


Critical aspects in the development of lithium–air batteries

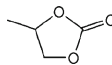
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Abstract Intensive research has been done on lithium–air batteries, especially in the last few years. Due to their very high theoretical specific energy, lithium–air batteries are one of the most promising candidates to power future electric vehicles. However, this new technology is in a very early stage of development, and several challenges must be overcome before there will be a commercially viable product. This review describes the most important critical aspects in the development of lithium–air batteries: the electrocatalysis of the oxygen electrode reactions, the degradation of the electrolyte and the oxygen electrode components, the structure of the oxygen electrode, and the passivation of the oxygen electrode during the discharge of the battery. Recent works in these areas are critically reviewed, and suitable research strategies to address these issues are discussed.

Abbreviations

DEMS	Differential electrochemical mass spectrometry
DME	1,2-Dimethoxyethane: $\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_3$
DMSO	Dimethyl sulfoxide: $(\text{CH}_3)_2\text{SO}$
DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone: 
$\text{EtV}^{2+}/\text{EtV}^+$	Ethyl viologen redox couple
FTIR	Fourier transform infrared spectroscopy

GC	Glassy carbon
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide: $\text{LiN}(\text{SO}_2\text{CF}_3)_2$
NMR	Nuclear magnetic resonance
ORR	O_2 reduction reaction
OER	O_2 evolution reaction
PC	Propylene carbonate: 
PFPBO	Pentafluorophenylboron oxalate
PVdF	Poly(vinylidene difluoride): $-(\text{CH}_2\text{-CF}_2)_n-$
SEI	Solid electrolyte interphase
Tetraglyme (also known as TEGDME)	Tetraethylene glycol dimethyl ether: $\text{CH}_3\text{-O-}[\text{CH}_2\text{-CH}_2\text{-O-}]_4\text{-CH}_3$
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
TPFPB	Tris(pentafluorophenyl)borane
Triglyme	Tri(ethylene glycol) dimethyl ether: $\text{CH}_3\text{-O-}[\text{CH}_2\text{-CH}_2\text{-O-}]_3\text{-CH}_3$
XANES	X-ray adsorption near edge structure
XRD	X-ray diffraction

Introduction

Alternative energy technologies need to be developed in order to decrease our dependency on oil, not only because its consumption generates CO_2 and other pollutants but also because its resources are limited and its price can only increase in the future [1]. The majority of oil is used for automobile and light truck applications, and therefore, the development of longer driving range electric vehicles is imperative. Lithium–air batteries are among the most promising candidates to power future electric vehicles since they are believed to offer potentially a gravimetric energy density similar to gasoline [2]. Because of its anticipated low

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weight, a lithium–air battery could also become a battery of choice for portable devices. For these reasons, the interest in lithium–air batteries has grown sharply, especially during the last few years. However, lithium–air batteries are still in a very early stage of development (the first reported demonstration of a non-aqueous lithium–air cell is from 1996 [3]), and many issues must be solved before they become commercially viable. The past research has been very fruitful in identifying the main weaknesses of lithium–air batteries and developing strategies for further steps. In this review, we will critically describe the most important contributions in this field with special focus on the most recent work.

A number of review articles have been published in the field of lithium–air batteries [4–17]. Among them, the exhaustive critical review of Christensen et al. [4] deserves special mention. However, since the field of lithium–air batteries is developing so fast, some of the most recent works have not been deeply discussed. The present article provides an up-to-date critical review focused on the progress made in understanding the main issues of lithium–air batteries. This review article is organized as follows: The next section describes the “Principle of operation and energy density of lithium–air batteries.” (We recommend skipping this section to readers familiar with the lithium–air battery concept.) Then, “Electrocatalysis of the oxygen electrode reactions,” “Degradation of the electrolyte and the oxygen electrode components,” “Structure of the oxygen electrode,” and “Passivation of the oxygen electrode” sections describe the most important challenges in the development of lithium–air batteries. Finally, in “Conclusions” section, we summarize the conclusions of this critical review.

Principle of operation and energy density of lithium–air batteries

Figure 1 shows the basic configuration of a lithium–air battery. (Note that in this review, we adopt the term “battery” as it is used in the primary literature, but in fact, a single cell is typically meant.) The electrical energy is provided by the chemical reaction between the lithium metal and O_2 from the air. The oxygen electrode has to be porous in order to allow the transport of gasses. The lithium electrode will be protected by a solid electrolyte interphase (SEI), which can be artificially prepared or spontaneously formed by the reaction of lithium with the electrolyte. The electrolyte can be an aqueous or aprotic solution, but in the former case, the protection of the lithium electrode requires the use of special membranes. Lithium–air batteries can also be built in the full solid state by using a solid electrolyte. The gas supply can be air, but then the interpretation of the results is complicated due to potential problems of

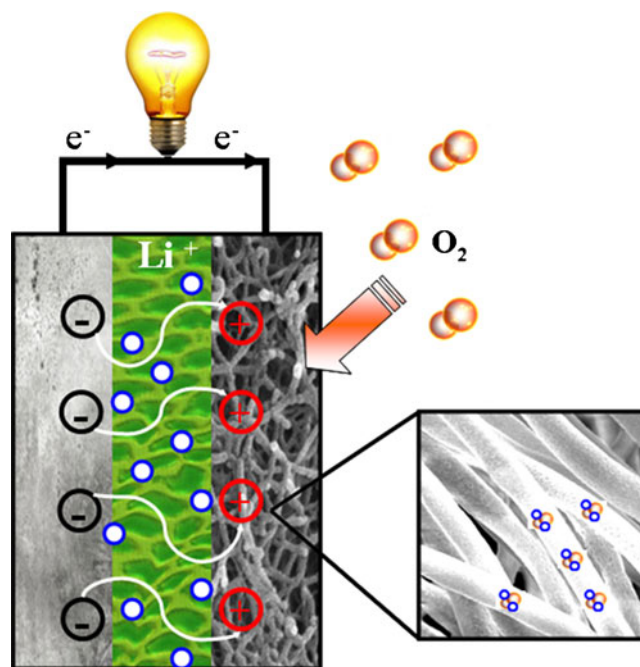
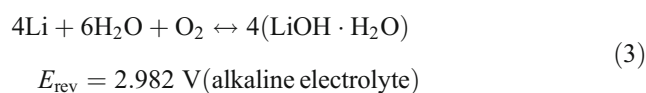
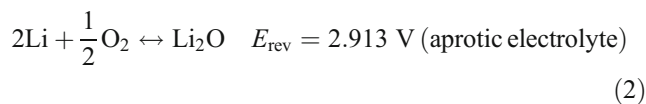
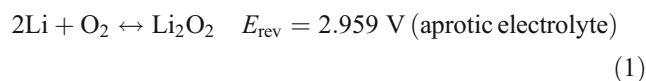


Fig. 1 Schematic representation of a lithium–air cell consisting of a negative lithium electrode, an aprotic organic electrolyte, and a porous positive oxygen electrode. The inset in the right panel illustrates the deposition of insoluble Li_2O_2 species on the oxygen electrode

contamination by water vapor, N_2 , or CO_2 . Therefore, most current works on lithium–air batteries are done by feeding the batteries with pure O_2 and, strictly speaking, these batteries should be called lithium–oxygen batteries (or better “lithium–oxygen cells”).

