharge to 500 mAh/g at 1000 mA/g. (d) A plot showing the statistics based on at least three replications (right pantel). (e) galvanostatic charge of pre-filled Li_2O_2/VC electrodes and (f) current normalized gas evolution rates for CO_2 and O_2 using 0.5 M LiTFSI + 50 mM LiI (RM) in diglyme in a 2-compartment cell. Electrode loading 0.39 mg/cm^2 (1:1 Li_2O_2:carbon ratio (90% Li_2O_2 purity), i.e., 0.35 mg/cm^2 of pure Li_2O_2). The cell was galvanostatically charged at 120 mA/cm^2 (corresponding to 82.8 μA). The voltage profile in a 2-compartment cell without LiI is superimposed for comparison (dotted gray line). The dotted black line indicates the specific capacity of 1051 mAh/g for the expected reaction Li_2O_2 → 2Li^+ + O_2 + 2e^−, whereas the blue dotted line indicates the expected oxygen evolution rate corresponding to 2e^-/O_2. (a–d) Reprinted with permission from ref 315. Copyright 2016 ACS and (e-f) from ref 197. Copyright 2014 Electrochemical Society.

Nitroxide compounds (such as TEMPO) are another highly promising family of RMs. An efficiency of 87% OER/ORR has been reported via pressure/DEMS measurements for TEMPO-containing Li-O_2 cells, containing a Li anode protected with a solid electrolyte. An efficiency of 70% OER/ORR has been reported for triphenylamines (such as TDPA) from the total amount of O_2 evolved during charging, these mediators have a very low redox potential (3.1 V vs. Li^+/Li for TDPA), but high activity for the oxidation of Li_2O_2 to O_2. TTF was the first reported charge mediator for Li-O_2 batteries, and the reaction of oxidized TTF, TTF^+, with Li_2O_2 was reported to produce a ratio of 2.01 electrons per O_2 evolved.
which can potentially translate in remarkable efficiencies of >99% OER/ORR. Addition of Cl⁻ in the electrolyte improves the mediation activity of TTF via the formation of an organic electronic conductor deposited on the cathode surface (TTF⁺-Cl⁻).\textsuperscript{325}

In conclusion, impressive improvements in performance have been achieved in recent years via the incorporation of RMs, and a good number of promising RMs has been identified (Tables 1-3). Major improvements are still required to reach the targets for commercialization, and the current main bottlenecks in performance are the poor OER/ORR recovery efficiency, insufficient stability against degradation, and lack of fundamental understanding of the key properties leading to high mediation activity.

4.3 Functional Additives

This section presents an in-depth discussion of the mechanism of phase-transfer catalysis (by water and alcohols) and singlet oxygen quenchers. (The use of electrolyte additives as RMs and to promote the solution-based mechanism of discharge has already been discussed in Sections 4.2 and 2.1, respectively). We believe that in order to reach the requirements for commercial applications, Li-O₂ batteries will need to exploit the synergistic combination of several functional additives, and that the combination of RMs, phase-transfer catalysts and singlet oxygen quenchers is particularly promising. The use of fluorinated electrolyte additives in Li-O₂ batteries is also discussed, since this approach has received considerable attention in recent years.

4.3.1 Water

The effect of water on the electrochemistry of Li-O₂ cells has been briefly discussed in Section 3.2.2. Drastic improvements in capacity have been reported upon water addition.\textsuperscript{31,74, 75, 238, 239, 341, 342} The observed increase in capacity has been ascribed to an increase in solubility of Li-O₂ cell reaction intermediates due to two possible effects: i) solvation effects, and ii) proton-transfer reactions. The following discussion demonstrates that, although solvation effects are definitively present and contribute to the increase in capacity, the dominant factor is the occurrence of proton-transfer reactions that enable a new reaction pathway involving a LiOOH intermediate, which overrides the “usual” reaction mechanism involving LiO₂ or O₂ intermediate formation.

The mechanistic understanding of the water-induced capacity enhancement is discussed below in light of older and recent studies of the electrochemistry of oxygen in aprotic media.

1. Solvation effects

Marked variations of the solvation energy of superoxide in different media were demonstrated in early work by Sawyer and coworkers: the change of the standard potential of the O₂/O₂⁻ couple, as measured with cyclic voltammetry experiments, showed that the solvation of superoxide by water was much stronger than in other solvents.\textsuperscript{343}

Such a strong superoxide-water interaction can be ascribed to the very high acceptor number of water, which readily accepts electron density from the superoxide, acting as a donor or
Lewis base. But water also has a very high donor number. Abraham and coworkers showed that lithium superoxide is stabilized in high-donor-number solvents, and Bruce and workers demonstrated that Li-O₂ cells with high-donor-number solvents discharge via a mechanism in which the high solubility of the lithium superoxide intermediate product enables the formation of large Li₂O₂ deposits away from the electrode surface: the solution-based mechanism described in Section 2.1, thus producing a marked capacity enhancement. Having a very high donor number, the incorporation of water as an additive or co-solvent produces a similar effect on the solubility of LiO₂. On the other hand, using a quantitative model of Li-O₂ cell reactions, Luntz and co-workers explained the observed enhanced capacities of Li-O₂ cells with added water by the strong interaction of water with superoxide due to the high acceptor number of water. Combining experiments and a computational analysis, Shao-Horn and coworkers studied the effects of donor number and acceptor number of water to the observed increase in lithium superoxide solubility. All these studies agree that water addition is expected to increase the solubility of the LiO₂ intermediate product. While that effect is expected to produce enhanced capacities, other effects might also be at play, or even dominate, in practical Li-O₂ cells.

2. Proton transfer reactions

Sawyer and coworkers demonstrated that, in aprotic media (e.g. dimethylformamide), protonation of superoxide by water is thermodynamically unfavorable; this is due to the very low pKₐ of water (low Bronsted acidity, pKₐ ≈33):³⁴⁵

\[
H₂O + O₂^− \leftrightarrow HO₂ + OH^−
\]

, where \(K_{eq}\) is equal to \(10^{-21}\), and \(\Delta G^°\) is equal to +119.7 kJ/mol.

However, it was found that this reaction is followed by the rapid disproportionation of protonated superoxide forming HO₂⁻ (which is the base of H₂O₂), and the net reaction is thermodynamically favorable:³⁴⁵

\[
H₂O + 2O₂^− \leftrightarrow HO₂⁻ + O₂ + OH^−
\]

, where \(K_{eq}\) is equal to \(10^5\), and \(\Delta G^°\) is equal to -28.5 kJ/mol.

Thus, in the presence of water, the oxygen reduction reaction may proceed via an alternative reaction pathway involving the formation of an HO₂⁻ intermediate, which is expected to have reasonably high solubility and diffusion coefficient in aprotic solvents. This would explain the fact that higher capacities are obtained in Li-O₂ electrolytes containing water, since the solubility of the HO₂⁻ intermediate will be higher than the solubility of the superoxide intermediate formed in the reaction in the absence of water. Once the saturation concentration of HO₂⁻ is reached, it will precipitate in the form or Li₂O₂. The following mechanism can be proposed for Li-O₂ discharge reactions in the presence of water:

\[
O₂ + e^- \leftrightarrow O₂^−
\]
\[ H_2O + 2O_2^- \leftrightarrow HO^- + O_2 + OH^- \]  (43b)

\[ HO^- + 2Li^+ + OH^- \leftrightarrow Li_2O_2 + H_2O \]  (43c)

\[ O_2 + 2e^- + 2Li^+ \leftrightarrow Li_2O_2 \]

The mechanism above shows that water acts as a catalyst that promotes an alternative reaction mechanism with faster kinetics, where the water is not consumed in the reaction. A variation of the above reaction mechanism can be proposed considering that anions are paired with lithium cations:

\[ O_2 + e^- + Li^+ \leftrightarrow LiO_2 \]  (44a)

\[ H_2O + LiO_2 \leftrightarrow LiOOH + O_2 + LiOH \]  (44b)

\[ LiOOH + LiOH \leftrightarrow Li_2O_2 + H_2O \]  (44c)

\[ O_2 + 2e^- + 2Li^+ \leftrightarrow Li_2O_2 \]

where LiOOH could be a soluble species \((HO^-_2\) and \(Li^+\) ion pair) or a solid intermediate product. Note that the thermodynamics and kinetics of these reactions are expected to change as the solvent is changed (due to solvation effects) and also as a result of the interaction of the anions with lithium ions.

In the first studies of the effect of water addition to Li-O_2 cells, Gasteiger and co-workers proposed that proton transfer effects could lead to a partial chemical “solubilization” of solid \(Li_2O_2\), but they also pointed out that full protonation of \(Li_2O_2\) to form \(H_2O_2\) was thermodynamically unfavorable: \(^{75}\)

\[ Li_2O_2 + 2H_2O \leftrightarrow H_2O_2 + 2LiOH; \Delta G^0 = +41 \text{ kJ mol}^{-1} \]  (45)

Thus, the formation of a LiOOH or \(HO^-_2\) intermediate would bring together these observations: water acts as a proton donor, but it favors the formation of LiOOH or \(HO^-_2\), not \(H_2O_2\), since the \(HO^-_2\) is not basic enough to be protonated by water. The formation of LiOOH in the discharge of water-containing Li-O_2 cells was first proposed by Wang and coworkers to explain the different reactivity of Li-O_2 cells upon addition of water (Fig. 27a). \(^{346}\) In addition, recent work has reported the presence of a Raman signal ascribable to hydroperoxide species \((HO^-_2\) or LiOOH) on wet, discharged cathodes from water-containing Li-O_2 cells (Fig. 27b). \(^{239}\) Interestingly, the \(HO^-_2\) or LiOOH Raman signal was found to appear at the beginning of discharge, prior to the formation of \(Li_2O_2\) or LiO_2, and formation of LiO_2 was not observed at high enough water concentrations. These findings support the hypothesis that proton-transfer reactions leading to the formation of LiOOH or \(HO^-_2\) intermediates constitute an alternative pathway in Li-O_2 reactions, which overrides the LiO_2 intermediate pathway for high enough water concentrations. The suppression of degradation reactions in water-containing Li-O_2 cells was, indeed, ascribed to bypassing LiO_2 formation, and Raman spectra of the dried electrodes (Fig. 27c) shows negligible formation of side reaction products at high water content (Fig. 27c). \(^{239}\) The delay in \(Li_2O_2\) deposition in the presence of water in
the electrolyte has also been observed in \textit{in situ} surface-enhanced Raman spectroscopy measurements.\textsuperscript{347}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig27.png}
\caption{Evidence of formation of LiOOH or HO\textsubscript{2} intermediates in Li-O\textsubscript{2} cells. (a): Raman spectra of Li\textsubscript{2}O\textsubscript{2}, LiOH, LiOOH-H\textsubscript{2}O and that of the discharge product collected from the cathode of a Li-O\textsubscript{2} cell without water or containing 9.1 vol.% H\textsubscript{2}O in the electrolyte.\textsuperscript{346} (b): Raman spectra and analysis on the discharged cathodes with differing water content in electrolytes (1 M LiTFSI/TEGDME); the spectra were collected with the wet, discharged cathodes. (c): Spectra of dry cathodes collected from the discharged electrodes (similar to (b)), but after washing and vacuum drying to clean off the residual electrolyte.\textsuperscript{239} (a) Reprinted with permission from ref 346. Copyright 2017 Macmillan Publishers Limited and (b-c) from ref 239. Copyright 2017 Wiley-VCH Verlag GmbH \& Co. KGaA, Weinheim.}
\end{figure}

In conclusion, the mechanism of the increased discharge capacity observed upon addition of water in electrolytes is mainly due to proton transfer reactions that, coupled to electron transfer reactions, produce the formation of a soluble LiOOH or HO\textsubscript{2}\textsuperscript{-} reaction intermediate and, as a result, the growth of Li\textsubscript{2}O\textsubscript{2} takes in solution, rather than on the electrode surface, thus resulting in the growth of large Li\textsubscript{2}O\textsubscript{2} deposits. The formation of LiOOH or HO\textsubscript{2}\textsuperscript{-} reaction intermediate is supported by thermodynamic considerations and the direct detection of the species by Raman spectroscopy. Therefore, water acts as a proton-donor phase-transfer catalyst that favors the formation of soluble reaction intermediates \textit{via} proton transfer reactions. Since the net reaction is the reduction of O\textsubscript{2} to Li\textsubscript{2}O\textsubscript{2}, water is not consumed in the reaction, but the effect on the electrochemistry of Li-O\textsubscript{2} cells can be dramatic. Interestingly, Nazar and coworkers have also shown that trace amount of water, incorporated in the cell as hydration water impurities in the electrolyte salt, can also produce a dramatic effect in the electrochemistry of Na-O\textsubscript{2} cells (increased discharge capacity and decreased charge overpotential).\textsuperscript{104}

\subsection*{4.3.2 Alcohols}

The discussion above (Section 4.3.1) has shown that, despite the very high pK\textsubscript{a} of water in organic media (that is, very low Bronsted acidity), water acts as a proton-donor catalysts in Li-O\textsubscript{2} cell discharge reactions by inducing the protonation of superoxide to form LiOOH or HO\textsubscript{2}\textsuperscript{-} reaction intermediates, which are soluble, and thus favor a solution-based discharge reaction that leads to Li\textsubscript{2}O\textsubscript{2} formation in solution, resulting in high discharge capacities.
The pK\textsubscript{a} of water in dimethylformamide is, pK\textsubscript{a} \approx 33.\textsuperscript{345} The pK\textsubscript{a} of alcohols is similar or lower than that of water: For example, in dimethylformamide, the pK\textsubscript{a}'s of phenol and of 3,5-di-tertbutylcatechol are pK\textsubscript{a} \approx 20. This is because of the stabilization of the PhO\textsuperscript{-} anion by resonance (electron delocalization in the benzene ring); for linear alcohols like 1-butanol the pK\textsubscript{a} is the same as water: pK\textsubscript{a} \approx 33.\textsuperscript{345} Therefore, these pK\textsubscript{a} values show that alcohols can be stronger Bronsted acids than water.

