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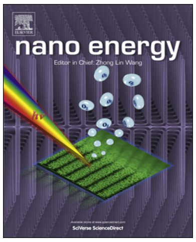

REVIEW

Challenges and opportunities of nanostructured materials for aprotic rechargeable lithium-air batteries

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Abstract

Rechargeable lithium-air (O_2) batteries have received much attention due to their extremely high theoretical energy densities, which far exceeds that of current lithium-ion batteries. The considerable high energy densities come from (i) pure metal lithium as anode and (ii) the cathode oxidant, oxygen, which comes from the surrounding air. However, there are still many scientific and technical challenges especially nanomaterial challenges to overcome before it turns into reality. In this review, the fundamental principles and understanding of the electrochemical reaction in the aprotic lithium-air batteries are first presented. We emphasized on the discussion of the nanomaterial's issues which prevent their practical implementation, including the material status and challenges from cathode, electrolyte, anode and other components. These problems will be discussed in detail and possible solutions are also suggested. Finally, we explore future research directions in the field of aprotic rechargeable lithium-air batteries.

Contents

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Introduction

The demand for energy is putting pressure on fossil fuel reserves, which in turn is responsible for the climate change. It has been reported that oil consuming accounts for 40% of the total CO_2 emission and is a major cause of geopolitical instability. On one hand, due to the fluctuation of oil prices and the serious environmental issues, there has been substantial interest in renewable energy sources. On the other hand, since the majority of oil is used for automobile and light truck applications, a transition to an electrified road transportation system should be a societal goal of utmost importance. This is heralded by the advent of hybrid electric vehicles (HEVs), and will be accelerated by plug-in hybrid vehicles (PHEVs) and ultimately pure electric vehicles (EVs). Therefore, the development of novel energy storage and conversion systems is required for effective utilization of renewable energy sources in future smart grids and power delivery systems.

Rechargeable battery systems may provide a feasible route to achieve this objective. Various battery systems have been developed and commercialized over the past few decades (Table 1) [1-6]. Figure 1 shows a range of battery technologies available or currently under development and compares their respective energy densities to gasoline [7]. Among them, the most successful rechargeable battery technology is lithium-ion battery (LIB), which was first commercialized in 1991 and has been widely used in a variety of portable electronic equipments and devices [8-10].

However, the maximum energy density of current lithium-ion batteries is limited by the intercalation chemistry occurring within the electrode materials [11]. While it is known that the theoretical energy density of gasoline is 13,000 Wh/kg, the energy density of lithium-ion batteries is usually less than 200 Wh/kg [7]. Considering the energy conversion efficiency of 12.6%, the practical energy density for automotive applications is 1700 Wh/kg, which is still much higher than lithium-ion batteries. There is no expectation that current or even future lithium-ion batteries will ever reach this target because of the intercalation reaction mechanism limit in lithium-ion battery system. A novel energy system must be considered.

Metal-air batteries (e.g. iron-air, aluminum-air, and zinc-air) have attracted much attention as a possible alternative due to their relatively high energy densities because the cathode of a metal-air battery utilizes oxygen from ambient air as reactant in the electrochemical reaction rather than storing heavy active materials as in other battery systems. Among them, Zn-air batteries have been studied for many years because they have many advantages such as a flat discharge voltage plateau, high safety, low cost, and long shelf life [12-14]. However, the theoretical specific energy density of Zn-air batteries is only 1084 W/kg [15], which is still much lower than gasoline and cannot fulfill the requirements of many high-energy applications of electric vehicles.

Lithium is the lightest metal element and its theoretical energy density is approximately 11,680 Wh/Kg [7], nearly equivalent to gasoline. Therefore, many efforts have been devoted to lithium-air battery research [7,16-18]. The

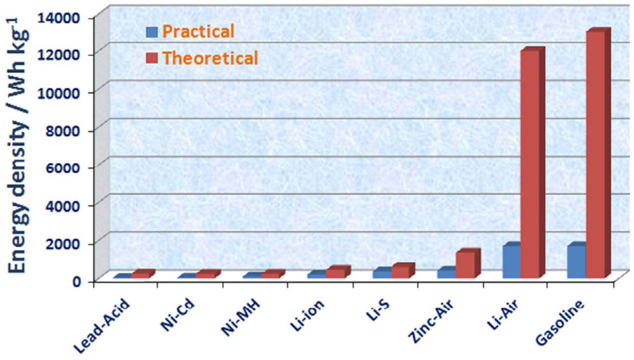


Figure 1 The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline.