Two main reasons contribute to the high theoretical specific energy of lithium–oxygen batteries: (1) the use of metallic lithium, which is very light, and (2) the use of O_2 , which is also quite light and, in addition, does not have to be carried on-board since it can be supplied from the air, reducing thus the weight of the battery in the charged state. It should be noted that the weight of the battery will significantly increase during the discharge, due to the incorporation of oxygen in the form of lithium oxide, peroxide, or hydroxide. The actual discharge product will depend on the battery design and, especially, on the electrolyte in the oxygen electrode compartment [18, 19]:



In the case of aprotic lithium–oxygen batteries, two main discharge products have been proposed: Li_2O_2 and Li_2O . The respective values of theoretical specific energies in the charged state are 11,426 (Li_2O_2 formation) and 11,248 Wh/kg (Li_2O formation), while in the discharged state, 3,457 (Li_2O_2 formation) and 5,226 Wh/kg (Li_2O formation). All these values are clearly higher than the specific energies of state-of-the-art lithium–ion batteries. For example, the theoretical specific energy of a graphite– LiCoO_2 battery is 387 Wh/kg [5]. On the other hand, the theoretical specific energy of gasoline is ca. 13,000 Wh/kg. However, the tank-to-wheel efficiency of combustion engines is very low (12.6 %) [13], giving a practical specific energy of only ca. 1,700 Wh/kg. In conclusion, in order to be competitive with gasoline, lithium–oxygen batteries should provide practical specific energies higher than ca. 1,700 Wh/kg, which appears to be a rather small percentage (15 % to 50 %) of the theoretical specific energies. In this regard, it should be noted that the practical specific energies of industrial lithium–ion batteries are typically 25 % to 30 % of the specific energy calculated considering the mass of the active materials only [20].

In the case of aqueous lithium–oxygen batteries, the theoretical specific energies are lower, due to the presence of hydrating water molecules in some of the species involved in the reactions. As a result, an excess of water has to be assumed in the battery, increasing its theoretical mass. In alkaline electrolytes ($\text{LiOH}\cdot\text{H}_2\text{O}$ formation), the respective theoretical specific energies are 2,353 Wh/kg in the charged state and 1,905 Wh/kg in the discharged state. However, a major challenge in the development of aqueous lithium–oxygen batteries is the protection of the lithium metal (or lithium alloy) counter electrode, which implies the use of lithium-conductive membranes that tend to be brittle, heavy, and poorly conductive [4, 6, 13]. For these reasons, most research on lithium–oxygen batteries has been done in aprotic organic electrolytes, and that will be the focus of this review. For the discussion that follows, it is convenient to summarize the theoretical specific energy and charge of lithium–oxygen batteries in organic and aqueous electrolytes, which are provided in Table 1.

Electrocatalysis of the oxygen electrode reactions

The deposition and dissolution of lithium on lithium–metal electrodes has sufficiently fast reaction kinetics. However, on the contrary, the reduction and evolution of O_2 on the oxygen electrode requires high overpotentials. The sluggish kinetics of these reactions is the main bottleneck in the development of fuel cells and water electrolyzers. While there is a vast literature about the electrocatalysts for both, the O_2 reduction reaction (ORR) and the O_2 evolution reaction (OER) in aqueous media, studies in organic electrolytes are scarce. In addition, it should be also noted that lithium–oxygen batteries require a bifunctional catalysis that lowers the overpotentials of both the ORR and the OER.

Improving the electrocatalysis of the oxygen electrode reactions in lithium–oxygen batteries is crucial. The overpotential of the ORR reaction causes a considerable loss in the battery voltage during discharge and hence decreases its specific energy and power. However, more importantly, the slow kinetics of the OER reaction have the consequence that very high voltages have to be applied in order to recharge the battery. At these very positive potentials of the oxygen electrode, most organic solvents degrade, and even some of the oxygen electrode components (binders and carbon materials) also corrode (see “Degradation of the electrolyte and the oxygen electrode components” section). Moreover, the overpotentials of the ORR and OER are awkward because their consequence is low round-trip energy efficiency. Therefore, many attempts have been undertaken to identify better electrocatalysts for lithium–oxygen batteries.

There are several aspects that differentiate the electrocatalysis in lithium–oxygen batteries, as compared with related technical systems such as fuel cells and water electrolyzers. One of the most salient features is the fact that the discharge of the battery leads to the formation of insoluble products. Both Li_2O_2 and Li_2O have a low solubility in organic electrolytes, and thus, they will precipitate on the surface of the oxygen electrode. As a result, even at an early stage of discharge, the oxygen electrode will be covered by the discharge products, and the catalytic active sites may be blocked. This reasoning has created skepticism about the

Table 1 Theoretical specific energy and charge of lithium–oxygen cells for different cell reactions

Cell reaction	Theoretical specific energy in the charged state (Wh/kg)	Theoretical specific charge in the charged state (Ah/kg)	Theoretical specific energy in the discharged state (Wh/kg)	Theoretical specific charge in the discharged state (Ah/kg)
$2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$	11,426	3,861	3,457	1,168
$2\text{Li} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Li}_2\text{O}$	11,248	3,861	5,226	1,794
$4\text{Li} + 6\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 4(\text{LiOH}\cdot\text{H}_2\text{O})$	2,353	789	1,905	639

The values are based on the weight of the reactants in the cell (lithium, reacting electrolyte, and in the discharged state the discharge product) and thermodynamic potentials

possibility of improving the kinetics of the oxygen electrode reactions by tuning the chemical composition of the electrode. Indeed, at present, there is a scientific debate about the feasibility of finding good catalysts for lithium–oxygen batteries [21, 22]. Another distinct aspect of the electrochemistry of lithium–oxygen batteries is the poor conductivity of the discharge products (Li_2O_2 and Li_2O) [23–25]. This point will be discussed in “Passivation of the oxygen electrode” section, but here it should be noted that, during the growth of Li_2O_2 and Li_2O layers, the voltage of the battery will be further decreased due to the ohmic IR drop across the insulating layer. Therefore, it is important to evaluate and correct this ohmic drop contribution in order to assess the effect of the catalysts on the oxygen electrode reaction. However, up to our knowledge, this has not yet been done in catalytic studies devoted to lithium–oxygen batteries.

In short, electrocatalysis studies on lithium–oxygen batteries should take into account that the overall reaction rates will be strongly affected by the formation of insoluble and poorly conductive discharge products. Consequently, the performance of lithium–oxygen batteries will be critically dependent on the structure of the oxygen electrode. Oxygen electrodes with higher surface area can provide higher specific charges and hence also higher specific energies (see “Structure of the oxygen electrode” section). In addition, the surface structure of the oxygen electrode can also affect the overpotentials of the ORR and OER in lithium–oxygen batteries. Indeed, works on the ORR and OER with single-crystal electrodes in aqueous media have demonstrated that these reactions are structure sensitive [26–28]. Thus, in order to demonstrate the presence of a true catalytic effect in lithium–oxygen batteries, experiments should be performed with oxygen electrodes with the same surface structure but different composition.

The work of Lu et al. on catalytic effects in lithium–oxygen cells deserves special attention [21]. Figure 2 shows the O_2 reduction current densities on flat electrodes of palladium, platinum, ruthenium, gold, and glassy carbon (GC) in 0.1 M LiClO_4 in 1,2-dimethoxyethane (DME). A clear effect of the electrode composition on the onset potential is observed, suggesting the presence of a true catalytic effect. However, as meticulously described in this work, the different electrodes employed in this study had different roughness factors. As a result, different trends in the O_2 reduction activities are obtained if the currents are normalized by the real or by the geometrical area of the electrodes (Fig. 2). Unfortunately, it is not clear if the real area of the electrode (i.e., the surface area in contact with the electrolyte), as determined by electrochemical measurements in aqueous media, will be the same in organic electrolytes since effects such as electrode wetting and pore clogging during battery discharge will be probably different.