In view of these considerations, it is not surprising that the addition of an alcohol as electrolyte additive in Li-O\textsubscript{2} batteries can produce an even more dramatic effect than water addition.\textsuperscript{76} Indeed, phenol was found to produce a very high value of discharge capacity of 9 mAh/cm\textsuperscript{2}, which was attributed to a phase-transfer catalysis effect, in line with the discussion above about proton-transfer induced reactions. It was also demonstrated that the increase in discharge capacity was not due to side reactions, since the reaction stoichiometry was found to be of two electrons consumed per O\textsubscript{2} (as obtained from \textit{in-situ} mass spectrometry measurements), and Li\textsubscript{2}O\textsubscript{2} was identified as the main discharge produce with FTIR and XRD measurements.\textsuperscript{76}

2,6-Di-Tert-Butyl-Hydroxytoluene (BHT) was also found to increase the discharge capacity of Li-O\textsubscript{2} cells,\textsuperscript{348} which could also be ascribed to the proton-donor phase-transfer catalysis effect. A mediation of BHT of the oxygen reduction reaction, as suggested in the original article,\textsuperscript{348} is unlikely, since BHT is already in the reduced form, thus if it was reductive enough to mediate the reduction of O\textsubscript{2}, the BHT present in solution would directly react with O\textsubscript{2} as the O\textsubscript{2} was incorporated in the cell, forming Li\textsubscript{2}O\textsubscript{2} even before the discharge of the cell started.

The proton-donor phase-transfer catalysis of alcohols and water is a promising venue to increase the discharge capacity of Li-O\textsubscript{2} cells because their Bronsted acidity is high enough to promote the formation of LiOOH or HO\textsubscript{2} soluble reaction intermediates, but it is low enough to preserve the Li\textsubscript{2}O\textsubscript{2} as the final discharge product. By contrast, introduction of stronger Bronsted acids, such as HClO\textsubscript{4}, was found to lead to various proton-triggered degradation reactions, and hence, should be avoided.\textsuperscript{75}

\textbf{4.3.3 Singlet Oxygen Quenchers}

Singlet oxygen has been identified as an important trigger of degradation reactions in Li-O\textsubscript{2} cells.\textsuperscript{139, 153} Singlet oxygen formation during the charge of Li-O\textsubscript{2} cells was first identified using a spin trap (4-oxo-TEMP, see structure in \textbf{Figure 28}) that reacts with singlet oxygen forming an stable radical (4-oxo-TEMPO), which was detected by \textit{operando} EPR spectroscopy.\textsuperscript{139} In a later work by Freunberger and coworkers, the specific emission of singlet oxygen at 1270 nm (involved in the decay of singlet oxygen to triplet oxygen) was detected in \textit{operando} measurements of Li-O\textsubscript{2} cells, and in addition, \textit{operando} fluorescence measurements using a chemical trap (dimethyl anthracene, DMA) that reacts irreversibly with singlet oxygen also demonstrated the formation of singlet oxygen during charge of Li-O\textsubscript{2} cells.\textsuperscript{153}
Interestingly, it has been shown that the damaging effects of singlet oxygen can be removed via the incorporation of a chemical trap or a physical quencher to deactivate singlet oxygen; this was shown to decrease the amount of side products formed during discharge and increase the amount of oxygen evolved during charge.\textsuperscript{153} While the first physical quencher of singlet oxygen (DABCO) used in Li-O\textsubscript{2} cells limited the operation voltage to \textit{ca.} \(3.5 \text{ V vs. Li}^{+}/\text{Li}\), due to instability of the quencher at higher voltages, a very efficient new quencher has been recently proposed (DABCOnium, which is the cation obtained by alkylation of the amine group of DABCO, see structure in Figure 28) that increases the upper voltage limit to \textit{ca.} 4.2 V vs. Li\textsuperscript{+}/Li.\textsuperscript{284} While the rechargeability of the Li-O\textsubscript{2} cells with the DABCOnium quencher was poor, due to the intrinsic slow kinetics of Li\textsubscript{2}O\textsubscript{2} oxidation, the incorporation of RM\textsubscript{s} to facilitate electron transfer reactions can enable further improvements in performance. For that purpose, the selection of suitable RM\textsubscript{s} is critical, since some organic RM\textsubscript{s} degrade in the presence of singlet oxygen.\textsuperscript{337} The selection of the redox potential of the mediator is also critical, since singlet oxygen can be generated by the reaction of superoxide anions with the oxidized RM. This occurs when the difference in redox potentials of RM\textsubscript{RED}/RM\textsubscript{OX} and \(\text{O}_2^-/\text{O}_2\) is higher than the energy difference between singlet and triplet oxygen, the latter being \textasciitilde 1 eV. For example, Bard and coworkers demonstrated that this is the case for electrochemically generated ferrocenium cations and superoxide anions:\textsuperscript{349}

\[
\text{O}_2^- + \text{Fc}^+ \rightarrow \text{^1O}_2 + \text{Fc} \quad (46)
\]

Other reactions generating singlet oxygen include the oxidation of Li\textsubscript{2}O\textsubscript{2} at potentials higher than 3.45-3.55 V vs. Li\textsuperscript{+}/Li\textsuperscript{139}:

\[
\text{Li}_2\text{O}_2 \rightarrow \text{^1O}_2 + 2\text{Li}^+ + 2\text{e}^- \quad (47)
\]

the chemical disproportionation of superoxide during discharge or charge:\textsuperscript{153}

\[
2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{^1O}_2 \quad (48)
\]

\[
2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{^1O}_2 \quad (49)
\]

where HO\textsubscript{2} could be formed due to water contamination, and the oxidation of Li\textsubscript{2}CO\textsubscript{3} (a typical degradation product in Li-O\textsubscript{2} cells):\textsuperscript{179}

\[
2\text{Li}_2\text{CO}_3 \rightarrow \text{^1O}_2 + 2\text{CO}_2 + 4\text{Li}^+ + 4\text{e}^- \quad (50)
\]

In summary, the following strategies can be proposed to avoid or minimize singlet oxygen formation: 1) introduction of singlet oxygen quenchers, 2) operation of the battery at potentials below 3.45-3.55 V vs. Li\textsuperscript{+}/Li, thus preventing singlet oxygen generation via reaction (47), 3) tuning the electrolyte properties so that the potential of LiO\textsubscript{2} formation, \(E_{\text{Red}}^{\text{O}_2/\text{Li}_2\text{O}_2}\) is close to the thermodynamic potential of O\textsubscript{2} reduction to Li\textsubscript{2}O\textsubscript{2}, \(E_{\text{Red}}^{\text{O}_2/\text{Li}_2\text{O}_2} = 2.96 \text{ V vs. Li}^+/\text{Li}\), thus making generation of singlet oxygen via reaction (48) thermodynamically unfavorable, 4) controlling the cell impurity levels to prevent formation of HO\textsubscript{2}, thus preventing singlet oxygen generation \textit{via} reaction (49), 5) minimizing degradation reactions leading to Li\textsubscript{2}CO\textsubscript{3} formation, thus preventing singlet oxygen generation via reaction (50), 6) selection of charge RM\textsubscript{s} with redox potential close to \(E_{\text{Red}}^{\text{O}_2/\text{Li}_2\text{O}_2} = 2.96 \text{ V vs. Li}^+/\text{Li}\), thus preventing singlet oxygen generation via reaction (50), 6) selection of charge RM\textsubscript{s} with redox potential close to \(E_{\text{Red}}^{\text{O}_2/\text{Li}_2\text{O}_2} = 2.96 \text{ V vs. Li}^+/\text{Li}\), thus preventing singlet oxygen generation via reaction (50).
2.96 V vs. Li⁺/Li, thus enabling the operation of the battery at low charging potential, and preventing singlet oxygen generation via reactions like (46) and (47).

![Fig. 28 Structures of 4-oxo-TEMP, TEMPO, DABCO, DMAn and DABCONium molecules.](image)

**4.3.4 Fluorinated Additives**

Fluorinated compounds have been used as O₂ carriers in artificial blood substitutes, due to their extremely high O₂ solubility, acting in a similar way as hemoglobin-based formulations. The high solubility of gases (such as O₂) in fluorinated liquids is attributed to the weak intermolecular interactions in these fluids. Inspired by their role as very efficient O₂ carriers in blood substitute formulations and breathing liquids, due to their outstanding O₂ solubility and low toxicity, several fluorinated compounds were added to Li-O₂ cells as electrolyte additives or cathode coatings in the early stages of development of Li-O₂ batteries. Significant improvements in capacity were reported, which were tentatively attributed to the increased O₂ solubility achieved by the fluorocompound. Unfortunately, those early studies were done in organic carbonate electrolytes (PC and others), which are now known to be unsuitable for Li-O₂ batteries due to poor stability against superoxides. Later work has used more suitable electrolytes, such as tetrurgyme, DME, DMSO, and significant improvements in capacity were again reported. To increase the miscibility of fluorinated compounds with the other co-solvent, the use of a perfluorinated lithium salt surfactant has been reported (lithium perfluorooctane sulfonate: LiPFOS, see structure in **Figure 29a**), which enabled an impressive solubility of >60 wt.% of BrC₆F₁₃ in tetrurgyme. Fluorine-functionalized ionic liquids are another interesting option with very high O₂ solubility. Since increasing the content of the fluorinated additive in the electrolyte has been shown to increase the O₂ solubility, the improved O₂ supply to the electrode surface has often been claimed to be the reason for the improved discharge performance. However, much further work is required to elucidate the origin of the capacity improvements, which, in some cases, is due to degradation reactions.

*Ab-initio* calculations predicted that fluorinated ethers are susceptible to degradation by superoxide attack. Fluorination of the α-carbon of the ether (for instance CH₃-O-CHFCF₃ or CH₃-O-CF₂CH₃) leads to low activation energy of nucleophilic attack by superoxide. In contrast, β-fluorinated ethers (e.g. CH₃-O-CH₂CHF₂ or CH₃-O-CH₂CF₃) are expected to be
much more stable. These predictions have been confirmed by experimental work\textsuperscript{,359, 366} as discussed below.

Yazami and coworkers used electrochemical and analytical techniques to demonstrate the degradation of an α-fluorinated ether (1-methoxyheptafluoropropane: 1-PFC, see structure in Figure 29a) in Li-O\textsubscript{2} cells.\textsuperscript{366} Cyclic voltammetry experiments at a glassy carbon electrode (Fig. 29b) showed that addition of 1-PFC increased the current due to reduction of O\textsubscript{2} to O\textsubscript{2}\textsuperscript{-}, but decreased the current due to oxidation of O\textsubscript{2}\textsuperscript{-} to O\textsubscript{2} in the reverse scan, evidencing the consumption of O\textsubscript{2} via irreversible degradation reactions with the 1-PFC additive. The degradation of 1-PFC was also supported by the finding that the increase in capacity upon addition of 1-PFC to Li-O\textsubscript{2} cells decreases at higher discharge current. If the only effect of 1-PFC was to increase the O\textsubscript{2} supply to the electrode surface, the opposite behavior would be expected: increasing the discharge current would make the effect of 1-PFC higher, due to the higher effect of the limited rate of O\textsubscript{2} supply. Furthermore, degradation of 1-PFC in Li-O\textsubscript{2} cells (most likely, upon reaction with O\textsubscript{2}) was also demonstrated by \textsuperscript{1}H-NMR and XPS measurements of the discharged electrolytes and cathodes, respectively.

![Fig. 29](image-url)
In contrast, the same group showed that a $\gamma$-fluorinated ether (1,1,1,2,2,3,3,4,4,4-nonafluoro-6-propoxyhexane: TE4, see Figure 29a) was stable against degradation in Li-O₂ cells. The improvement of the discharge capacity and discharge voltage of Li-O₂ cells upon TE4 addition was more pronounced at high discharge current, were the O₂ supply is more critical, in agreement with the hypothesis that the beneficial effect of TE4 is due to the increase in O₂ solubility. Direct measurement of the increase of O₂ solubility in the electrolyte upon TE4 addition were reported, as obtained by monitoring changes in pressure in O₂ uptake experiments (see Figure 29c). The absence of degradation of TE4 during discharge of Li-O₂ cells was confirmed by $^1$H and $^{19}$F-NMR of the discharged electrolytes and FTIR and XPS measurements of the discharged cathodes.