concept of Li-air chemistry was first introduced by Littauer and Tsai at Lockheed in 1976 [19], but it received little attention until a lithium-O_2 battery system based on non-aqueous electrolyte was presented by Abraham in 1996 and the rechargeability of the system was explored by Bruce in 2006 [20,21]. These pioneering works have attracted world-wide attentions and triggered numerous research works into lithium-air field. However, current lithium-air battery (most of the current research on lithium-air batteries has focused on pure oxygen rather than air as air contains H_2O and CO_2 which interferes with the desired electrochemical behavior) still suffers from a relatively low practical energy density as compared to the theoretical one and internal combustion engine that uses gasoline. Numerous fundamental and systematic studies are required to mature this novel electrochemical energy system. Undoubtedly, lithium-air battery is a pivotal research area for next-generation power source and could bring electric vehicles to the mass market in the future.

Currently, there are four architectures of lithium-air batteries being pursued, which are categorized based on the applied electrolyte species (aprotic, aqueous, hybrid, and all solid-state electrolytes) [22-44]. All the four types of lithium-air batteries use lithium metal and oxygen (air) as anode and cathode active materials, respectively. Their fundamental electrochemical reaction mechanisms depend on the electrolytes used, which is listed in Table 2. The aprotic system is advantageous because it has been proved that the reduction product of Li_2O_2 can be reversed into the original reagents of the oxygen reduction reaction (ORR). This is aptly named the oxygen evolution reaction (OER) and signifies the rechargeability of the aprotic lithium-oxygen battery. Because only the aprotic lithium-air battery has shown promise of electrical rechargeability, this configuration has attracted the most effort worldwide to date compared to other electrolyte systems, and we will focus principally on this configuration in the following sections.

In this review, Section 2 mainly emphasizes on the understanding of aprotic lithium-air batteries including the fundamental electrochemical reaction mechanism, the discharge products, and the capacity limit. Our focus is primarily on the following two sections: the material's status and challenges including electrolyte material (Section 3) and cathode (catalysis) materials (Section 4). In addition, the current development at anode, air dehydration membranes, and collectors are also reviewed. Finally, perspective materials development directions in lithium-air batteries are suggested.

Understanding of aprotic lithium-air batteries

Oxygen reduction/evolution reactions

During the discharge of an aprotic lithium-air battery, an oxidation reaction occurs at the anode ($Li \rightarrow Li^+ + e^-$). The electrons flow through an external circuit and the lithium ions generated from this reaction react with oxygen to form Li_2O_2 (and possibly Li_2O) in the cathode. At the cathode, oxygen is reduced in either a two or four electron process as described by the following half cell reactions (Figure 2) [45,46]:

$$O_2 + 2e^- + 2Li^+ \rightarrow Li_2O_2 \ (3.10\ V) \tag{1}$$

$$O_2 + 4e^- + 4Li^+ \rightarrow 2Li_2O \ (2.90\ V) \tag{2}$$

The reactions above are thought to be reversible at externally applied potentials, i.e., lithium metal is plated out on the anode, and O_2 is evolved or generated at the cathode. The potentials of reactions (1) and (2) are close, so

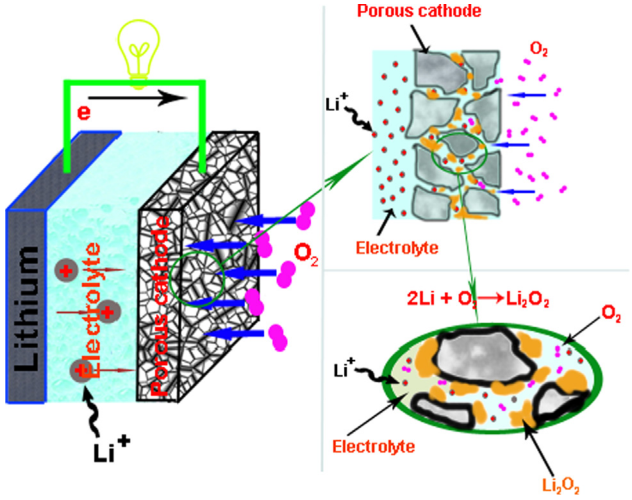


Figure 2 The schematic figure of an aprotic lithium-air battery and the oxygen electrode structure.