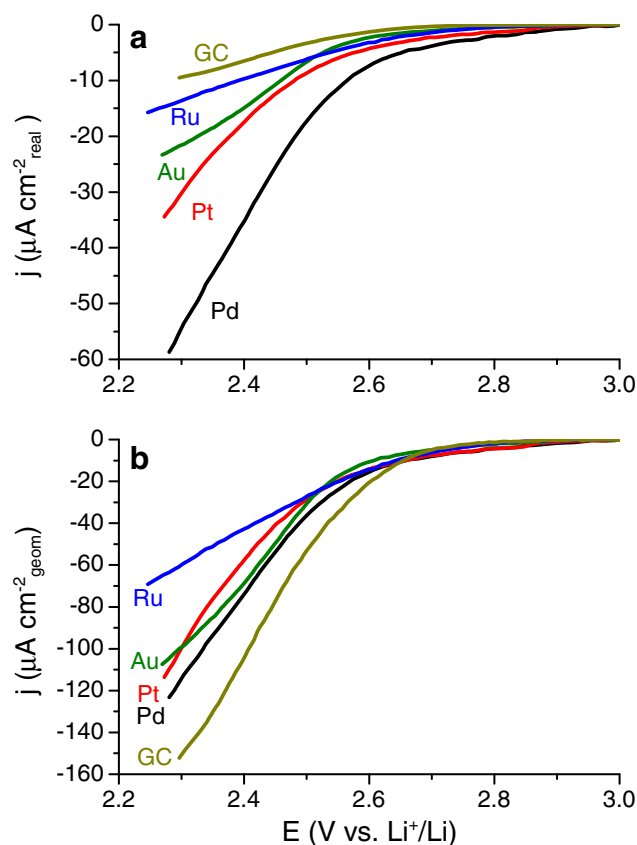


Fig. 2 Capacitive- and IR-corrected ORR polarization curves of polycrystalline Pd, Pt, Ru, Au, and GC electrodes, plotted against the applied potential, E . The normalization of currents to current densities has been done with the real surface area of the electrodes (a) and with their geometrical area (b). Electrolyte: O_2 saturated 0.1 M LiClO_4 in DME. Rotation speed, 100 rpm. Scan rate, 20 mV/s. Adapted with permission from [21]. Copyright (2011) American Chemical Society

Another complication in the study of lithium–oxygen batteries stems from the interference of side reactions such as electrolyte degradation (see “Degradation of the electrolyte and the oxygen electrode components” section). Some materials promote the degradation of the electrolyte and, on the basis of electrochemical measurements alone, such degradation of the electrolyte could be misinterpreted as an improved catalysis of the desired reactions. For this reason, it is necessary to combine electrochemical measurements with analytical techniques in order to elucidate the reactions taking place in lithium–oxygen batteries. It is now well understood that the reactions taking place in lithium–oxygen batteries using organic carbonate electrolytes involve the degradation of the electrolyte [29–33]. This takes place even if the electrode is composed of carbon and binder only, regardless of the presence of catalysts [29, 31]. On the other hand, ethers have been shown to be more stable against degradation, but the most popular catalyst for lithium–oxygen batteries, $\alpha\text{-MnO}_2$ nanowires [34], was seen to enhance the degradation of the ether-based electrolyte [35]. In order

to evaluate the presence of a true catalytic effect in lithium–oxygen batteries, McCloskey et al. performed quantitative DEMS measurements on lithium–oxygen batteries containing different catalysts (platinum, gold, and α -MnO₂ nanowires) in ether electrolytes [22]. They demonstrated that more CO₂ and less O₂ is evolved during the charge of lithium–oxygen batteries containing platinum nanoparticles or α -MnO₂ nanowires, as compared with batteries containing gold nanoparticles or carbon only (Fig. 3), demonstrating that platinum and α -MnO₂ nanowires promoted the degradation of the ether electrolyte. The authors of this work also noted that the onset potential of the OER was the same in all these batteries, suggesting the absence of a true catalytic effect.

A recent electrocatalysis work by Harding et al. was performed with electrodes pre-filled with Li₂O₂ [36]. This

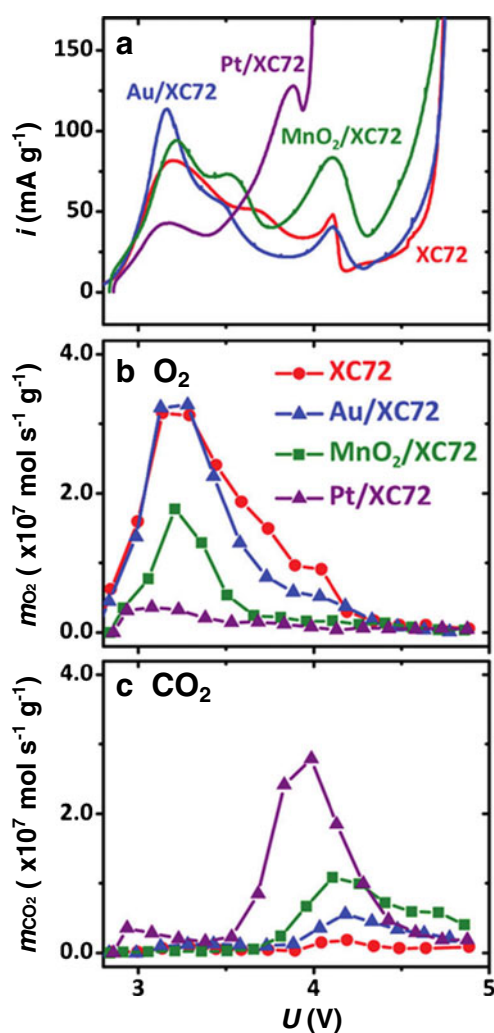


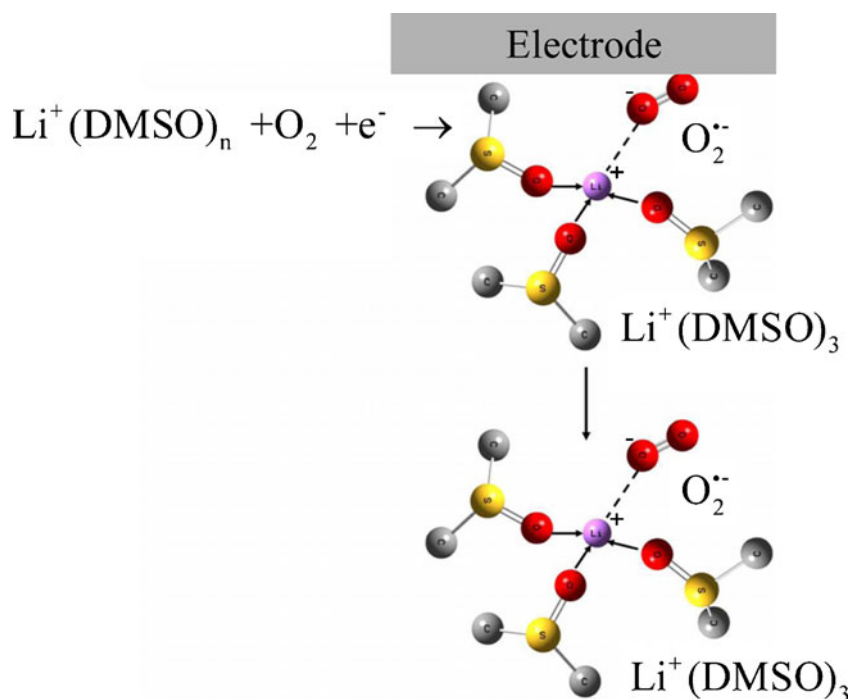
Fig. 3 Specific current (a) and evolution rate of O₂ and CO₂ (b, c) measured during the charge of lithium–oxygen cells containing a Vulcan carbon (XC72)-based oxygen electrode with and without catalyst (Au and Pt nanoparticles and α -MnO₂ nanowires, respectively), plotted as a function of the applied voltage, U . Electrolyte: 1 M LiTFSI in DME. Scan rate, 0.5 mV/s. Reprinted with permission from [22]. Copyright (2011) American Chemical Society