Another interesting advantage of fluorinated additives is their flame retardant behavior. Figure 29d (bottom) illustrates the ignition tests of glass fiber separators pre-soaked in different electrolytes, which demonstrate that the separators do not ignite in any of the electrolytes containing fluorinated additives. Figure 29d (top) illustrates the improved wettability facilitated by the addition of fluorinated additives: a drop placed on top a pre-soaked glass fiber separator fully wets the separator with electrolytes containing fluorinated additives, whereas the drop does not wet (small contact angle) in the conventional electrolytes containing LiTFSI in tetraglyme.

In summary, fluorinated additives exhibit some highly beneficial properties that can potentially lead to major improvements in Li-O₂ batteries, such as their very high O₂ solubility, good wettability and flame retardant properties. From a broader perspective, the role of mass transport limitations in Li-O₂ batteries needs to be investigated further. Mass transport limitations in ionic-liquid based Li-O₂ batteries were evidenced by the fact that drastic improvements in capacity could be achieved by either stirring or flowing an electrolyte saturated with O₂ through the cell. Due to the high viscosity of ionic liquids, mass transport limitations were shown to be important even at low current densities of around 0.1 mA cm⁻². For less viscous electrolytes, combination of experiments and simulations concluded that mass transport limitations could be an issue for current densities in the range of 1-10 mA cm⁻². Those current density values are relevant for commercial applications in, for example, electric vehicles, thus improving mass transport should be addressed in further studies of Li-O₂ batteries. Of note, in mediated Li-O₂ cells, the transport of the RM from the cathode/electrolyte to the O₂/electrolyte interface will substitute the transport of O₂, thus in that case the transport rate of the RM will be the most critical. In conclusion, further studies assessing mass transport limitations (from all species involved in the reactions: lithium ions, RMs, dissolved O₂, superoxide, etc.) are required for the development of batteries able to fulfil the power requirements for commercial applications.
4.4 Protection Strategies for Li Metal in Lithium-Air Batteries

In the previous discussion of Section 4, we focused on approaches addressing the challenges associated with the O₂ electrochemistry. In this section, we present strategies that can mitigate the problems at the reaction interface of Li metal anodes and the electrolyte. We summarize the protection strategies into two categories: 1) solid-electrolyte interface (SEI) formed on Li metal anode surface by reacting Li metal with additives, electrolytes, salts and air constituents; 2) inorganic/organic protective layers used as separators or coatings on Li metal anode. Literature examples are selected with emphasis on the interplay between the protection method and effect of air constituents.

4.4.1 Solid Electrolyte Interface

The SEI is a protective surface layer, with low electronic conductivity but that enables lithium ion transport. It is formed on reaction of Li metal with organic electrolytes, and consists of a complex mixture of inorganic and organic components. It can be formed by reactions among electrolyte, salt, additives and Li metal during chemical pre-treatment or during electrochemical cycling. A stable SEI enables a prolonged stripping/plating cycles of a Li metal anode at high Coulombic efficiencies. In principle, any effective electrolyte system that has been reported to sustain a reversible Li stripping/plating process and is compatible with the oxygen redox chemistry at the cathode is worth considering as a candidate for the lithium-air battery system. Many functional additives have been proposed to facilitate the formation of a stable SEI, including dissolved O₂ and CO₂ species, trace H₂O contamination, lithium nitrate, boric acid, germanium, polyphosphoric acid, 1,4-dioxacyclohexane, Super P® carbon, tetraethyl orthosilicate, Indium and cesium iodide. Some of them have been reported to be beneficial to processes at both electrodes, their effects on the Li anode being discussed below.

Lithium nitrate is an electrolyte additive widely used in lithium sulfur batteries. It is thought that LiNO₃ reacts with Li to form a protective layer (likely to be Li₂O due to the reduction of LiNO₃ by Li), which prevents further reactions of Li with polysulfide intermediates shutting from the cathode. Li₂O being an active component in a stable SEI layer has been confirmed by cryo-TEM and Raman spectroscopy. Addison and coworkers found that the salt LiNO₃ is also effective in generating a stabilized SEI in lithium-air battery systems, where an amide-based electrolyte would otherwise be incompatible with a Li anode. The authors further added that O₂ also plays a beneficial role in stabilizing Li metal anodes, which is consistent with the observation by Edström, Zhou and Wang and coworkers (Section 3.3.2). Although the causes of Li₂O formation in SEI layers may vary case to case, these studies suggest that its presence is beneficial to a stable SEI.

Water at ppm levels is usually an inevitable contamination in a battery system. It can serve as a solvating additive to improve the ORR at the cathode, as discussed in Sections 2.1.1 and 4.3.1. At trace quantities, it can also benefit the anode. Zhang and coworkers found that when 25–50 ppm water is used together with a LiPF₆ salt in the electrolyte, a more reversible
Li deposition/dissolution reaction can be promoted. Instead of forming a mossy structure, Li anodes with 50 ppm water exhibit a columnar morphology for the deposited lithium (Fig. 30a). Detailed analysis revealed that HF is generated via the reaction of LiPF$_6$ and H$_2$O, the generated HF being subsequently reduced during the initial Li deposition and forming a LiF-rich SEI layer. LiF as a critical component in SEI for reversible Li deposition has been previously demonstrated by many groups,$^{374,392-397}$ the fluorinated SEI is proposed to enable much faster Li$^+$ diffusion at the Li anode-electrolyte interface, and guide an ordered columnar Li deposition.

The use of redox mediators is an important strategy to improve the cell reversibility (Section 4.2). One common issue facing their successful implementation concerns their incompatibility with the Li anode. For example, the oxidized form of an iodide mediator, i.e., I$_3^-$, tends to shuttle over to the Li anode and becomes chemical reduced thereby corroding the Li anode. Zhou and coworkers$^{388}$ demonstrated that by using InI$_3$ additives, the lithium anode can be protected against I$_3^-$ attack (Fig. 30b); the In$^{3+}$ becomes electrochemical reduced at the Li anode on charging, forming a protective indium layer on Li, which was also found to suppress lithium dendrite formation. While the In layer is likely reduced further to form a lithium indium alloy, redox shuttling is most likely prevented by the formation a stable SEI.

When a single electrolyte system is used in the lithium-air battery, finding an optimal electrolyte to satisfy the requirements from both anode and cathode is challenging, especially in the complex (electro-)chemical environment of lithium-air batteries. However, once a dual compartment cell structure is employed, more strategies in the general Li metal research can
be transferred to lithium-air batteries, because the anolyte and catholyte are separated by a solid electrolyte membrane so that they can be optimized independently.

### 4.4.2 Inorganic/Organic Protective Membranes

Inorganic, organic and hybrid membranes have been used in lithium-air batteries to prevent the reactions occurring between the air electrode constituents and the Li anode. While the membrane can be used as a separator between the cathode and anode, i.e. a protected anode design, it can also be applied at the interface of the cathode and ambient air, i.e. a protected cathode design. In the protected anode design, a membrane should have high Li⁺ ionic conductivity. Proton transport and reaction with water and CO₂ should also be minimised. In the protected cathode design, a membrane should have high O₂ permeability, high rejection rate of H₂O, CO₂, and high immiscibility with organic electrolytes to suppress electrolyte evaporation.

The first example of using inorganic solid state electrolytes to protect Li metal anode was demonstrated by Visco and coworkers in 2007. They developed an aqueous/organic hybrid Li-O₂ system, where the two compartments in the battery were separated by a NASICON-type (Li₂M₂(PO₄)₃) solid state electrolyte with high Li⁺ conductivity, thus protecting the Li metal anode from reaction with the aqueous electrolyte contained in the oxygen electrode compartment. The authors reported a stable discharge up to 14 hours. Following the dual-compartments design, a number of studies reported improved stability and energy efficiency by optimizing the activity of oxygen reduction catalyst, using protective layers for solid state electrolyte against water and Li corrosion, better electrolyte, and adjusting operational temperatures. The concept of dual-compartments was later adapted to non-aqueous lithium-oxygen batteries; in this approach two different electrolytes are used at the oxygen and lithium electrode compartments, thus enabling a higher flexibility that allows separate optimization of electrolytes, salts, redox mediators, etc. for the cathode and anode.

For example, the cell can be separated by an Ohara glass, L₁₁⁺ₐ+Al₂⁻_$\text{Ti}_{12}^{-}$$_{-}$Si$_3$P$_3$-$\gamma$O₁₂. Figure 3a shows an example of a dual-compartment Li-O₂, where the cathode compartment contains LiTFSI /TEGDME with a redox mediator dimethylphenazine (DMPZ), while in the anode compartment contains fluoroethylene carbonate (FEC) and the salt LiTFSI which is known to form a stable SEI on Li metal anode. The SEM image revealed the smooth surface morphology on the cycled Li metal anode. Due to the isolation from TEGDME/DMPZ that would otherwise react to form an unstable SEI, the Li metal anode shows much improved cycling stability in the FEC electrolyte (Fig. 3a(ii)). Many other protection methods can be potentially applied in the dual-compartment configuration, including the solvent-in-salt (A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries), self-healing electrostatic shield, 3D current collectors (Accommodating lithium into 3D current collectors with a submicron skeleton towards long-life lithium metal anodes), additives (Dendrite-free Li deposition using trace-amounts of water as an electrolyte additive), and nanoengineering methods.

Recently, there has been growing interests in applying polymer membranes to protect Li metal anode, because of the flexibility in materials design and the potentially low cost.
This field builds on the extensive work on polymer electrolytes for lithium-ion batteries. A representative example is the application of poreless polyurethane (PU) membrane (Fig. 31b(i)). As shown in Figure 31b(ii), the PU membrane is composed of two domains: hard and soft domains. Because of the poreless structure, the Gurley time (the time required for 100 cm$^3$ of air to pass through a separator under air pressure of 0.862 kgf cm$^{-2}$) was out of the detection range in an air permeability test (Fig. 31b(iii)), suggesting that the PU membrane is air-impermeable. The PU membrane also has excellent electrolyte wettability and Li ion conductivity (Fig. 31b(iv)), and therefore affords an improved cycling lifetime of the Li metal anode. Compared to the Li metal anode protected by porous polyethylene (PE) separator in which particulate LiOH was detected by XRD and SEM, only Li metal signals were detected after 100 cycles when the anode is protected by the PU separator.

While the PU separator successfully prevents the crossover of H$_2$O and O$_2$, Li dendrite still grows, possibly due to the low mechanical strength. This is a problem common to many polymer membranes, which can be improved by inorganic additives. For example, aluminum oxide (Al$_2$O$_3$) nanoparticles have been added into a lithiated Nafion membrane to form a composite protective layer. As schematically illustrated in Figure 31c(i,ii) pulverization of the protective layer during Li plating/stripping experiments occurs without the Al$_2$O$_3$ nanoparticles (Nafion layer: NL), whereas the protective layer remains intact when Al$_2$O$_3$ nanoparticles (Nafion-based composite layer: NCL) are included. This composite layer has also been shown to suppress dendrite growth. A symmetric Li cell protected by the composite layer shows an improved cycling lifetime compared to the unprotected or Nafion-only protected cells (Fig. 31c(iii)). Furthermore, the authors stress that the chemical stability of the membrane must be tested in the presence of reactive oxygen species in lithium-oxygen batteries: the stability of the Nafion-based composite membranes were compared to that of a polyvinylidene fluoride (PVdF)-based composite membrane (composite protective layer: CPL). As measured by online electrochemical mass spectrometry (OEMS), irreversible O$_2$ reduction and CO$_2$ evolution were observed in the latter case (Fig. 31c(iv,vi)), likely due to the decomposition of PVdF, whereas the O$_2$ reduction and evolution are more reversible when Nafion-based membrane is used (Fig. 31c(v,vi)). This result is in agreement to an earlier work that reported the instability of PVdF against the O$_2^-$ radical. In contrast, the NCL affords a more reversible O$_2$ reduction and evolution.
Fig. 31 Inorganic/organic membranes to protect Li anodes. (a) The bicompartimental cell configuration with dual organic electrolytes for optimized stability of Li-O_2 batteries. (i) Schematic illustration of the cell showing the two compartments, separated by a Li^+ ion conducting solid electrolyte, with the Li anode compartment containing Li SEI protective additives such as fluoroethylene carbonate (FEC), and the oxygen electrode compartment containing redox mediators (RM). (ii) The voltage profiles of Li/TEGDME/Li and Li/FEC/Li symmetrical cells during repeated plating/stripping at 1 mA/cm^2. The cell voltage is below 50 mV in FEC (labelled at FE in the figure legend) while the cell voltage increases to 3V in TEGDME (labelled as TE in the figure legend). Reprinted with permission from ref 288. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) A supported poreless polyurethane (PU) separator used to protect Li metal anode (i) Schematic illustration of the rejection of O_2 and H_2O by the poreless PU separator. In a cell, the PU membrane was placed between the Li metal anode and the glass fiber. The salt/electrolyte are LiClO_4/TEGDME. (ii) Molecular structure of the PU separator, containing hard and soft domains. The hard domain consists of 4,4'-diphenylmethane diisocyanate (MDI), providing the mechanical rigidity through the \( \pi-\pi \) interactions and the hydrogen bonding between the end urethane groups. The soft domain consists of poly(ethylene oxide) and polytetramethylene glycol (PTMEG), providing the softness and wettability. (iii) The air permeability test results showing the Gurley time for glass fiber (GF), polyethylene (PE) and PU. (iv) The electrolyte (TEGDME) contact angle (top) to PE and PU, 5s after the electrolyte drop; the Li ion conductivities of the PE and PU separators (bottom). Reprinted with permission from ref 289. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Schematic illustration of the pulverization of the Nafion-based membrane without (i)
and with (ii) Al₂O₃ nanoparticles. (iii) Voltage profiles of Li symmetric cells without protection, with Nafion-only (NL) and Nafion-Al₂O₃ composite layer (NCL) during plating/stripping reactions at 0.5 mA/cm² for 1000 hours. Schematic illustration of the O₂ radical attack to the PVdF-based protective layer (CPL) (iv) and the Nafion-based protective layer (NCL) (v). (vi) The OEMS signal of O₂ evolved at different specific capacities from the cells with CPL and NCL protection. The dotted line shows the theoretical 2e⁻/O₂ relationship. 