Table 1 Electrochemical reactions and energy densities of the various rechargeable batteries.

Types	Cell reactions	Theoretical energy density (Wh/Kg)	Practical energy density (Wh/Kg)
Lead-Acid	$Pd + PdO_2 + 2HSO_4^- + 2H^+ \rightarrow 2PdSO_4 + 2\ H_2O$	170	30-50
Ni-Cd	$2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$	245	45-80
Ni-MH	$xNi(OH)_2 + M \rightarrow xNiOOH + MH_x$	280	60-120
Li-ion	$LiCoO_2 + C \rightarrow Li_xC + Li_{1-x}CoO_2$	400	110-160
Li-S	$xLi^+ + S_8 + e \rightarrow Li_2S_x$ $Li_2S_x + Li^+ + e \rightarrow Li_2S_2$ or Li_2S	2600	~400
Zn-air	$2Zn + O_2 \rightarrow 2ZnO$	1084	~400
Li-air	$2Li + O_2 \rightarrow Li_2O_2$	11,680	~2000

both Li_2O_2 and Li_2O are the most abundant reduction products after the discharge process. However, based on the studies from Abraham [20] and Bruce [21] using Raman spectrometry, Li_2O_2 was identified as the dominant reduction product formed after discharge. Moreover, Li_2O_2 exhibits a better rechargeability than Li_2O since Li_2O is believed to be electrochemically irreversible. Despite the fact that both Li_2O_2 and Li_2O are bulk insulators, a recent study indicated that the stable surfaces of Li_2O_2 are half-metallic [47]. In contrast, the stable surfaces of Li_2O are insulating and non-magnetic. The distinct surface properties of these compounds may explain the observations of electrochemical reversibility for systems with Li_2O_2 as the discharge product, and the irreversibility of systems that discharge product is Li_2O.

Considering Li_2O_2 is more desirable for rechargeable aprotic lithium-air batteries, currently the net discharge/charge reactions in an aprotic lithium-air battery is the oxidation/reduction involving of lithium peroxide

$$2Li+O_2 \rightarrow Li_2O_2 \text{ (discharge)} \tag{3}$$

$$Li_2O_2 \rightarrow 2Li+O_2 \text{ (charge)} \tag{4}$$

In the mechanism study, there are various different proposed mechanisms for O_2 reduction in Li^+ electrolytes over past years [48-53]. Recently, Bruce applied spectroscopic methods to directly identify the reaction products and their intermediates. A possible mechanism has also been suggested in order to further elucidate the chemical reactions that occur at the cathode during discharge

$$O_2+e^- \rightarrow O_2^- \tag{5a}$$

$$O_2{}^- + Li+ \rightarrow LiO_2 \tag{5b}$$

$$2LiO_2 \rightarrow Li_2O_2+O_2 \tag{5c}$$

Reduction of O_2 in the presence of Li ions in a nonaqueous electrolyte first forms O_2^-, which binds to Li^+ forming LiO_2 on the surface of the electrode. Here LiO_2 is unstable and disproportionates to the more stable Li_2O_2, that is, $2LiO_2 \rightarrow Li_2O_2+O_2$. Therefore, Li_2O_2 is the final discharge product.

Further, a charging process mechanism was also suggested by Bruce [54]. During the charging process, oxidation occurs by direct decomposition according to the reaction

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2 \tag{6}$$

In other words, the pathways followed on reduction and oxidation are different. On charging, Li_2O_2 decomposes directly, in a one-step reaction to evolve O_2 and does not produce LiO_2 as an intermediate.

Discharge products and capacity limit

The lithium-air battery may achieve a high practical specific energy as its theoretical specific energy is 11,431 Wh/kg Li, assuming that Li_2O_2 is the product, starts with Li (0.006941 kg/mol) and the equilibrium potential is 2.96 V

$$Spec.E = \frac{2.96\ \text{V} \times 96{,}500\ \text{C/mol}}{3600\ \text{C/Ah} \times 0.006941\ \text{kg/mol}} = 11{,}431\ \text{Wh/kg}$$

However, currently the practical specific energy of an aprotic lithium-air battery is significantly lower than the theoretical one. There are many factors including the conductivity, pore clogging, and electrolyte decomposition which limit the discharge capacity.