approach has the advantage that the reaction products are known: During charge of the battery, Li₂O₂ is electrochemically decomposed to form Li⁺ and O₂. In addition, by performing additional experiments with the same electrodes but without Li₂O₂, the potential window where the electrolyte decomposition is negligible was identified. It was concluded that platinum and ruthenium nanoparticles are better catalysts than gold or Vulcan carbon. However, as the same group pointed out [19], the respective size of the platinum and ruthenium nanoparticles used in their work was much smaller than those of gold and Vulcan carbon, and therefore, the increased charging current may be due to their higher electrochemical specific surface area. In addition, differences in the overpotential during charge could also be related to variations in the conductivity of the Li₂O₂ composite, as discussed in “Passivation of the oxygen electrode” section. For example, composites of Li₂O₂ and Super S required higher charging potentials than in the case of Li₂O₂ and Vulcan carbon [19, 37], and this effect is more likely to be due to differences in conductivity rather than electrocatalysis.

Laoire et al. demonstrated that the selection of the electrolyte in lithium–oxygen batteries can also have a major effect on the kinetics of the ORR and OER reactions and even on the reaction mechanism [38–40]. It was shown that superoxide anions are stabilized by soft cations like tetraalkylammonium cations, resulting in a reversible one-electron transfer of O₂ to O₂⁻. On the contrary, hard cations like Li⁺ have a higher affinity for peroxide and oxide anions and, as a result, the main O₂ reduction products are Li₂O₂ and Li₂O. However, the acidity of Li⁺ can be modulated with the selection of the solvent since strongly solvated lithium cations will be soft. In conclusion, solvents with high affinity to coordinate lithium cations (high donor number) increase the reversibility of the O₂/O₂⁻ redox couple. This, in turn, affects the solubility of the discharge product. For example, the solvent DMSO has a high affinity to solvate lithium ions and, therefore, increases the reversibility of the reduction of O₂ to superoxide, and facilitates also the dissolution of the complex formed between the superoxide and the solvated lithium (Fig. 4) [40].

Finally, another aspect that should be taken into consideration in studies of lithium–oxygen batteries is the interference of contamination effects. Meini et al. have shown that lithium–oxygen batteries are extremely sensitive to contamination by water vapor from the air [41]. Remarkably, the presence of water vapor results in a dramatic increase in the specific charge for discharge of test cells and lowers the discharge overvoltage (Fig. 5), and therefore, these effects can be erroneously attributed to a better electrocatalysis. These complications arise with cells that are not properly sealed from the environment or/and with cells whose O₂ supply contains cavities difficult to be flushed properly and where water may be trapped. Trace water present in the electrolyte results in a similar, although less dramatic effect. It should be stressed that the contamination

Fig. 4 Sketch of the reduction of O_2 in the presence of DMSO-solvated lithium cations, illustrating the formation of a stable complex between superoxide and the solvated lithium cation, which is subsequently dissolved in the solution. Adapted with permission from [40]. Copyright (2011) The Electrochemical Society



by trace water is not easy to avoid, and special attention should be devoted to this issue in future studies.

Degradation of the electrolyte and the oxygen electrode components

The degradation of both the electrolyte and some of the oxygen electrode materials is one of the major challenges

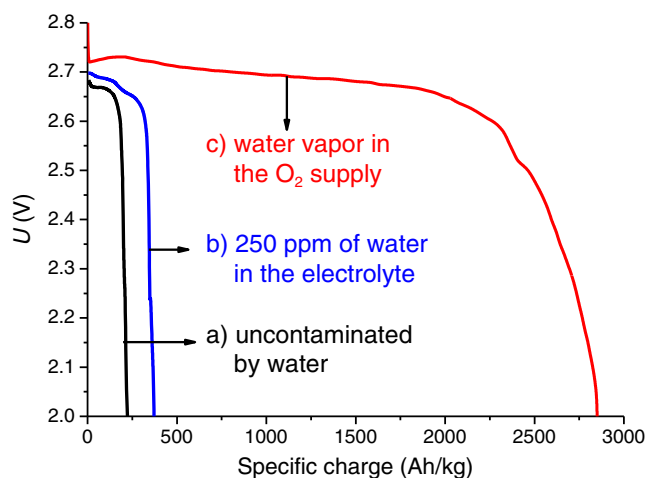


Fig. 5 Variation of the discharge voltage, U , and the specific charge of the positive electrode of lithium–oxygen test cells when uncontaminated by water (a), with 250 ppm of water in the electrolyte (b), and with water vapor in the O_2 supply (c). Electrolyte: 0.1 M $LiClO_4$ in 1,2-dimethoxyethane. Specific current: 120 A/kg. Oxygen electrode: Vulcan XC72 carbon deposited on a Celgard C480 Separator. Adapted with permission from [41]. Copyright (2012) The Electrochemical Society

in the development of lithium–air batteries. The origin of the degradation reactions is associated to the formation of the superoxide radical anion after the first electron transfer to the O_2 molecule:



$O_2^{\cdot-}$ is a highly reactive nucleophile that is likely to attack all known types of electrolytes. The reactivity of $O_2^{\cdot-}$ is an advantage for the reduction of O_2 in aqueous media because the attack of $O_2^{\cdot-}$ to a H_2O molecule is just one of the fast (and necessary) steps of the global reaction. On the contrary, the attack of $O_2^{\cdot-}$ to known organic solvents is irreversible and, hence, detrimental for the battery performance. As a result of degradation reactions, the reaction taking place during the battery charging is not the reverse reaction on discharging, and therefore, the battery is not truly rechargeable.

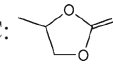
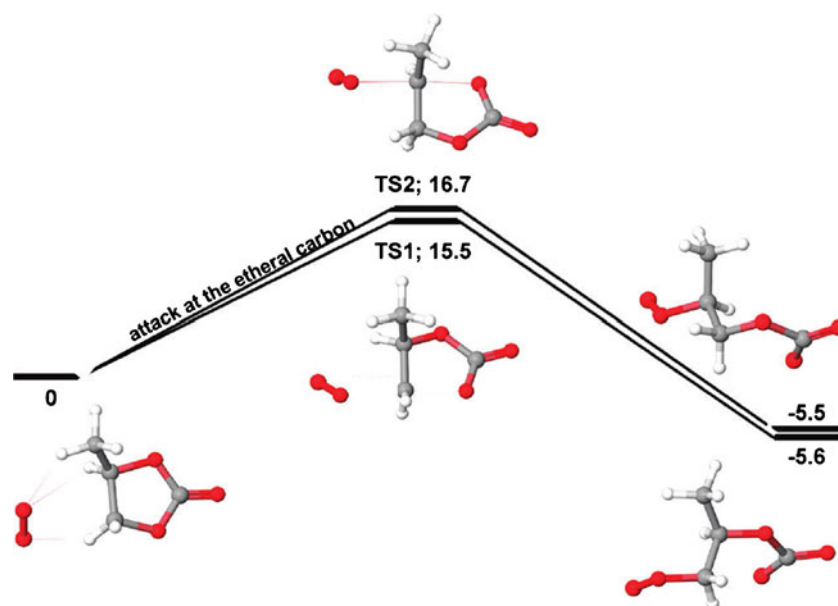