Reprinted with permission from ref 421. Copyright 2019 The Royal Society of Chemistry.

In the protected cathode design, an oxygen selective membrane (OSM) was placed at the interface of cathode and ambient air. The OSM should allow the fast transport of O₂ while rejecting or trapping other air constituents, such as H₂O and CO₂. Since the molecular size of H₂O is smaller than O₂, simply tuning the porosity of the membrane will not achieve a selective transport of O₂. A non-polar membrane with a high solubility and diffusivity of the non-polar molecule O₂ should achieve the high selectivity of O₂ over the polar molecule H₂O. For example, low-density polyethylene was applied to dehydrate ambient air and greatly prolonged the cycling lifetime of the lithium-air battery. Silicone oil loaded into a porous metallic Ni substrate also achieved a good O₂/H₂O separation. Compared to O₂/H₂O separation, separation of O₂ from CO₂ is more challenging since both molecules are non-polar. While considerable research has been performed to separate CO₂ from the air (for CO₂ sequestration, for example), literature reporting O₂/CO₂ separation in Li-air batteries is scarce. In one example, a composite membrane made of a polydopamine-coated metal organic framework CAU-1-NH₂ dispersed in a polymethylmethacrylate (PMMA) was attached to the cathode and the battery showed an improved cycling life in ambient air. The functional group -NH₂ in CAU-1-NH₂, -OH in the polydopamine and -C=O in PMMA were demonstrated to trap CO₂ and afford a high selectivity of O₂ over CO₂. In another work, perfluoropolyether-based membrane was demonstrated to dehydrate ambient air and suppress DMSO evaporation effectively. Interestingly, the allowed permeation of CO₂ through the membrane stabilizes the Li metal anode by forming a protective layer of Li₂CO₃. On the cathode, however, Li₂CO₃ that could be potentially formed from the reaction of discharge product Li₂O₂ and CO₂ (reaction 14) was not detected. Therefore, the permeation of CO₂ without H₂O appears to improve Li metal anode stability without compromising the cathode stability by the irreversible formation of Li₂CO₃.

In summary, Li-metal protection strategies have been demonstrated in lithium-air battery systems, including the protected anode design by forming stable SEI using electrolyte additives or inorganic/organic protective membranes, and the protected cathode design by applying oxygen selective membranes. Significant progress has been made in prolonging battery cycling lifetime. With further demand for more practical and scaled up lithium-air batteries, more stringent requirements will be placed on the materials involved in the proposed strategies. At the anode side, many protective solid-state layers are reactive to Li metal causing side reactions and reduction in Coulombic efficiencies; buffer layers between solid state electrolyte and Li metal can greatly circumvent the problem, but they also increase system cost/complexity and reduce energy density. Meanwhile, even with protective solid state layers, lithium dendrites still form in some cases; a more complete picture of the origins of this dendritic growth needs to be obtained to come up with effective strategies to resolve this. At the cathode side, the chemical stability of gas selective membranes against reactive
oxygen species may be an issue, which should not be overlooked. Finally, other air constituents (CO₂, H₂O) might have impact on the material properties and interfacial processes (such as the stability of SEI, solid state electrolyte etc.) involved in these proposed strategies. Further fundamental studies are required in this direction to aid any rational materials design.

5. Alternative Battery Chemistries

While tremendous efforts are being devoted to developing strategies that mitigate the issues of a Li₂O₂-based non-aqueous Li-O₂ battery, many researchers also exploited alternative chemistries. For instance, one-electron superoxide based metal-oxygen batteries were found to exhibit much smaller voltage hysteresis than the peroxide chemistry. A nickel-based cathode together with a LiNO₃-KNO₃ inorganic electrolyte at 150°C has been reported to promote Li₂O formation and decomposition in a Li-O₂ battery. The synergistic effects of water additives and catalysts can be used to modulate the battery chemistry as a nominal four-electron oxygen electrochemistry via LiOH formation and decomposition. These novel strategies shed new light on how to tackle the long-standing issues of high overpotentials, organic electrolyte decomposition, battery chemistry sensitive to H₂O and CO₂ contamination and so on, further deepening and widening the mechanistic understanding of metal-oxygen electrochemistries. In this section, we discuss the fundamental characteristics and implications of these battery electrochemistries.

5.1 MO₂ or M₂O as the Potential Discharge Products?

It has been long established that the cation size (or softness) can significantly impact on the O₂ redox processes in non-aqueous media. According to the Hard Soft Base and Acid Theory, larger cations, such as Na⁺, K⁺, TBA⁺, tend to afford the one-electron O₂/O₂⁻ redox reaction, whereas smaller Li⁺ induces Li₂O₂ formation, the oxygen CVs measured with the former larger cations show narrower redox peak separations, while with Li⁺ CVs show wider separations and irreversibility. These phenomena are rooted in the thermodynamic properties of superoxide, peroxide and oxide species for these alkali metals, as summarized in Table 4.

The one-electron KO₂ formation reaction has a standard potential of 2.48 V vs. K⁺/K, higher than that of two-electron K₂O₂ formation (2.20 V vs. K⁺/K). Therefore, in a K-O₂ battery, electrochemical KO₂ formation is both thermodynamically and kinetically favored. In Na-O₂ batteries, the standard potential of the NaO₂ formation reaction is slightly lower than Na₂O₂ formation by 60 mV, Na₂O₂ thus being thermodynamically preferred. Nonetheless, in practice NaO₂ is still observed to form preferentially during experiments; this preference can be attributed to a higher kinetic barrier associated with the two-electron charge transfer for Na₂O₂ formation. In the case of Li-O₂ batteries, LiO₂ is thermodynamically unstable at standard conditions and thus does not form as a stable discharge product. Once it is transiently generated upon electro-reduction, LiO₂ chemically disproportionate to form Li₂O₂, which is then electrochemically decomposed at anodic potentials. The high
irreversibility typically observed in CVs for a Li-O<sub>2</sub> battery is in part a reflection of the asymmetric operating mechanisms for Li<sub>2</sub>O<sub>2</sub> formation (an electrochemical then chemical steps) and decomposition (electrochemical processes), in contrast to the symmetric processes for KO<sub>2</sub>, NaO<sub>2</sub> formation and decomposition (both are one-electron electrochemical processes). The formation of Li<sub>2</sub>O<sub>2</sub> is both thermodynamically and kinetically favored over Li<sub>2</sub>O formation, because the former has a higher equilibrium voltage and the O-O bond does not need to be cleaved. However, at above 150°C, formation of Li<sub>2</sub>O becomes the thermodynamically more favorable reaction over Li<sub>2</sub>O<sub>2</sub> and with the right catalyst, Li<sub>2</sub>O can be formed electrochemically during cell discharge; this is discussed further in Section 5.1.2.

Table 4. Thermodynamics of possible discharge reaction products in K-O<sub>2</sub>, Na-O<sub>2</sub> and Li-O<sub>2</sub> batteries and corresponding specific capacity as well as energy density.

<table>
<thead>
<tr>
<th>Product</th>
<th>Reaction</th>
<th>ΔS (J/(mol·K))</th>
<th>ΔH (kJ/mol)</th>
<th>ΔG (kJ/mol)</th>
<th>z</th>
<th>E° (V)</th>
<th>Specific Capacity (mAh/g)</th>
<th>Energy Density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>K + O&lt;sub&gt;2&lt;/sub&gt; → KO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>116.7</td>
<td>-284.9</td>
<td>-239.4</td>
<td>1</td>
<td>2.48</td>
<td>377.0</td>
<td>934.9</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 K + O&lt;sub&gt;2&lt;/sub&gt; → K&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>102.1</td>
<td>-494.1</td>
<td>-425.1</td>
<td>2</td>
<td>2.20</td>
<td>486.4</td>
<td>1070.2</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 K + 1/2 O&lt;sub&gt;2&lt;/sub&gt; → K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>94.1</td>
<td>-363.2</td>
<td>-322.2</td>
<td>2</td>
<td>1.67</td>
<td>569.1</td>
<td>950.3</td>
</tr>
<tr>
<td>NaO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Na + O&lt;sub&gt;2&lt;/sub&gt; → NaO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-140.6</td>
<td>-260.7</td>
<td>-218.8</td>
<td>1</td>
<td>2.27</td>
<td>488.2</td>
<td>1108.2</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 Na + O&lt;sub&gt;2&lt;/sub&gt; → Na&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-212.9</td>
<td>-513.2</td>
<td>-449.7</td>
<td>2</td>
<td>2.33</td>
<td>689.0</td>
<td>1605.4</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Na + 1/2 O&lt;sub&gt;2&lt;/sub&gt; → Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-130.1</td>
<td>-415.1</td>
<td>-376.3</td>
<td>2</td>
<td>1.95</td>
<td>867.4</td>
<td>1691.4</td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 Li + O&lt;sub&gt;2&lt;/sub&gt; → Li&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-206.9</td>
<td>-632.5</td>
<td>-570.8</td>
<td>2</td>
<td>2.96</td>
<td>1168.3</td>
<td>3458.3</td>
</tr>
<tr>
<td>Li&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2 Li + 1/2 O&lt;sub&gt;2&lt;/sub&gt; → Li&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-123.2</td>
<td>-597.9</td>
<td>-561.2</td>
<td>2</td>
<td>2.91</td>
<td>1793.9</td>
<td>5220.2</td>
</tr>
</tbody>
</table>

Note: ΔS, ΔH and ΔG are the standard entropy, enthalpy and Gibbs energy of the reaction, z is the number of electrons involved, E° is the standard voltage of the associated metal-O<sub>2</sub> battery. (Data used for calculating Na-O<sub>2</sub> and Li-O<sub>2</sub> batteries are from the article by Ji et al. Reprinted with permission from refs 421 and 428. Copyright 2013, 2017 ACS.

In light of the aforementioned properties of alkali metal oxides, NaO<sub>2</sub> and KO<sub>2</sub> as the discharge products in Na-O<sub>2</sub> and K-O<sub>2</sub> batteries, respectively, have been demonstrated under galvanostatic cycling conditions. By contrast, LiO<sub>2</sub> as a stable final discharge product in non-aqueous Li-O<sub>2</sub> batteries was not observed until Amine and coworkers’ work. They suggested that Ir metal catalysts on a reduced graphene oxide electrode can stabilize LiO<sub>2</sub> due to the lattice match between LiO<sub>2</sub> and Ir<sub>3</sub>Li, allowing them to realize a LiO<sub>2</sub>-based Li-O<sub>2</sub> battery. Although doubts were raised by McCloskey and coworkers on the existence of LiO<sub>2</sub> as the final discharge product, another group later on also reported LiO<sub>2</sub> formation on a Pd/rGO catalyst, supporting the concept of LiO<sub>2</sub>-based Li-O<sub>2</sub> batteries. It is clear from Table 4 that the theoretical energy densities of NaO<sub>2</sub> and KO<sub>2</sub> are 3-4 times lower than that of Li<sub>2</sub>O<sub>2</sub>, which is the main reason why less research input has been devoted to developing Na-O<sub>2</sub> or K-O<sub>2</sub> batteries. (The uses of Na and K metals are also associated with higher safety concerns). Nevertheless, the practical capacities obtained for Na-O<sub>2</sub> or K-O<sub>2</sub> batteries are
significantly higher than typical Li-O₂ batteries under similar operational conditions, and the fundamental insights gained for Na- and K-O₂ cells can motivate new strategies to further improve Li-O₂ cells. Next, we compare the superoxide-based electrochemistry reported for Li-, Na- and K-O₂ batteries and focus our discussion on the reversibility and stability of the battery chemistry.