The first factor is electrical passivation at the cathode. Albertus et al. [55] identified capacity limitations of the lithium-air battery by experiments and modeling. While pore clogging may occur in the cathode as the discharge products forms, the electrical passivation is the dominant capacity-limiting mechanism in their cells [56]. Therefore, the currently achievable energy density of aprotic lithium-air batteries is much lower than what we expect. Design of novel porous cathode structure with oxygen diffusion channels may relieve the pore clogging problems and improve the discharge performance.

Second, the low conductivity of discharge products and the resulting high electronic resistance also present big challenges for aprotic lithium-air batteries. Both Li_2O_2 and Li_2O are considered as bulk insulators (Figure 3), resulting in serious electrochemical resistance. However, a recent study indicated that the stable surfaces of Li_2O_2 are half-metallic as mentioned above [47]. The presence of conductive surface pathways in discharged Li_2O_2 could offset capacity limitations expected from limited electron transport through the bulk. Therefore, electron transport through well-connected Li_2O_2 particles may not significantly hinder performance in lithium-air batteries (Figure 4) [57]. However, the underlying mechanisms relevant to the performance of lithium-air batteries are not well understood. The structure, chemical composition, and electronic proprieties of the primary discharge phases Li_2O_2 and Li_2O are needed to be further investigated.

In addition, the electrolyte decomposition and associating problems also reduce the performance and life time of lithium-air batteries. There has been recent experimental

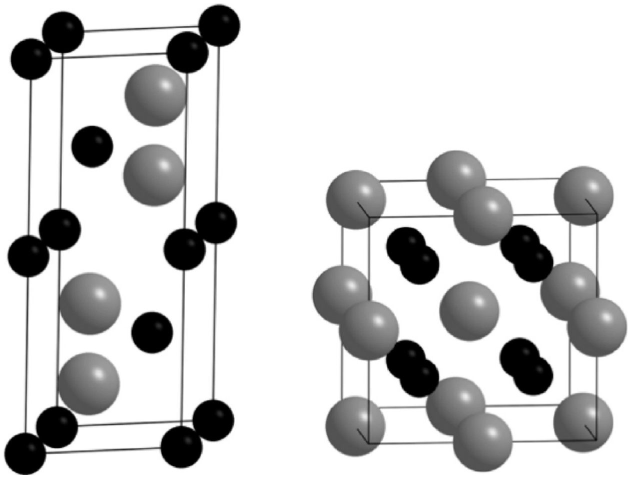
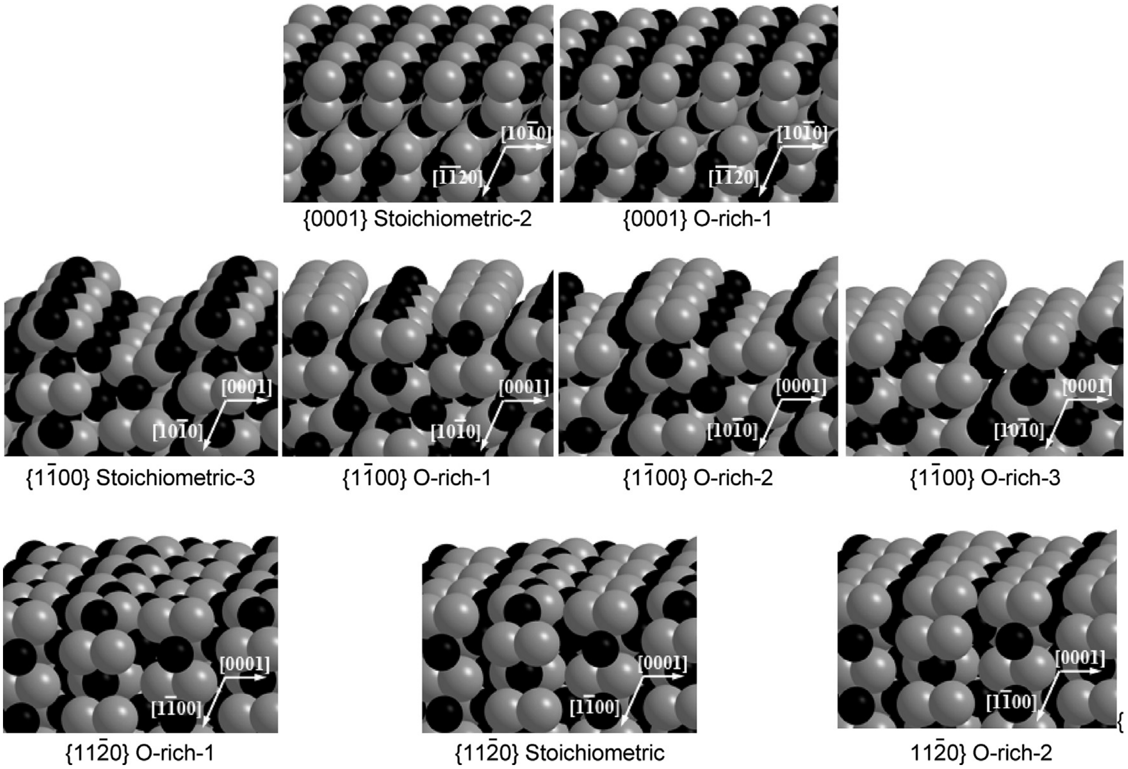