Early works on lithium–oxygen batteries were performed using organic carbonate-based electrolytes (e.g., $LiPF_6$ in propylene carbonate, PC:  [4, 5]. The reason for this selection was the formation of the so-called SEI on the lithium metal counter electrode, which is then protected in these electrolytes. Unfortunately, the reactions on the oxygen electrode involve the degradation of the carbonate-based electrolytes producing lithium alkyl carbonates, esters, Li_2CO_3 , CO_2 , and H_2O instead of the formation of lithium peroxide (Li_2O_2) as originally assumed [29–33, 42]. The degradation reactions are initiated with the nucleophilic attack of the superoxide radical $O_2^{\cdot-}$ to the alkyl carbonate electrolyte (Fig. 6) [29–33]. On charge, the oxidation of the

Fig. 6 Reaction free-energy profile for the nucleophilic attack of the superoxide radical $O_2^{\cdot-}$ to propylene carbonate showing that the reaction is favorable ($\Delta G_{\text{reaction}} = -5.5$ to -5.6 kcal/mol), and the activation energy is low ($\Delta G_{\text{activation}} = 15.5$ to 16.7 kcal/mol). Adapted with permission from [33]. Copyright (2011) American Chemical Society



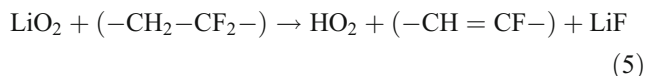
degradation products involves the evolution of a mixture of gases (CO_2 , O_2 , H_2O , H_2 , etc.). Therefore, the battery is not truly rechargeable, which explains the observed rapid capacity fading during cycling. The electrolyte decomposition also results in a drastic decrease in the expected specific energy of practical batteries since a large excess of electrolyte would have to be added to the battery, increasing thus the total mass of the battery and, as a result, lithium–oxygen batteries would obviously not be competitive to lithium–ion batteries. In conclusion, it is now clear that lithium–oxygen batteries cannot be operated with organic carbonate-based electrolytes, and thus, it is necessary to identify alternative electrolytes resistant to degradation under the conditions in which the lithium–oxygen batteries operate, i.e., highly oxidative potentials and presence of O_2 radicals.

Ethers (e.g., tetraglyme, TEGDME: $CH_3-O-[CH_2-CH_2-O]_4-CH_3$ or 1,2-dimethoxyethane, DME: $CH_3-O-CH_2-CH_2-O-CH_3$) have proved to be more stable against degradation than organic carbonates [22, 35, 43–46]. The discharge reaction in ether electrolytes mainly involves the formation of Li_2O_2 , even though partial electrolyte degradation has been observed [35, 44, 45]. During the charge of the battery, O_2 is principally evolved, although CO_2 is also evolved when the battery is polarized at high potentials (≥ 4 V) [22, 43]. Acetonitrile (CH_3CN), on the contrary, does not show any problems with electrolyte degradation in the oxygen electrode during the discharge of the battery [47]. However, acetonitrile is not a practical solvent for lithium–oxygen batteries because it would decompose in contact with the lithium metal electrode [48]. Other polar solvents such as dimethyl sulfoxide, DMSO: $(CH_3)_2SO$, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, DMPU: , and oligoether silane compounds, INMx:

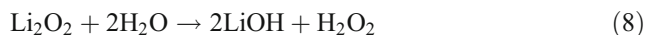
$(CH_3)_3Si(OCH_2CH_2O)_xCH_3$ with $x=1-5$ have also been tested in lithium–oxygen batteries [39, 49, 50]. All-solid-state lithium–oxygen batteries have also been reported in the literature [3, 51–53]. Hydrophobic ionic liquids have been investigated as electrolytes in lithium–oxygen batteries as well [50, 54–61]. Very recently, promising results have been obtained with lithium–oxygen batteries containing a sulfone-based electrolyte [62]. However, further work in this area is necessary in order to evaluate quantitatively the stability of these electrolytes, especially after cycling the test cells for more than a few cycles. In a recent work by Chen et al., a variety of techniques was employed to demonstrate that amida electrolytes are not suitable for lithium–oxygen batteries because of degradation problems [63]. The stability of salts such as $LiBF_4$, $LiPF_6$, $LiClO_4$, and lithium bis(trifluoromethanesulfonyl)imide, LiTFSI: $LiN(SO_2CF_3)_2$ was evaluated in a recent study by Veith et al. [64] finding that these salts decompose at the surface of the oxygen electrode during the discharge of the batteries, but it remains an open issue if salt decomposition is extensive enough to be a challenge. FTIR measurements indicate that siloxane ethers also decompose in lithium–oxygen batteries [65].

A useful strategy of screening for suitable solvents in lithium–oxygen batteries is to test the solvent's stability towards the attack by the superoxide radical $O_2^{\cdot-}$. Such stability has been evaluated by ab initio calculations [33, 66–68], and also experimentally by simply dissolving KO_2 in the solvent to be tested (with or without a lithium salt to evaluate the reactivity towards both $O_2^{\cdot-}$ and LiO_2) [69, 70]. Several solvents have been identified whose reactivity towards superoxide attack is lower than the detection limit of this method, but further tests of these solvents in lithium–air batteries are necessary in order to verify the solvents' stability because the sensibility of this method is limited. This

approach has also been used to test the stability of commonly used electrode binders such as poly(vinylidene difluoride), PVdF, which was found to degrade according to [69]:



In addition, it was found that the degradation of PVdF in the presence of the α - MnO_2 nanowires catalyst leads to the formation of LiOH. This is because α - MnO_2 nanowires catalyze the decomposition of H_2O_2 to form H_2O which then reacts with Li_2O_2 to form LiOH [69]:

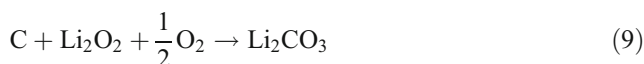


The degradation of PVdF in lithium–oxygen batteries has been recently confirmed experimentally by hard X-ray photoelectron spectroscopy, as well of the decomposition of the salt $\text{LiB}(\text{CN})_4$ [71].

A very recent article by Jung et al. reported a lithium–air battery providing a specific charge of 5,000 Ah/kg at a specific current of 500 A/kg for >30 cycles [72]. The electrolyte was ≈ 1 M LiCF_3SO_3 in tetraglyme, and the oxygen electrode was a thin Super P film coated on a gas diffusion layer. The improved performance of the battery was tentatively ascribed by the authors to a shorter lifetime of the superoxide radical $\text{O}_2^{\cdot -}$ under the optimized experimental conditions of this battery. Unfortunately, the authors do not report experimental data obtained with other electrolytes and/or oxygen electrode compositions, which would help to quantify the synergetic effect proposed in their work. In view of the remarkable electrochemical performance and based on XRD and TOF-SIMS measurements, it was claimed that electrolyte degradation is negligible in this battery design. However, this conclusion is in disagreement with other works done under very similar experimental conditions [35, 52, 73–75]. This controversial issue could be clarified by performing additional measurements using techniques able to detect electrolyte degradation products (FTIR, NMR, DEMS, ...) with batteries discharged and charged for more than a few cycles. In addition, degradation of the PVdF binder employed in their work can also be expected in view of the work done by Black et al. [69].