5.1.1 Reversibility and Stability of Superoxide-Based Electrochemistry

The reversibility and stability of LiO₂, NaO₂ and KO₂ batteries are shown in sequence on the top, middle and bottom panels of Figure 32. In contrast to the behavior observed in Li₂O₂-based Li-O₂ batteries, in LiO₂-based Li-O₂ batteries, the formation and decomposition of LiO₂ exhibit a smaller voltage hysteresis (~0.5 V, Fig. 32a(i)). The majority of charge capacity finishes below 3.5 V. DEMS measurements of the 1st electrochemical cycle lead to an e/O₂ molar ratio of 1.00, implying that the OER/ORR ratio is very close to 1, although the cycle life of the battery is poor (40 cycles). Moving from LiO₂ to NaO₂ and KO₂, a progressively smaller voltage hysteresis is observed in superoxide-based metal-O₂ batteries, e.g., typically <200 mV for NaO₂ (Fig. 32b(ii)) and <100 mV for KO₂ (Fig. 32c(ii)), and the oxygen recovery efficiency (OER/ORR) based on operando pressure and DEMS measurements are reported to be >95% for NaO₂ and 99% for KO₂. Different from the LiO₂ electrochemistry, both NaO₂ and KO₂ exhibit charging profiles that rapidly polarize to the cutoff value when the charge capacity approaches that of the discharge, marking the end of charge (Fig. 32b,c(i)). These NaO₂- or KO₂-based batteries can typically cycle more than 100 times continuously, that is, when there is no resting between discharge and charge processes. Compared to the peroxide chemistry, the higher reversibility of superoxide-based battery can be attributed to the following reasons: 1) a smaller kinetic barrier associated with the one-electron redox chemistry; 2) higher solubility (KO₂>NaO₂>LiO₂) or better solvation of superoxides than peroxides in non-aqueous electrolytes that provides facile solution-mediated redox processes; 3) fewer parasitic reactions involved in the formation and decomposition of superoxides – both a consequence and a cause for the low voltage hysteresis.

Apart from the electrochemical reversibility, the chemical stability of the discharge product in the cell environmental is another critical requirement to evaluate the feasibility of a practical superoxide-based battery, because it determines both the cycle life and shelf life. This demand raises issues with LiO₂ and NaO₂, because of their relative thermodynamic instability versus their peroxide counterparts (Table 4). After only 12 hours resting period after discharge, significant amounts of LiO₂ and NaO₂ products have been transformed to Li₂O₂ (Fig. 32a(iii)) or Na₂O₂ (Fig. 32b(ii)), this transformation may initiate or involve parasitic reactions with electrolyte (Fig. 32b(iii)); As a result, the reversibility of the battery in the following cycles becomes worse. By contrast, KO₂ is both thermodynamically and kinetically favored product. Wu and coworkers found that after 30 days of resting the cell following discharge, the subsequent recharge still holds a Coulombic efficiency of 94%, and quantitative titration experiments show that only 1.4% KO₂ degraded after 10 days’ resting in the cell (Fig. 32c(ii-iii)). These observations certainly suggest that
from a chemical stability point of view, KO$_2$ is a better choice for realizing a superoxide battery with both a long cycle life and shelf life.

Indeed, Lu and coworkers$^{430}$ recently demonstrated a novel organic-oxygen battery operating with highly reversible and sustainable KO$_2$ formation. The quasi-reversible K metal anode (due to an unstable SEI) was replaced by a more reversible aromatic hydrocarbon solution
(e.g., 2-methyl b-phenyl in DME) acting as an anolyte, which was combined with a cathode undergoing reduction of O₂ to KO₂ (Fig. 33a,b). Such novel cell design based on KO₂-electrochemistry in a KPF₆/DMSO electrolyte could be cycled for 3000 times, at 4 mA/cm² and 0.25 mAh/cm² per cycle (Fig. 33c). The oxygen recovery efficiency (OER/ORR) at 500th cycle was measured to be 99.1%, the side products being quantified as low as 0.15% per cycle (Fig. 33d-f). As a result, the cell shows an impressive average Coulombic efficiency of 99.8% over the course of 3000 cycles.

These findings of Wu, Lu and coworkers⁴³⁰, ⁴³⁷, ⁴⁴⁹ are certainly surprising, because they challenge the consensus that superoxide anion is a strong base and nucleophile causing significant electrolyte degradation over time,¹⁷⁰ as repeatedly observed in non-aqueous Na-O₂ and Li-O₂ batteries. It has been reported that superoxide anions in Na-O₂ batteries can abstract protons from DMSO or glyme solvents,⁴²⁵ the HO₂, so generated, causing further degradation via disproportionation or reacting with trace water impurities, releasing reactive ¹O₂ during both discharge and charge.¹⁷⁸ It is still an open question as to whether ¹O₂ is also formed during the operation of K-O₂ batteries. Nonetheless, the impressive battery performance reported by Wu, Lu and coworkers seems to suggest that the ¹O₂ formation in K-O₂ batteries is largely avoided, if any occurs at all. The origin of this long-term stability of KO₂ in an organic solvent compared to its counterpart in Li- and Na-O₂ batteries warrants further investigation and may lead to pathways to more stable Li-O₂ and Na-O₂ batteries. Despite of the many intriguing unanswered questions, it is encouraging to see that an alkali metal-O₂ battery can be reversibly cycled thousands of times without significant capacity decay (albeit at a low reversible capacity), especially based on the stereotyped ‘reactive’ superoxide.

Fig. 33 Characteristics of a long-life organic-oxygen battery. (a): CVs of biphenyl (Bp), naphthalene (Nap), triphenylene (Tph) and Phenanthrene (Pha) in a 0.5 M KPF₆/DME electrolytes and saturated O₂ in a 0.5 M KPF₆/DMSO electrolyte. (b): Configuration of the bi-compartmental BpK-O₂ cell, separated by a polymer-sealed K-β’’-Al₂O₃ disc. (c): Rate capability tests of the BpK-O₂ cell in a 100% DOD mode in the range 1.5-3.0 V versus BpK/Bp (0.1-2.0 mA/cm²) and 1.0-3.5 V versus BpK/Bp (4.0 mA/cm²). (d): Galvanostatic charge profile (blue) and gas evolution (purple) profiles of the BpK-O₂ cell at 2.0 mA/cm² during the 500th charge. (e):
Galvanostatic voltage profiles of the BpK-O₂ cell at 2.0 mA/cm², except 51st, 102nd and 153rd charge, during which the current density was reduced to 0.2 mA/cm². (f): The corresponding Coulombic efficiencies of the BpK-O₂ cell in (e); the inset shows the pie chart distributions of reversible KO₂ (could be recharged at 2.0 mA/cm², yellow area), ‘loose KO₂’ (accumulated KO₂ that could be recharged only under a lower current density of 0.2 mA/cm², rose red area) and non-rechargeable product (blue area). The percentages are averaged over the 1st-51st, 52nd-102nd and 103rd-153rd cycles, respectively. Reprinted with permission from ref 430. Copyright 2019 Macmillan Publishers Limited.

5.1.2 A Molten-Salt Li-O₂ Battery Based on Li₂O Formation and Decomposition

Li₂O is another tantalizing energy storage material, because two electrons can be stored in a Li₂O molecule, giving rise to the highest energy density, 5.2 kWh/kg (Table 4). Furthermore, Li₂O is more stable than Li₂O₂ and LiO₂, and thus can probably improve the chemical instability issues that have plagued the non-aqueous Li-O₂ battery. Although at room temperature electrochemical formation of Li₂O₂ is thermodynamically favored over Li₂O, the situation is reversed beyond 150°C (Fig. 34a). Nazar and coworkers recently reported that by using an Ni-based cathode, an inorganic LiNO₃/KNO₃ molten salt electrolyte and a Li metal anode at an operating temperature of 150°C (Fig. 34b), a Li-O₂ battery based on Li₂O formation and decomposition could be realized. This battery shows a major discharge plateau at 2.7 V and a charging plateau slightly below 3.0 V, which gradually polarizes towards 3.5 V at the end of charge (Fig. 34c). Li₂O titration experiments on discharge and DEMS measurements on charge suggest that Li₂O formation is a four-electron oxygen reduction reaction and the oxygen recovery efficiency (OER/ORR) is close to 1 (Fig. 34d). As a result, the cell could cycle for 150 times without significant performance decay (at 0.2 mA/cm², 0.5 mAh/cm² per cycle). The authors demonstrated that the nickel cathode is essential to overcoming the kinetic barriers involved in cleaving the O₂ intramolecular bond on discharge, as well as O-O reformation during charge: when a carbon electrode is used under the same conditions, Li₂O₂ is the discharge product. The mechanism of Li₂O formation is proposed as: two-electron Li₂O₂ formation over the Ni catalyst surface, followed by disproportionation of Li₂O₂ to form Li₂O and O₂, and finally solution-mediated Li₂O nucleation and growth (Fig. 34e).
The Li₂O battery system reported by Nazar and coworkers is intriguing and has at least the following implications. First, it shows that Li-O₂ batteries are not intrinsically limited and that with principle-guided design and wise choice of materials, a highly reversible battery reaction approaching theoretical Coulombic efficiency is indeed feasible. Secondly, the four-electron ORR and OER in the Li₂O battery system exhibit a remarkably small voltage hysteresis, ~0.3 V, much lower than the regenerative proton exchange membrane fuel cell system, ~0.7 V. Further investigation is required to provide atomistic insights into the discharge and charge reactions in the system and to account for the origin of the observed low overpotentials. When an inorganic electrolyte is used, little electrolyte decomposition occurs, even in the presence of large charging overpotentials, which reiterates the critical stability issue with organic electrolytes. This work by Nazar et al. highlights the tremendous opportunities for fundamental research to understand the oxygen redox reactions that may lead to novel battery technologies that can potentially rival the current Li-ion battery and other energy storage systems.

5.2 Cycling Based on LiOH Formation and Decomposition?

Another critical challenge facing all Li₂O₂, LiO₂ and Li₂O-based batteries is their sensitivity to H₂O and CO₂ contamination from air, and eventually LiOH and Li₂CO₃ are generally formed to varying degrees. Table 5 summarizes the thermodynamic driving forces of relevant reactions. It is clear that the thermodynamic tendency to form LiOH or Li₂CO₃...
increases from Li$_2$O $<$ Li$_2$O$_2$ $<$ KO$_2$ $<$ NaO$_2$ $<$ LiO$_2$. The issue is particularly severe for Li$_2$CO$_3$ formation, as the driving forces for most compounds are more than -300 kJ/mol; any small contamination of the battery atmosphere by CO$_2$ would induce carbonate formation, resulting in a high overpotential on charging (to remove the carbonate), as observed experimentally. By contrast, the free energy (per Li$_2$CO$_3$ formation) for the conversion of LiOH to Li$_2$CO$_3$ is less than $\frac{1}{2}$ of the other types of active materials. In addition, water is typically the proton source in many LiOH-based battery systems (as introduced later), the battery chemistry is thus highly immune to water contamination. Given its higher resistance to both H$_2$O and CO$_2$ contamination, LiOH can be considered as a more promising alternative energy storage material in a lithium-air battery, especially when simple and effective gas separation membranes are also used in the battery. Rechargeable aqueous Zinc-air batteries based on Zn(OH)$_2$ are good examples to circumvent the CO$_2$ contamination issue, even though there is a small thermodynamic driving force (-21 kJ/mol) to convert Zn(OH)$_2$ to ZnCO$_3$.

Table 5. Thermodynamics of superoxide, peroxide, hydroxide reactions with water and CO$_2$.  

<table>
<thead>
<tr>
<th>Product</th>
<th>Chemical Reactions at Standard Conditions</th>
<th>$\Delta G^\circ_{\text{rxt}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>4LiO$_2$ + 2H$_2$O $\rightarrow$ 4LiOH + 3O$_2$</td>
<td>-274.3</td>
</tr>
<tr>
<td>NaO$_2$</td>
<td>4NaO$_2$ + 2H$_2$O $\rightarrow$ 4NaOH + 3O$_2$</td>
<td>-168.4</td>
</tr>
<tr>
<td>KO$_2$</td>
<td>4KO$_2$ + 2H$_2$O $\rightarrow$ 4KOH + 3O$_2$</td>
<td>-84.4</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>2Li$_2$O + 2H$_2$O $\rightarrow$ 4LiOH + O$_2$</td>
<td>-152</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>Li$_2$O + H$_2$O $\rightarrow$ 2LiOH</td>
<td>-80.1</td>
</tr>
<tr>
<td>LiO$_2$</td>
<td>4LiO$_2$ + 2CO$_2$ $\rightarrow$ 2Li$_2$CO$_3$ + 3O$_2$</td>
<td>-467.7</td>
</tr>
<tr>
<td>NaO$_2$</td>
<td>4NaO$_2$ + 2CO$_2$ $\rightarrow$ 2Na$_2$CO$_3$ + 3O$_2$</td>
<td>-424.6</td>
</tr>
<tr>
<td>KO$_2$</td>
<td>4KO$_2$ + 2CO$_2$ $\rightarrow$ 2K$_2$CO$_3$ + 3O$_2$</td>
<td>-380.4</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>2Li$_2$O + 2CO$_2$ $\rightarrow$ 2Li$_2$CO$_3$ + O$_2$</td>
<td>-345.4</td>
</tr>
<tr>
<td>LiOH</td>
<td>Li$_2$O + CO$_2$ $\rightarrow$ Li$_2$CO$_3$</td>
<td>-176.8</td>
</tr>
<tr>
<td>LiOH</td>
<td>2LiOH + CO$_2$ $\rightarrow$ Li$_2$CO$_3$ + H$_2$O</td>
<td>-96.7</td>
</tr>
</tbody>
</table>

Note: the free energy of Li$_2$O used here is from theoretical calculation (-251.8 kJ/mol), which is in reasonable agreement with the value of -260.5 kJ/mol obtained using a redox potential value of 2.7 V vs. Li$^+/Li$ estimated from cyclic voltammogram experiments (Fig. 3a).