Figure 3 Unit cell for (left) bulk Li_2O_2 and (right) bulk Li_2O. Gray and black spheres represent O and Li atoms, respectively. Reproduced with permission from Ref. [47]. Copyright 2012 American Chemical Society.



{0001} Stoichiometric-2 {0001} O-rich-1

{1$\bar{1}$00} Stoichiometric-3 {1$\bar{1}$00} O-rich-1 {1$\bar{1}$00} O-rich-2 {1$\bar{1}$00} O-rich-3

{11$\bar{2}$0} O-rich-1 {11$\bar{2}$0} Stoichiometric {
11$\bar{2}$0} O-rich-2

Figure 4 Structures of low-energy Li_2O_2 surfaces. Gray and black spheres represent O and Li atoms, respectively. Reproduced with permission from Ref. [47]. Copyright 2012 American Chemical Society.

and theoretical evidence that the organic carbonates (e.g. propylene carbonate, ethylene carbonate, and dimethyl carbonate) commonly used in Li-ion batteries are not stable against oxygen reduction reaction during discharge [58–60]. Neither Li_2O_2 nor Li_2O are major components of the insoluble discharge products; instead, the products are mainly Li_2CO_3 and others resulting from the decomposition of carbonate electrolytes. Li_2CO_3 is not electrochemically reversible in an aprotic lithium–air battery system, which will limit the rechargeability, cycle life, and stability in lithium–air batteries. Currently, the stability issue of electrolytes is urgent for development of aprotic lithium-air batteries. More detailed discussion about electrolytes is contained in later sections of this review.

Improvement of ORR/OER kinetic

In order to improve the ORR/OER kinetic in an aprotic lithium–air battery, intensive research efforts have been devoted to various aspects including electrolytes, cathode structure, discharge products, and catalysts.

Electrolyte formulation has a determining effect on ORR kinetic and discharge capacity in lithium-air battery systems [52]. The cations in the electrolyte solutions of hexafluorophosphate of the general formula A^+PF6^- (where A= tetrabutylammonium (TBA), K, Na, and Li) strongly influence the reduction mechanism of O_2. Larger cations displayed reversible O_2/O_2^- redox couple. In contrast, those containing the smaller Li (and other alkali metal) cations exhibit an irreversible one-electron reduction of O_2 to LiO_2, and other alkali metal superoxides. Therefore, it would be advantageous to use a mixture of Li and K and/or TBA salts as supporting electrolytes in order to dissolve the oxygen reduction products. This in turn would deliver higher capacity and promote the rechargeability for lithium–air system.