The degradation of the electrolyte and the oxygen electrode binder is not the only undesired side reaction in lithium–oxygen batteries. The corrosion of the carbon-containing oxygen electrode also creates a serious challenge

for the durability and rechargeability of lithium–oxygen batteries. By means of DEMS measurements with isotopically substituted samples, McCloskey et al. demonstrated that around 50 % of the CO_2 evolution during charge is due to carbon corrosion, the remaining being associated to the degradation of the ether electrolyte used in their study [45]. Due to these side reactions, the complete charge of the battery is never achieved; even for the most stable solvent studied so far (acetonitrile), less than 90 % of the O_2 consumed during discharge is evolved during charge [73]. Carbon corrosion has been explained by the chemical reaction between carbon and the main discharge product, Li_2O_2 [45]:



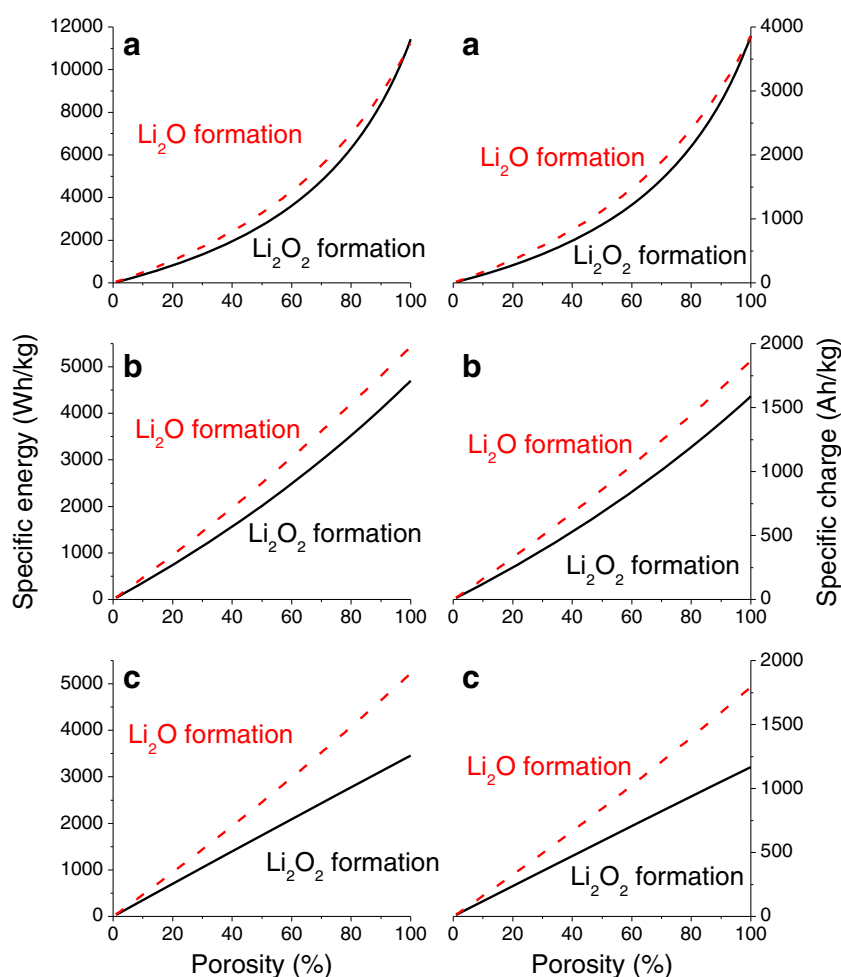
resulting in the formation of a layer of Li_2CO_3 on the carbon oxygen electrode, which decomposes at potentials ≥ 4 V vs. Li^+/Li . The formation of Li_2CO_3 during discharge was confirmed by XPS [45]. Later, XANES measurements provided experimental evidence that Li_2CO_3 is formed at the carbon– Li_2O_2 interface but not at the Li_2O_2 –electrolyte interface [76].

In a very recent work by Peng et al., it was demonstrated that all the problems of side reactions in lithium–air batteries (i.e., the degradation of both the electrolyte and the oxygen electrode components) can be solved at once by selecting a proper combination of electrolyte and oxygen electrode composition [74]. A nanoporous electrode made of gold (without carbon) was used as the oxygen electrode, and 0.1 M LiClO_4 or LiTFSI in DMSO was used as the electrolyte. These batteries exhibited a 95 % of specific charge retention during 100 cycles and ca. ten times faster kinetics during charge than on carbon electrodes. FTIR measurements showed that, after 100 cycles, the extent of electrolyte decomposition was <1 %. SERS measurements showed that >99 % of the discharge product is Li_2O_2 . Quantitative DEMS measurements showed that nearly all the O_2 that is consumed during discharge is evolved during charge. In conclusion, these new lithium–oxygen batteries exhibit an excellent electrochemical behavior, and the challenge is now to achieve similar results with cheaper and lighter oxygen electrode materials.

Structure of the oxygen electrode

The oxygen electrode in lithium–oxygen batteries must have a structure with high porosity in order to accommodate a high amount of the Li_2O_2 or Li_2O precipitate during the discharge of the battery. Figure 7 shows the theoretical specific charge and specific energy of hypothetical lithium–oxygen batteries as a function of the assumed porosity of the oxygen electrode (which is here considered to be made of

Fig. 7 Theoretical specific charge of the positive electrode and specific energy of lithium–oxygen cells containing a porous oxygen electrode made of carbon. The calculations were done assuming that the oxygen electrode is (a) in the charged state with all the pores filled by O_2 , (b) in the charged state with all the pores filled by electrolyte, and (c) in the discharged state with all pores filled by the discharge product (Li_2O_2 or Li_2O). In these calculations, all the pores of the oxygen electrode were filled by Li_2O_2 or Li_2O at the end of discharge. The weight of the cell includes (a) the weights of the lithium and carbon electrodes, (b) the weights of the lithium and carbon electrodes and the electrolyte filling the pores, and (c) the weights of the carbon electrode and the Li_2O_2 or Li_2O filling the pores. The density of the electrolyte is assumed to be 1 g/cm^3 , and the density of carbon is taken as that of graphite, 2.27 g/cm^3 . The weight of other parts of the cell (current collector, housing, membrane, etc.) is not included in the calculations, following [18]



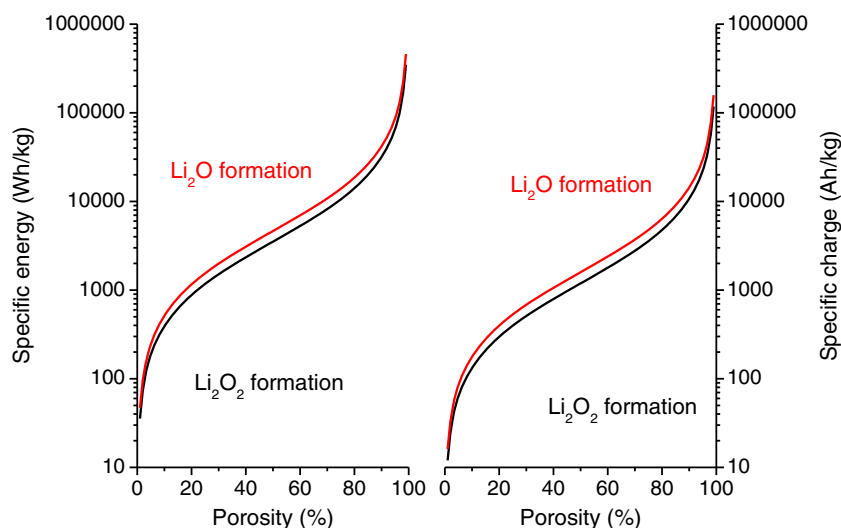
carbon). As described in “Principle of operation and energy density of lithium–air batteries” section, both the specific charge and the specific energy of lithium–oxygen batteries depend on their state of charge. In the fully discharged state, all the pores of the oxygen electrode should be filled by the discharge product(s) (Fig. 7, c). In the fully charged state, two extreme situations can be considered: the pores of the oxygen electrode will be filled by O_2 (Fig. 7, a) or by the electrolyte (Fig. 7, b). Note that, in these calculations, the values represent the minimum weight of the hypothetical battery as they are based on the directly involved compounds only, which includes the weight of the lithium counter electrode. If the calculation is done using the weight of the oxygen electrode only, even much higher hypothetical values of specific charge and energy are obtained (Fig. 8), and the effect of the porosity becomes even more evident (note the logarithm scale in the y-axes).