Indeed, in aqueous Li-O$_2$ batteries, LiOH formation and decomposition have been demonstrated as the battery reactions on cycling, as described by reaction (51). In nonaqueous media, LiOH precipitates out of the organic electrolyte as a solid phase, as described by reaction (52). In this case, a specific capacity of 1116.7 mAh/g can be derived and given a standard voltage of 3.32 V, the theoretical specific energy density of 3707.4 Wh/kg is calculated.

$$4e^- + 2H_2O_{(l)} + O_2(g) \leftrightarrow 4OH_{(sol)}$$ \hspace{1cm} \text{(51)}$$

, where $E^\circ$ is equal to 3.4 V at pH=14, versus Li$^+/Li$.

$$4Li^{+}_{(sol)} + 4e^- + 2H_2O_{(l)} + O_2(g) \leftrightarrow 4LiOH_{(s)}$$ \hspace{1cm} \text{(52)}$$

, where $\Delta G^\circ$ is equal to -1281.6 kJ/mol, and $E^\circ$ is equal to 3.32 V, versus Li$^+/Li$.  

92
Thus far, two non-aqueous Li-O$_2$ battery systems have been reported to produce LiOH as a stoichiometric discharge product, as opposed to a byproduct due to organic electrolyte decomposition. One involves the use of metal catalysts and water additives in the battery and the other is a result of synergistic effects due to lithium iodide and water additives in the organic electrolyte. We next discuss in sequence the fundamental understanding and unresolved questions concerning these two systems.

### 5.2.1 Metal-catalyzed LiOH Electrochemistry

Zhou and coworkers first reported the observation that LiOH forms and decomposes over extended cycles in a range of Li-O$_2$ battery systems, including ether-, DMSO-, and ionic liquid-based electrolytes. The essential element in all these systems that enables the LiOH chemistry is the use of Ru/MnO$_2$ or RuO$_2$/MnO$_2$ catalysts and water as an additive in the electrolyte. In one example, where Ru/MnO$_2$/SP and LiClO$_4$/DMSO (containing 120 ppm water) are used as the cathode and electrolyte respectively, Zhou and coworkers observed a superior cycling performance of 200 cycles without any capacity decay (Fig. 35a). The charge voltage is at ~3.2 V and a small voltage gap of around 0.4 V is obtained on cycling. XRD, FTIR (Fig. 35b), SEM results suggest that a mixture of Li$_2$O$_2$ and LiOH is formed on discharging and removed on charging. By chemical titration, the authors derived a stoichiometry of two electrons per reduced O$_2$ on discharging, that is, dominated by the typical Li$_2$O$_2$ formation. On charging, the authors proposed that Li$_2$O$_2$ is first converted to H$_2$O$_2$ in the presence of water, H$_2$O$_2$ being subsequently decomposed by the MnO$_2$ catalyst, which effectively converts Li$_2$O$_2$ to LiOH (reactions (i-ii) in Fig. 35e); at charging voltages, the generated LiOH in the prior steps is concomitantly oxidized by Ru catalyst to evolve O$_2$, via a common four-electron OER (reaction (iii)). Overall, it is claimed to be two-electron per evolved O$_2$ on charging. The feasibility of Ru catalysts decomposing LiOH is further supported by performing linear sweep voltammetry on a LiOH-prefilled Ru/SP cathode in DMSO electrolytes, where an anodic current is observed from 3.27 V and O$_2$ gas is detected by gas chromatography (Fig. 35c). With increasing concentrations of added water in the electrolyte, LiOH formation and decomposition become the dominant battery chemistry, the charging voltage remaining at ~3.2 V (Fig. 35d).

This work reported by Zhou and coworkers inspired several fundamental questions: 1) is LiOH formation a four-electron ORR on discharging?; 2) does LiOH formation involve side reactions as reported for Li$_2$O$_2$ formation?; 3) is O$_2$ indeed evolved on electrochemically charging? and so on. These mechanistic questions remained to be answered. As such, some of the current coauthors subsequently performed a systematic study on a similar Li-O$_2$ battery system.
Grey and coworkers discovered that when there is sufficient water in the DMSO-based electrolyte, a range of metal catalysts can lead to predominant LiOH formation, where Ru catalysts exhibit the best catalytic effects on promoting LiOH formation and decomposition. On discharging, *operando* pressure measurement suggests that the LiOH formation is a stoichiometric four-electron ORR reaction process (Fig. 36a), where the H in LiOH comes predominantly from added water, but O in LiOH originates from both gaseous $\text{O}_2$ and $\text{H}_2\text{O}$ (Fig. 36b,c). Even without MnO$_2$ that was used in earlier work, the Ru catalyst is found adequate to promote the conversion of Li$_2$O$_2$ to LiOH in the presence of water, probably by decomposing the $\text{H}_2\text{O}_2$ intermediate. This observation of four-electron ORR highlights the high catalytic efficiency of Ru in promoting the decomposition of soluble peroxide species ($\text{H}_2\text{O}_2$, LiOOH, $\text{HO}_2^-$), as illustrated in Figure 36e. When the added water is insufficient, the discharge is first dominated by four-electron ORR to form LiOH until all water is consumed, and then Li$_2$O$_2$ formation takes over. On charging, a striking observation was the decomposition of LiOH at voltages as low as 3.1 V, where it is thoroughly and quantitatively removed (Fig. 36d) after a full charge with high Coulombic efficiencies (>95%). The battery could typically cycle for more than 100 cycles without capacity fade, in agreement with the work by Zhou and coworkers. Nevertheless, we did not observe O$_2$ evolution on charging in either pressure (Fig. 36a) or DEMS measurements. The LiOH decomposition is found to be coupled with DMSO oxidation to form DMSO$_2$ (Fig. 36e).
36e), the oxygen being effectively trapped in the electrolyte.\textsuperscript{297} DMSO\textsubscript{2} is a soluble species in the DMSO electrolyte, as also widely observed as the decomposition product in Li\textsubscript{2}O\textsubscript{2}-based Li-O\textsubscript{2} cells,\textsuperscript{87, 88, 91, 132, 205} and thus it does not cause rapid cell failure (by surface passivation) as observed for example in the case of Li\textsubscript{2}CO\textsubscript{3} formation. As a result, the cells can have extended cycles even though the O\textsubscript{2} recovery ratio (OER/ORR) is extremely low.\textsuperscript{297}

\textbf{Fig. 36} Ru-catalyzed LiOH formation and decomposition in a water-added LiTFSI/DMSO electrolyte. (a): Electrochemical profile and pressure responses during discharge and charge of a Li-O\textsubscript{2} cell using Ru/SP cathodes. (b) \textsuperscript{1}H magic angle spinning (MAS) solid state NMR measurements on Li-O\textsubscript{2} cells discharged using D\textsubscript{2}O-DMSO or H\textsubscript{2}O-d6 DMSO electrolytes. (c) \textsuperscript{17}O MAS solid state NMR measurements on Li-O\textsubscript{2} cells discharged using \textsuperscript{17}O\textsubscript{2} or \textsuperscript{17}O enriched H\textsubscript{2}O in the electrolyte, respectively. (d) Quantitative \textsuperscript{1}H MAS solid state NMR measurements of cathode cycled to different states of charge, to evaluate how much LiOH is removed.\textsuperscript{297} (e): Schematic illustration showing the mechanisms for cell discharge and charge processes. Reprinted with permission from ref 297. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

LiOH decomposition without O\textsubscript{2} evolution in nominally dry electrolyte has been previously reported in batteries using LiOH-prefilled carbon electrodes by Gasteiger and coworkers,\textsuperscript{242} where concomitant electrolyte decomposition was observed on charging, similar to our observation for the Ru system.\textsuperscript{297} A major difference, though, is that the charging voltage in their work is above 4.0 V (as opposed to 3.1 V in ours), even in the presence of a Pt catalyst.\textsuperscript{242} A theoretical study by Ling and coworkers\textsuperscript{453} suggests that the largest energy barrier to decompose LiOH is connected to the first delithiation step (where high voltages > 4.67 V is needed) and that once a Li\textsuperscript{+} deficient surface is generated, the subsequent steps are thermodynamically downhill. The difficulty in Li\textsuperscript{+} extraction is suggested to correlate with the inertness of OH\textsuperscript{−} to participate in a redox reaction and soluble redox mediators may be useful to facilitate LiOH decomposition.\textsuperscript{453} From an experimental point of view, however, LiOH ionization /dissolution can be readily achieved by adding water to the non-aqueous electrolyte. Grey and coworkers have shown that in the presence of water solvation, the decomposition voltage of LiOH in non-aqueous media is quite sensitive to the type of catalyst: LiOH decomposition starts at 3.1, 3.5, 4.0 and above 4.0 V on Ru, Ir, Pd and Pt surfaces,
respectively; this observation indicates that the initial electrochemical \( \text{Li}^+ \) delithiation of \( \text{LiOH} \) cannot be the only dominant barrier, as implied by the theoretical work; the subsequent OH oxidation steps also involve barriers that dictate the charging overpotential. On the other hand, the decomposition of electrolyte observed is likely to be initiated by certain reaction intermediates (e.g., hydroxyl radicals) generated during OH oxidation on catalyst surfaces. The typical strategy of tuning catalyst surface-oxygen binding energy to modulate and circumvent the formation of specific reaction intermediates may help promote OER on charging. Further systematic studies are required to understand the \( \text{LiOH} \) decomposition reaction in a non-aqueous Li-O\(_2\) battery.

Despite of the absence of oxygen release, the Ru-catalyzed \( \text{LiOH} \) electrochemistry actually represents a highly rechargeable and energy-efficient (voltage gap=0.25 V) battery. During discharge, electricity is generated via \( \text{LiOH} \) formation that involves little side reactions compared to the \( \text{Li}_2\text{O}_2 \) formation; the charging process, on the other hand, can be seen as electrochemical DMSO\(_2\) production. DMSO\(_2\) itself is a useful industrial high-temperature solvent for inorganic and organic substances, and it also has several medical applications. If one couples the lithium-oxygen battery with an electrolyte flow system that circulates the solvent and can afford solvent separation, a much longer battery cycle life and useful chemical production can be achieved. The same idea may be applied to other useful solvent conversion reactions.

### 5.2.2 Synergistic Effect of \( \text{LiI} \) and \( \text{H}_2\text{O} \) on Modulating the \( \text{O}_2 \) Electrochemistry

The other battery system that promotes \( \text{LiOH} \) formation involves the use of both \( \text{LiI} \) and \( \text{H}_2\text{O} \) as additives in an organic electrolyte. \(^{130}\) \( \text{LiI} \) is a widely studied redox mediator that can also help decompose \( \text{Li}_2\text{O}_2 \) on charging. \(^{277, 388, 455}\) Its combined use with water can also be applied to modulate the \( \text{O}_2 \) electrochemistry on discharge.

Some of us \(^{130}\) first reported that \( \text{LiI} \) and \( \text{H}_2\text{O} \) together lead to \( \text{LiOH} \) formation in ether-based electrolytes, and proposed a stoichiometric four-electron oxygen reduction reaction (52), for the battery discharge; this was later confirmed by other groups using \textit{operando} pressure measurements. \(^{448}\) Using solid state NMR aided by isotopic labeling, Grey and coworkers showed that H of \( \text{LiOH} \) is predominantly from water rather than the electrolyte \(^{130}\) and that O can come from either \( \text{H}_2\text{O} \) or \( \text{O}_2 \) gas, \(^{342}\) which is the same as observed for Ru-catalyzed \( \text{LiOH} \) formation. \(^{297}\) This stoichiometry of four electrons per reduced \( \text{O}_2 \) was verified by \textit{operando} pressure tests. \(^{342, 448}\) Of note, the authors found that the chemical purity of the ether solvent has a critical impact on the \( \text{LiI} \)-promoted chemistry: \(^{342}\) without prior distillation of the nominally anhydrous solvent to remove the impurities, \( \text{LiOH} \) formation together with Li formate and acetates, have been observed even in the absence of water, \(^{347}\) which likely results from other proton donor species rather than decomposition of the ether electrolyte.

Figure 37a(i-iii) show a series of pressure measurements of cells with increasing water contents in the electrolyte: \(^{342}\) when the added water is insufficient (Fig. 37a(i)), the cell discharge initially shows four-electron \textit{ORR} to form \( \text{LiOH} \), followed by two-electron peroxide formation, as indicated by the slopes of the pressure curve; at intermediate water
contents (Fig. 37a(ii)), LiOH formation dominates the entire discharge; interestingly when water content increases further (Fig. 37a(iii)), the pressure slope \(e/O_2\) lies between 2 and 4, indicating that \(\text{Li}_2\text{O}_2\) formation is reactivated. The corresponding XRD patterns (Fig. 37b) also capture the transition from \(\text{Li}_2\text{O}_2\), to LiOH, and finally to a mixture of \(\text{Li}_2\text{O}_2/\text{LiOH}\), when the water content gradually rises.

![Fig. 37 Modulation of the Li-O2 electrochemistry by the synergistic effect of LiI and H2O in a LiTFSI/DME electrolyte. (a): pressure measurements performed on Li-O2 cells using the DME electrolyte with increasing amount of added water from 0.2% (i), 1% (ii) to 5% (iii); where LiOH formation is dependent on added water quantities. (b): XRD measurements on discharged electrodes using LiTFSI/DME electrolytes with 0.2%, 0.5%, 1%, 2% and 5% added water. (c): molecular dynamic simulations revealing that clustering of water-LiI molecules occurs at high water concentrations, which can retard the LiI catalyzed LiOH formation and as a result, \(\text{Li}_2\text{O}_2\) formation reactivates. Reprinted with permission from ref 342. Copyright 2019 ACS.](image-url)

Later on, through in situ Raman and FTIR measurements, Zhou, Shao-Horn and coworkers have identified reaction intermediates such as HO\(_2\), LiOOH and \(\text{H}_2\text{O}_2\) during discharge. Their formation is proposed to occur via water induced superoxide disproportionation in non-aqueous media (reactions (i-ii) in Figure 38), consistent with previous studies. Iodide was suggested to play a key role in the catalytic decomposition of \(\text{H}_2\text{O}_2\) (or HO\(_2\), LiOOH), as verified by a wide range of chemical assay and analysis: at low water contents, iodide reduces \(\text{H}_2\text{O}_2\) to form LiOH, and the resulting \(\text{I}_3^-\) is concomitantly reduced at discharge potentials (reactions (iii-iv)); at high water contents, iodide decomposes \(\text{H}_2\text{O}_2\) into \(\text{H}_2\text{O}\) and \(\text{O}_2\) (reactions (v-vi)). Both pathways give an overall nominal four-electron ORR on discharging. However, at high water contents, the efficacy of iodide catalysis on \(\text{H}_2\text{O}_2\) decomposition is retarded due to the formation of large LiI-\(\text{H}_2\text{O}\) clusters, where iodide anions are highly coordinated and surrounded by a large number of water molecules, as revealed by molecular dynamics simulations (Fig. 37c). Because the iodide anions are deeply embedded inside the water clusters, the accessibility for \(\text{H}_2\text{O}_2\) to interact with iodide is considerably reduced. The remaining \(\text{H}_2\text{O}_2\) molecules will eventually
be converted to \( \text{Li}_2\text{O}_2 \), as if in the case without LiI. This is suggested to be the origin of the observed mixed \( \text{Li}_2\text{O}_2 \) and LiOH formation at higher water contents.\(^{342}\)

![Synergistic Effect of LiI and H2O on the ORR](image)

Fig. 38 A summary of synergistic effect of H\(_2\)O and LiI on modulating oxygen reduction reaction in a Li-O\(_2\) battery.\(^{342}\) Reprinted with permission from ref 342. Copyright 2019 ACS.

On charging, LiOH was reported to be removed at two distinct voltages in a DME electrolyte, at around 3.0 V\(^{130}\) and 3.5 V,\(^{448}\) which correspond to processes mediated by I\(_3^-\) and I\(_2\), respectively (reactions (53-54)). Given that evolved O\(_2\) signals was detected after charging a LiOH-prefilled cell in Ar, Grey and coworkers initially proposed that LiOH can be decomposed by I\(_3^-\) to evolve O\(_2\) on charging (reaction (55)) in a DME electrolyte,\(^{130}\) although alternatively LiOH removal pathways are also possible via LiIO\(_3\) formation in the presence of significant water concentrations (reaction (56)), as indicated by UV-vis measurements.\(^{456}\)\(^{457}\) LiOH formation and decomposition mediated by LiI/LiI\(_3\) couple was later supported by \textit{in situ} XRD in the same DME-electrolyte (Fig. 39a).\(^{449}\) Nonetheless, using pressure and DEMS measurements, others suggest that LiOH cannot be decomposed to evolve O\(_2\) at 3.0 V in ether-based electrolytes (DME and TEGDME),\(^{347}\)\(^{448}\) and that any O\(_2\) signal should be due to decomposition of some coexisting Li\(_2\)O\(_2\). On charging to 3.5 V, LiOH removal was observed to occur via LiIO\(_3\) formation (reaction (57)),\(^{448}\)\(^{452}\) but still no O\(_2\) evolution was observed. Shao-horn and coworkers\(^{452}\) further argued that the Gutmann acceptor number (AN) of an electrolyte solvent has a large impact on the oxidizing power of LiI mediator: stronger solvation of iodide in DMA, DMSO and Me-Im raises the oxidation potential of I\(_3^-\) so that it can oxidize LiOH (reaction (56)), whereas in weaker solvents (TEGDME and DME), the more oxidizing I\(_2\) is needed for the oxidation reactions (reaction (57)).

\[
6\text{I}^-\text{(sol)} \leftrightarrow 2\text{I}_3^-\text{(sol)} + 4e^- \quad (53)
\]

\[
2\text{I}_3^-\text{(sol)} \leftrightarrow 3\text{I}_2\text{(sol)} + 2e^- \quad (54)
\]

\[
4\text{LiOH}\text{(s)} + 2\text{I}_3^-\text{(sol)} \leftrightarrow 4\text{Li}^+\text{(sol)} + 6\text{I}^-\text{(sol)} + 2\text{H}_2\text{O}\text{(l)} + \text{O}_2\text{(g)} \quad (55)
\]

\[
6\text{LiOH}\text{(s)} + 3\text{I}_3^-\text{(sol)} \leftrightarrow 6\text{Li}^+\text{(sol)} + 1\text{O}_3^-\text{(sol)} + 8\text{I}^-\text{(sol)} + 3\text{H}_2\text{O}\text{(l)} \quad (56)
\]

, which is under alkaline conditions.

\[
6\text{LiOH}\text{(s)} + 3\text{I}_2\text{(sol)} \leftrightarrow \text{LiI}_3\text{(s)} + 5\text{LiI}\text{(sol)} + 3\text{H}_2\text{O}\text{(l)} \quad (57)
\]
Fig. 39 LiI mediated LiOH decomposition in organic electrolytes during a cell charge. (a): Operando X-ray diffraction measurements performed in a LiI (50 mM)-added 0.5 M LiTFSI/DME electrolyte with 4000 ppm water, which shows LiOH formation and decomposition (between 3-4 V) for the initial 3 cycles.\(^{49}\) (b): operando pressure tests performed on cells using LiI/LiTFSI/DME electrolytes and XC-72 carbon electrodes, which shows that when Li$_2$O (2e$^-$/O$_2$) forms in the prior discharge, there is O$_2$ evolution on charging (i), whereas when LiOH forms on the prior discharge, no O$_2$ evolution is observed on the following charge (ii). (c): A scheme illustrating a potential mechanism for the observed electrochemistry in a DME-based electrolyte with LiI and water additives: the lower charging plateau at ~3.0 V corresponds to either LiI$_3$/LiI mediated Li$_2$O$_2$ decomposition or LiI$_3$/LiI shuttling, and the higher charging plateau at ~3.5 V is related to LiOH oxidation by I$_2$ to form LiO$_3$ or alternatively the I$_2$/LiI$_3$ shuttling process.\(^{48}\) (a) Reprinted with permission from ref 449. Copyright 2017 ACS and (b,c) from ref 448. Copyright 2016 ACS.

Another route that can play a role in LiI$_3$-mediated LiOH decomposition is via the actions of H$_2$O$_2$.\(^{342, 451, 458}\) At high water contents, where Li$_2$O$_2$ and LiOH are both the discharge products,\(^{342, 346}\) the coexistence of H$_2$O$_2$ with LiOH is certainly possible. Zhou and coworkers\(^{458}\) introduced H$_2$O$_2$ to a LiOH-prefilled carbon electrode, and they observed quantitative LiOH removal on charging at ~3.4 V, that is, an e$^-$/LiOH molar ratio of 1, as well as concomitant O$_2$ evolution (Fig. 40a-c). Their observation\(^{458}\) appears to be consistent with the stoichiometry in reaction (52). Further analysis by Raman aided with isotopic labeling shows that H$_2$O$_2$ reacts with LiOH to form Li$_2$O$_2$ and H$_2$O (Fig. 40d),\(^{342}\) where the oxygen in Li$_2$O$_2$ originates from H$_2$O$_2$ and the oxygen in LiOH likely ends up in H$_2$O, as described by reaction (i) in Figure 40e. When LiOH is added to a LiI$_3$ electrolyte containing H$_2$O$_2$, O$_2$ is indeed observed\(^{342}\) similar to the observation by Zhou and coworkers.\(^{458}\) Nonetheless, the generated O$_2$ is a result of peroxide decomposition by either a chemical reaction with LiI$_3$ (reactions (i-ii) in Figure 40e) or direct electrochemical oxidation on the carbon electrode (reactions (i-iii) in Figure 40e), both giving an e$^-$/LiOH molar ratio of 1. The LiOH/O$_2$ and LiOH/H$_2$O molar ratios (reaction (iv), Fig. 40e), however, are half of those in a standard
reaction of electrochemical LiOH decomposition (reaction (52)). Therefore, this observation does not provide direct evidence to support four-electron LiOH decomposition via O₂ evolution in a non-aqueous electrolyte.

Fig. 40 H₂O₂ assisted LiOH removal during a charging process in nonaqueous Li-O₂ batteries. (a) Electrochemical charging profile of a Li-O₂ cell using LiOH-prefilled Ketjen Black cathode and TEGDME-based electrolytes with H₂O and H₂O₂ additives. (b): the corresponding DEMS measurement of (a), showing O₂ evolution on charging. (c): Chemical LiOH titration on charging for a similar cell described in (a), supporting a LiOH/e⁻ molar ratio of 1.45⁸ (d): Raman measurements on the reaction between LiOH and H₂O₂, revealing that LiOH is progressively converted by H₂O₂ to LiOH monohydrate, then LiOOH and finally Li₂O₂, where the O in Li₂O₂ originates H₂O₂ and O in LiOH likely ends in the water (described in reaction (i) in (e)). ₃₄₂ (e): Schematic illustration of H₂O₂ assisted electrochemical removal of LiOH in organic electrolytes: H₂O₂ helps convert LiOH to Li₂O₂ and H₂O; direct electrochemical charging or mediated charging by LiI₃ decomposes Li₂O₂, giving an overall reaction described by (iv) in (e). (a–c) Reprinted with permission from ref 4₅₈. Copyright 2017 Macmillan Publishers Limited and (d) from ref 3₄₂. Copyright 2019 ACS.

Thus far, the very central question concerning the LiOH chemistry in non-aqueous media is whether LiOH can be decomposed via the O₂ evolution route (reaction (52)). Theoretical consideration suggests that this is feasible at 3.32 V. Given that water is not at its standard state in a Li⁺ organic electrolyte (as revealed by solution NMR and FTIR results ₃₄₂, ₄₅₀), derivation from this standard voltage value will occur: a simple calculation estimates that at 100 ppm water, the equilibrium voltage for LiOH decomposition (reaction (52)) can be as low as 3.2 V. The standard voltage/potential, however, is not the only decisive factor to promote O₂ evolution; high reaction overpotentials would imply much higher charging voltages than 3.4 V, which would lead to other competing parasitic reactions associated with the electrolyte ²⁴₂, ²⁹⁷ or redox mediator ⁴₄₈, ⁴₅₂ during LiOH decomposition. How various catalysts can be used to modulate the binding energies of reaction intermediates, i.e., the reaction coordinate, and potentially help avoid the parasitic reactions during LiOH decomposition warrant further systematic studies. Despite that some early work reports the detection of O₂ evolution when charging LiOH by Ru catalysts ⁴₃₂ or by reacting with LiI₃/I₂ ¹₃₀, ³₄₆ operando and quantitative gas analysis aided with isotopic labeling awaits to be
demonstrated. Recent work (currently under review) by some of us shows that LiOH decomposition via four-electron OER is indeed feasible.

6. Summary and Outlook

Significant progress has been made in the research field of lithium-air batteries. We have now understood that the discharge mechanism of Li$_2$O$_2$ formation, i.e., surface versus solution processes, of a non-aqueous Li-O$_2$ battery is largely dictated by the solvating properties of the electrolyte, which can be tuned independently by either the salt or the solvent. By judiciously choosing the combination of salt and solvent, both high discharge capacity and good chemical stability of the electrolyte can be achieved. With the aid of a RM that chemically reduces O$_2$, the power density of the battery can be enhanced even further. The mechanism of battery recharge, namely, Li$_2$O$_2$ decomposition, is also dependent upon the solvating properties of electrolytes, and analysis suggests that the first delithiation step of Li$_2$O$_2$ to form Li$^+$-deficient Li$_{2-x}$O$_2$ determines the largest charge overpotential. Strategies that can potentially facilitate this specific step, e.g., using solvent/additives that can readily dissolve Li$_2$O$_2$, should be explored.

Nevertheless, to move towards a practical lithium-air battery, the charge voltage should be brought well below 3.5 V; this is because carbon cathode corrosion, singlet oxygen generation and its associated electrolyte decomposition are all sensitive to higher voltages. Solid catalysts have been widely explored to reduce the charging overpotential. But a common issue is that although the onset charge voltage is low, they all gradually polarize toward 4.0 V or higher with deeper states of charging, which is usually connected to parasitic product accumulating at the reaction interfaces. Electrocatalysts that readily decompose LiOH and Li$_2$CO$_3$ and electrolytes with high solubilities of these byproducts can help maintain a low charge voltage and thus improve the rechargeability of the battery.