It is clear that, in order to build lithium–oxygen batteries with high specific energy, it is crucial that the oxygen electrode has high porosity, while still maintaining good electrical conductivity and mechanical stability. The oxygen electrode structure should also have an appropriate pore distribution and minimal tortuosity in order to facilitate fast

O_2 transport to the whole surface area of the electrode. In practical batteries, flooding of the pores with the electrolyte should be avoided since O_2 transport across the electrode will be faster if part of the pores is filled with O_2 . Ideally, a thin layer of electrolyte will cover most of the oxygen electrode structure, thus providing a high electrochemical specific surface area that will enhance the overall reaction kinetics. The pore size distribution should also be optimized taking into account the transport rate of O_2 and Li^+ in order to avoid pore clogging.

In conclusion, the development of suitable structures for the oxygen electrode is one of the major challenges of lithium–oxygen batteries. Unfortunately, most works focused on structure development in lithium–oxygen batteries were done in organic carbonate electrolytes [77–90]. Now, it is clearly established that the reactions in these batteries are dominated by electrolyte decomposition. Therefore, the electrode architectures developed in these works need to be tested again in suitable electrolytes. More recently, advantageous electrode structures have been developed and tested in lithium–oxygen batteries with ether electrolytes, as summarized in Table 2. Although some degradation of the ether electrolyte takes place, the main discharge product is

Fig. 8 Theoretical specific charge and specific energy of hypothetical lithium–oxygen cells calculated by using the weight of the porous oxygen electrode (made of carbon only), assuming that at the end of discharge, all the pores are filled by Li_2O or Li_2O_2 . The potential of the negative electrode was assumed 0 V vs. Li^+/Li



Li_2O_2 ; therefore, these results are a good indication of the true effect of the morphology of the electrode on the (desired) electrochemistry of lithium–oxygen batteries. The high surface area of these electrode structures is one of the reasons for their remarkable discharge capacities, although catalytic effects are probably also be involved [75, 91–95]. In the case of hierarchically porous electrodes, the high

capacities are probably due to the combination of big tunnels for the flow of O_2 and small pores to accommodate the discharge product [76, 94–98].

As discussed by Christensen et al. [4], the volume fraction of the active material in electrodes of standard lithium–ion batteries is typically in the order of 50 % to 80 %, and therefore, a comparable volume fraction of the discharge

Table 2 Technical data of selected lithium–oxygen cells delivering high specific charge

Oxygen electrode	Electrolyte	Specific charge for the first discharge	BET specific surface area	Fraction of pore volume filled by Li_2O_2	References
Super P on GDL	≈ 1 M LiCF_3SO_3 in tetraglyme	$>10,000$ Ah/kg of Super P	NA	>50 %	[72, 99]
Mixed lead or bismuth ruthenium oxides supported on carbon	1 M LiPF_6 in tetraglyme	$\approx 10,000$ Ah/kg of carbon	66–103 m^2/g (catalyst powder)	≈ 100 %	[91]
Hierarchically porous carbon on nickel foam	1 M LiTFSI in DME	11,060 Ah/kg of carbon	378 m^2/g of carbon (final electrode)	≈ 2 %	[97]
Iron–nitrogen–carbon composite	1 M LiCF_3SO_3 in tetraglyme	4,320 Ah/kg of composite	NA	NA	[75]
Mesoporous Co_3O_4 on acetylene black carbon	1 M LiTFSI in DME	$\approx 2,000$ Ah/kg of carbon	100 m^2/g (catalyst powder)	NA	[92]
Free-standing electrode made of vertically aligned carbon nanotubes	0.1 M LiClO_4 in DME	$\approx 10,000$ Ah/kg of carbon	NA	≈ 8 %	[76]
Nitrogen-doped graphene nanosheets	1 M LiPF_6 in tetraglyme	3,700 Ah/kg of carbon	278 m^2/g (powder)	NA	[94]
Carbon nanofibers	0.1 M LiClO_4 in DME	$\approx 5,000$ Ah/kg of carbon	NA	≈ 45 %	[98]
Hierarchically porous graphene	1 M LiTFSI in triglyme	15,000 Ah/kg of carbon	590 m^2/g (powder), 186 m^2/g (final electrode)	≈ 35 %	[96]
Nitrogen-doped graphene nanosheets	1 M LiPF_6 in tetraglyme	11,660 Ah/kg of carbon	599 m^2/g (powder)	NA	[95]

Note that the BET specific surface area is usually given for the catalyst powder instead of for the final electrode. The fraction of pore volume filled by Li_2O_2 at the end of discharge is calculated taking into account the electrode packing density and considering that only Li_2O_2 is formed during the discharge of the cells

The component used for the normalization of specific charges and specific surface areas is noted as follows: for example “Ah/Kg of carbon” indicates that the charge is normalized by the mass of carbon in the electrode

NA non-available

products (Li_2O or Li_2O_2) should be achieved in lithium–oxygen batteries. This quantity is not reported explicitly in most published manuscripts on lithium–oxygen batteries, but it can be estimated from the values of specific charge, thickness, and carbon loading of the oxygen electrode. As it is seen from Table 2, the volume fraction filled by Li_2O_2 at the end of discharge is small for some batteries with high specific charge. In other cases, the volume fraction is very promising [72, 91, 99]. However, it should be noted that the values given in Table 2 might be overestimated since these calculations do not consider electrolyte degradation. Further work is necessary in order to characterize and suppress electrolyte degradation in these batteries with advanced electrode structures, and also to guarantee the stability of the structure with cycling.

Passivation of the oxygen electrode

In order to identify which are the limiting factors in lithium–oxygen batteries, Albertus et al. compared experimental data obtained with porous and flat electrodes and made a simulation of the results by means of a physics-based model [86]. With this, it was demonstrated that the practical specific charge of lithium–oxygen cells is limited by the high electronic resistivity of the discharge products, while other factors such as pore clogging or O_2 diffusion have little effect. Following a similar approach, Lu et al. also concluded that the diffusion of O_2 within the electrolyte is not a limiting factor in the current lithium–oxygen cells, contrary to what was previously believed [100]. In conclusion, the insufficient practical specific charge provided by the state-of-the-art lithium–oxygen batteries, as discussed in the previous section, is mainly due to the poor electronic conductivity of the discharge products (Li_2O_2 and Li_2O).

The resistance of the Li_2O_2 layer produced during the discharge of lithium–oxygen batteries has been evaluated by means of electrochemical impedance measurements in the presence of an outer-sphere reversible redox couple (ferrocene/ferrocenium) [23]. As the depth of discharge increased, it was observed that the measured charge-transfer resistance of the ferrocene/ferrocenium couple, R_{ct} , markedly increased (Fig. 9). This was ascribed to the growth of the passivating Li_2O_2 layer on the surface of the electrode. It was found that, with glassy carbon model electrodes, the end of discharge takes place when the average thickness of the passivating film is only around 5–10 nm [23, 86]. These findings explain the fact that, in most lithium–oxygen batteries, only a small fraction of the pore volume is filled by Li_2O_2 at the end of discharge, as described in “Structure of the oxygen electrode” section. Furthermore, the insulating character of Li_2O_2 (and Li_2O) layers is also responsible for the fact that charging the battery requires the application of very positive potentials to the positive electrode at which most electrolytes and battery materials degrade

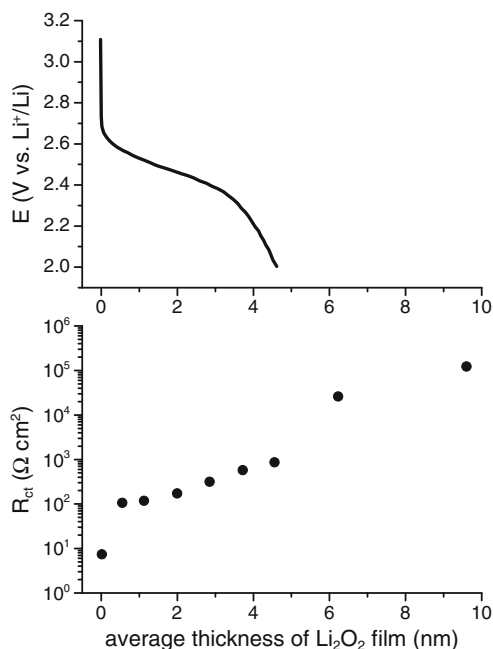


Fig. 9 Potential of a glassy carbon electrode, E , and corresponding effective charge-transfer resistance of the ferrocene/ferrocenium couple, R_{ct} , plotted as a function of the average thickness of the Li_2O_2 discharge product. Electrolyte: 1 M LiTFSI in DME+3 mM ferrocene. Adapted with permission from [23]. Copyright (2011) American Institute of Physics

(“Degradation of the electrolyte and the oxygen electrode components” section). These problems can be mitigated by limiting the depth of discharge [34, 40, 72], or by means of the formation of very thin Li_2O_2 layers [101], but then the battery does not provide a sufficient specific charge for practical applications. In summary, the formation of insoluble products limits the practical specific charge of the battery, hampers the rechargeability, and contributes to the specific charge fading with cycling.

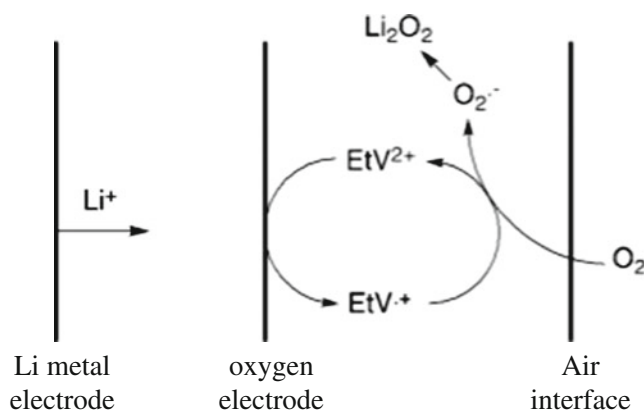


Fig. 10 Schematic diagram showing how a redox shuttle relocates the oxygen reduction reaction from the electrode surface to the air interface. $\text{EtV}^{2+}/\text{EtV}^{+}$: ethylene viologen redox couple. Reprinted from [108] with permission from Elsevier

Electrolyte additives could be used in order to increase the solubility of Li_2O and Li_2O_2 . It has been shown that the solubility of lithium oxides can be increased considerably with additives such as pentafluorophenylboron oxalate (PFPBO) [102], tris(pentafluorophenyl) borane (TPFPB) [50, 103, 104], and boron compounds with formula $\text{B}(\text{OR})_3$ [where R is a (carbonyl) alkyl chain] [105]. However, a final evidence of the absence of degradation reactions when these additives are used in lithium–oxygen batteries is not yet available, and further studies are needed.

Theoretical works have shown that the conductivity of Li_2O_2 can be increased by the introduction of lithium vacancies (i.e., presence of LiO_2) [24]. Interestingly, DFT calculations predict that the surface of Li_2O_2 is oxygen-rich and, as a result, half-metallic as opposed to the Li_2O surface, which is stoichiometric and insulating [25, 106]. DFT calculations of the thermodynamics of Li_2O , Li_2O_2 , and LiO_2 , in both bulk phases and nanoparticles showed that decreasing the nanoparticle size below 5 nm results in stabilization of Li_2O_2 over Li_2O (in terms of surface energy) [107]. However, it is necessary to test experimentally the conclusions from these works since these calculations do not take into account that, in practical lithium–oxygen batteries, the electrodes will be covered by a complex layer containing solvent molecules, salt, and degradation products (SEI-like layer).

Very recently, Lacey et al. have proposed a redox shuttle mechanism that solves the problem of electrode passivation by insulating reaction products (Fig. 10) [108]. A reversible redox couple (in their work $\text{EtV}^{2+}/\text{EtV}^+$) is dissolved in the electrolyte, and during the discharge of the battery, the reduced form of this couple (EtV^+) is generated. This species diffuses to the gas–electrolyte interface where it is oxidized by O_2 , forming Li_2O_2 (or Li_2O or LiO_2). In this way, the discharge product does not block the electrode surface since it is generated at the gas–electrolyte interface. Moreover, this approach can potentially lead to enhanced overall reaction kinetics compared to the ORR, although further improvements are necessary in order to improve the cyclability, the practical specific charge, and the durability of the battery.

Conclusions

The recent research has clearly demonstrated that the realization of practical lithium–oxygen batteries is far from being easy and fast, due to fundamental challenges. The first electron transfer to molecular oxygen forms superoxide radical species that attack all known types of electrolytes and electrode materials. Finding solvents, binders, catalysts, and catalyst supports that remain stable under the harsh

conditions of lithium–air batteries is a formidable challenge. However, the latest results by Peng et al. [74] have brought reasons for optimism. By combining a gold electrode with a suitable electrolyte, they have developed lithium–air test cells with unprecedented specific charge retention. Jung et al. [72] have also developed lithium–air test cells with remarkable electrochemical performance, but it remains to be clarified why this work is not in line with previous studies by other authors [35, 73]. In both cases, it seems that the key for success is the decrease in the lifetime of the superoxide radical (achieved through the proper combination of solvent and electrode materials), and the use of materials very resistant to degradation/corrosion (such as the pure gold electrode). Clearly, electrocatalysis is one of the keys to lithium–air batteries since the performance of the battery critically depends on the lifetime of some intermediate species. Electrocatalysis is also critical for the rechargeability of the battery since high overpotentials during charging of the battery enhance degradation reactions in a larger extent than the desired electrooxidation of Li_2O_2 or Li_2O [73]. The main factor that decreases the overall rate of the reactions in lithium–air batteries is the passivation of the electrode by the deposition of discharge products [86], and this is a subject that needs further investigation. Related to this is the insufficient amount of discharge products formed in most lithium–oxygen batteries [4], an issue that also requires further studies.

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