The nature of the species that are the dominant source or trigger of the side reactions involved in the lithium-oxygen electrochemistry remains an open question and worthy of further investigation. Previously, reaction intermediates, such as LiO$_2$, Li$_{2-x}$O$_2$, were considered to be the main cause. Recent evidence however shows that singlet oxygen plays a major role. The example of a KO$_2$-based battery that can sustain thousands of cycles indicates that parasitic reactions originating from the chemical reactivity of superoxide (in solid form or as ions in solution) do not dominate the chemistry of K-O$_2$ batteries using ethereal electrolytes. This raises the question as to whether superoxide is the main culprit for the parasitic reactions observed in Li-O$_2$ batteries. Further fundamental studies are required to separate superoxide-from singlet-oxygen induced parasitic reactions in Li-O$_2$ batteries. Circumventing the formation of singlet oxygen (e.g., by minimizing the overpotentials) or by quenching it immediately as it forms are possible ways of mitigating the issues due to singlet oxygen generation and for potentially untangling the two degradation pathways.

In the regard of lowering the charging voltage, the use of a RM seems the most promising, as its charging profile is typically flat and the RM has the ability to decompose products formed
remotely from the cathode surface (as formed in a solution mediated discharge), thereby circumventing the issues caused by the low charge transport rate through discharge products. A variety of RMs have been explored in recent years, but the underlying principles leading to efficient mediation are yet to be established. A key step for the development of RMs for Li-O2 batteries will be to perform systematic studies comparing different mediators under the same conditions. The ultimate goal is to establish an understanding of the key properties affecting the mediator activity and to determine how different experimental conditions alter their activity. In light of newly discovered role of singlet oxygen, a few common organic RMs are found to be unstable in the presence of $^1$O$_2$. On the other hand, inorganic RMs, such as LiI and LiBr, promotes Li$_2$O$_2$ decomposition with O$_2$ recovery efficiencies of up to 92% and 98% respectively, which are among the highest reported values so far. Whether these inorganic RMs are more stable against singlet oxygen, and whether mediated product decomposition still involves singlet oxygen generation are open questions and warrant further studies. To develop Li-O$_2$ batteries with suppressed degradation, high capacity and reversibility, the combination of singlet oxygen quenchers and RMs as electrolyte additives currently appears as an interesting approach, and additional complementary approaches to minimize voltage gaps for the ORR and OER as much as possible are always beneficial.

The effect of other components (H$_2$O, CO$_2$, N$_2$) in the air on Li-O$_2$ electrochemistry has been investigated. At the cathode, significant H$_2$O and CO$_2$ contamination leads to conversion of Li$_2$O$_2$ to LiOH and Li$_2$CO$_3$, considerably polarizing the battery on recharging. Although Li$_2$CO$_3$ can be removed at 3.6-4.0 V (and at lower potentials when certain catalysts are used) on charging, recent evidence suggests that no oxygen is evolved in the process making the charge irreversible, and that this lack of oxygen is associated with side reactions due to singlet oxygen generation. At current stage, Li$_2$CO$_3$ formation should therefore be avoided in a Li-O$_2$ battery. On the other hand, the effect of O$_2$, H$_2$O, N$_2$ and CO$_2$ on the Li metal anode stability has been less systematically investigated. In several cases, opposing opinions, e.g., in the effect of O$_2$ crossover to Li anode on the Li cycling stability, exist. These studies underscore the need for fundamental understandings of the interaction between O$_2$, CO$_2$, N$_2$ and Li metal anode surface in different electrolytes/salts, and establishment of the role of SEI in protecting the metal anode.

Most Li-O$_2$ cell studies focus on elucidating the mechanism of the reactions in the first few cycles. While these fundamental studies are essential, with advances of lithium-air batteries further work should also be dedicated to study longer cycles. The amounts of electrolyte then becomes particularly important in longer cycling studies, since depletion of the electrolyte via, for example, reaction with the lithium-air batteries can markedly affect battery performance. To date, all Li-O$_2$ cell studies have been conducted with a large excess of electrolyte. Gallagher and coworkers considered an electrolyte loading of 25% of the Li$_2$O$_2$ electrode volume for their calculations, which for a 100 μm electrode would imply a volume of electrolyte per geometric electrode area of 2.5 μL cm$^{-2}$ (5 μL cm$^{-2}$ for a 200 μm electrode). Decreasing the electrolyte amount not only brings new challenges from a cell assembly perspective, it also implies that the growth of Li$_2$O$_2$ during discharge would be much more restricted in volume, thus making the achievement of high capacities more challenging. The implementation of
low electrolyte loadings also requires a realistic protection of the lithium metal anode with a suitable lithium protective membrane. These longer term studies should also be conducted with a realistic excess of capacity of the lithium anode (Gallagher and coworkers considered a 50% excess capacity) which again is an area that has not been addressed in Li-O₂ cell studies.

Of note, many groups have started to explore alternative electrochemistries for a Li-O₂ battery, such as those based on superoxide, oxide and hydroxide. Although LiO₂ and NaO₂-based cells exhibit lower overpotentials during cycling, they face insufficient chemical stability issues, which induce parasitic reactions. KO₂-based cells, however, exhibit much better reversibility and chemical stability. When coupled with a K⁺ source from an organic anode, the cell can be cycled for up to 3000 times, with an unprecedentedly high O₂ recovery efficiency (99.8%); this finding challenges the consensus that superoxide anion is a strong base and nucleophile causing significant electrolyte degradation over time and thus is not suitable as a basis for a long-lived battery. The origin of this long-term stability of KO₂ in an organic solvent compared to its counterpart in Li- and Na-O₂ batteries warrants further investigation, which may in turn aid the development of other alkali-oxygen batteries. A higher temperature molten-salt Li-O₂ battery based on Li₂O formation and decomposition is demonstrated via nominal four-electron ORR and OER. The cell cycles with an outstanding energy efficiency for 150 times without evident capacity decay. Further investigation is required to provide atomistic insights into the discharge and charge reactions in the system and to account for the origin of the observed low overpotentials. Li-O₂ cells based on LiOH formation and decomposition are also demonstrated, where water is the proton source participating in the nominal four-electron ORR. Thermodynamic analysis shows that LiOH is more resistant to H₂O and CO₂ contamination and thus, more promising to help realize an open system and maintain the high energy density of lithium-air batteries. All these new types of battery chemistry clearly highlight the tremendous opportunities for research to understand and modulate the versatile O₂ electrochemistry, which may lead to novel battery designs outperforming the more established Li-O₂ or Li-ion battery chemistry.

Acknowledgments

Tao Liu thanks Schlumberger Fellowship from Darwin College, the National Natural Science Foundation of China (Grant No. 21802102), Recruitment Program of Global Experts and Tongji University start-up grant, Science and Technology Commission of Shanghai Municipality (19DZ2271500) for funding. Nuria Garcia-Araez thanks EPSRC for the award of an early-career fellowship (EP/N024303/1). Clare P. Grey thanks the EPSRC for support via the LIBATT grant (EP/M009521/1).

References


(20) Blorton, K. F.; Sammells, A. F. Metal/air batteries: their status and potential — a review. J. Power Sources. 1979, 4, 263-279.


(38) Yu, Q.; Ye, S. In situ study of oxygen reduction in dimethyl sulfoxide (DMSO) solution: a fundamental study for development of the lithium-oxygen battery. J. Phys. Chem. C. 2015, 119, 12236-12250.


(111) Kang, S.; Mo, Y.; Ong, S. P.; Ceder, G. A facile mechanism for recharging Li$_2$O$_2$ in Li-O$_2$ batteries. *Chem. Mater.* 2013, 25, 3328-3336.


Assary, R. S.; Lau, K. C.; Amine, K.; Sun, Y.-K.; Curtiss, L. A. Interactions of dimethoxy ethane with Li$_2$O$_2$ clusters and likely decomposition mechanisms for Li$_2$O$_2$ batteries. *J. Phys. Chem. C* 2013, 117, 8041-8049.


112


197) Xie, J.; Dong, Q.; Madden, I.; Yao, X.; Cheng, Q.; Dornath, P.; Fan, W.; Wang, D. Achieving low overpotential Li2O2 battery operations by Li2O2 decomposition through one-electron processes. *Nano Lett.* **2015**, *15*, 8371-8376.


(457) Viswanathan, V.; Pande, V.; Abraham, K. M.; Luntz, A. C.; McCloskey, B. D.; Addison, D. Comment on "Cycling Li-O₂ batteries via LiOH formation and decomposition". Science. 2016, 352, 667.

Bios:

Prof. Tao Liu obtained his Bachelor’s degree in Beijing University of Aeronautics and Astronautics in 2008. He received his PhD degree in 2013 in the field of Surface Science under the supervision of Profs. Sir David A. King and Stephen J. Jenkins at the University of Cambridge. Then, he worked as a postdoctoral researcher on the study of non-aqueous lithium-air batteries with Prof. Clare P. Grey in Cambridge, UK. He was elected as the Schlumberger Research Fellow in 2016, at Darwin College in Cambridge, and appointed a professorship of chemistry at Tongji University, Shanghai, in 2018. His current research interests include electrocatalysis and batteries, and development of *in situ* spectroscopy/spectrometry techniques to study energy conversion and storage devices.

Dr. Nuria Garcia-Araez obtained her PhD in 2007 in the field of single-crystal electrochemistry under the supervision of Profs. Juan Feliu and Victor Climent at the University of Alicante, in collaboration with Prof. Jacek Lipkowski (University of Guelph). Then, she worked as postdoctoral researcher on the study of water-metal interaction with Profs. Marc Koper and Huib Bakker (The Netherlands), and as senior scientist on battery research with Prof. Petr Novak (Paul Scherrer Institute). In 2012, she was appointed lecturer in electrochemistry at the University of Southampton. Her current research focuses on the rational development of rechargeable metal-oxygen/sulfur/ion batteries.

Dr. J. Padmanabhan Vivek is a research fellow in Dr. Nuria Garcia-Araez’s group at the University of Southampton. He received his PhD in chemistry from the University of Saskatchewan, Canada, for the work carried out in the area of interfacial electrochemistry under the supervision of Prof. Ian J. Burgess. In his first postdoctoral position, at the Technical University of Munich, he explored titania based anode materials for lithium-ion batteries. Then he worked as a postdoctoral research associate at the Stephenson Institute for Renewable Energy (University of Liverpool), with Prof. Laurence J. Hardwick in collaboration with Prof. Richard J. Nichols, where he employed *in situ* surface enhanced infrared spectroscopy to investigate interfacial processes relevant to metal-oxygen batteries. His current research focuses on *in situ* and operando methodologies to interrogate the role of redox mediators in lithium-oxygen batteries.

Jiang Lei received his B.Eng. degree from the Hefei University of Technology in 2019. He worked as a project student with Dr. Ling Qin on the subject of metal-organic framework for photodegradation of dyes. He then joined the group of Professor Tao Liu at the Tongji university for M.Sc. studies. His research interest is non-aqueous lithium-oxygen batteries.

Dr. Evan Wenbo Zhao received his Bachelor’s degree in 2012 at the Nanyang Technological University. He obtained his PhD in 2017 under the supervision of Prof. Clifford Russell Bowers at the University of Florida, where his research focused on developing parahydrogen-enhanced nuclear magnetic resonance spectroscopy. He is currently a postdoctoral research associate working with Prof. Clare P. Grey at the
University of Cambridge, focusing on the fundamental understanding of redox processes in flow and Li-air batteries, via in situ magnetic resonance (NMR and EPR) and optical spectroscopy.

Professor Clare P. Grey is the Royal Society Research Professor of Chemistry at the University of Cambridge and a Fellow of Pembroke College Cambridge. She received a BA and D.Phil. (1991) in Chemistry from the University of Oxford. After postdoctoral fellowships in The Netherlands and at DuPont CR&D in Wilmington, DE, she joined the faculty at Stony Brook University (SBU) as an Assistant (1994), Associate (1997) and then Full Professor (2001 to 2015). She moved to Cambridge in 2009, maintaining an adjunct position at SBU. She was director (2009 to 2010) and associate director (2011 to 2014) of the Northeastern Chemical Energy Storage Center, a DOE Energy Frontier Research Center. Recent honors/awards include the Research Award from the International Battery Association (2013), the Royal Society Davy Award (2014), the Arvedson-Schlenk-Preis from the German Chemical Society (2015), the Société Chimique de France, French-British Prize (2017), the International Solid State Ionics Galvani-Nernst-Wagner Mid-Career Award (2017) and Royal Society of Chemistry John B. Goodenough Award (2019). She is a Fellow of the Royal Society and in 2017 has been elected as a Foreign member of the American Academy of Arts and Science and Fellow of the Electrochemical Society. Her current research interests include the use of solid state NMR and diffraction-based methods to determine structure-function relationships in materials for energy storage (batteries and supercapacitors), conversion (fuel cells) and carbon capture.