Some additives for electrolytes may be helpful for ORR kinetic in lithium–air batteries. In organic synthesis, quaternary ammonium salts are often used as the phase transfer (solid phase to liquid phase) catalyst to promote heterogeneous reactions [61,62]. Based on a similar principle [63], tetrabutylammonium triflate was proposed as an additive or a co-salt of the nonaqueous electrolyte to improve the discharge characteristic of lithium–air batteries. It is assumed that in ORR, the ammonium cations can combine peroxide anions to form slightly soluble tetrabutylammonium peroxide, $(NBu_4)_2O_2$, which is believed to change the morphology of Li_2O_2 and Li_2O precipitates on the surface of carbon and promote the reaction of "$2Li+Li_2O_2 \rightarrow 2Li_2O$". This function not only reduces the polarization of Li_2O_2 reduction but also increases the overall discharge capacity. In addition, some additives may increase the solubility and diffusivity of oxygen in an aprotic electrolyte which is another limitation for lithium-air battery. Oxygen concentration in an aprotic electrolyte is dependent on the electrolyte formulation and others parameters (e.g. gaseous oxygen partial pressure). The lithium–air batteries were limited by oxygen diffusion and the dissolved oxygen diffusivity and concentration are of critical importance for the battery's performance [64]. By introducing perfluorinated compounds, the solubility of oxygen in a non-aqueous electrolyte can be significantly increased, which leads to the increase in the diffusion-limited current of oxygen reduction on the gas diffusion electrode in a lithium-air battery [65].

In addition to electrolytes, the optimization of the air electrode and pursuit of an efficient catalyst for Li_2O_2 or Li_2O decomposition at a lower charge potential play very important roles in improving the performance of rechargeable lithium-air batteries. The optimization of the air electrode with more porous structure is critical for both oxygen diffusion and accumulation of discharge products, contributing higher capacity for lithium-air batteries [66]. Various catalysts including carbon-based nanomaterials, metal-metal oxides (e.g. MnO_2), noble PtAu/C catalysts have been widely studied for ORR and/or OER in lithium-air batteries [67-71]. In addition, catalysts' distribution in cathode may also influence on the specific capacity and energy density. A recent study indicated that it is more efficient to use a nonuniform catalyst that enhances the reaction rate only at the separator-cathode interface than a catalyst uniformly distributed. Using uniformly distributed catalysts enhances the current and power density of the cell but does not significantly increase the specific capacity and energy density. The specific capacity and energy density can be increased by suppressing the reaction rate at the oxygen-entrance interface to delay the pinch-off of the conduction channel in this region [72].

There are other ways to improve the ORR/OER kinetics. Recently, Ceder studied the oxygen evolution reaction of lithium peroxide in the lithium-air battery by first-principle method [73]. The result indicated that the OER processes are kinetically limited by the high energy barrier for the evolution of oxygen molecules and that the rate of the OER processes is highly dependent on the surface orientation of Li_2O_2. The kinetics of OER is slow on the abundant surfaces, such as the $(11\bar{2}0)$ and (0001) surfaces, but is faster on the higher energy surfaces. Therefore, in order to improve the poor kinetics of OER, the discharge product of Li_2O_2 with high energy surfaces is more desirable. Nevertheless, it is a big challenge since those higher energy surfaces generally are not as stable as these (0001) and $(11\bar{2}0)$ surfaces.

Electrolytes materials' status, challenges and opportunities

Electrolyte catalog

Currently, the applied electrolytes in non-aqueous lithium-air battery systems can be divided into two catalogs based on the types of solvent: carbonates (ethylene carbonate, propylene carbonate, dimethyl carbonate) and ethers (tetrahydrofuran, dioxolane, dimethoxyethane, tetraethylene glycol dimethyl ether), which solvate lithium salts, such as $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiN(SO_2CF_3)_2$, and $LiSO_3CF_3$ (Table 3) [74-78].

Carbonates are typically employed as solvents in state-of-the-art rechargeable Li-ion batteries as a result of its high oxidation potential (high stability) and relatively low viscosity (low activation energy for Li+ ion diffusion) [79-81]. For the same reason, most nonaqueous lithium-air batteries have initially used carbonate solvent-based liquid electrolytes. However, recently it has been reported that such electrolytes decompose in lithium-air batteries during discharge. Bruce indicated that the discharge product in a non-aqueous rechargeable lithium-air battery is a mixture of lithium propyl dicarbonate (mainly Li_2CO_3), rather than

Table 2 Catalogs of lithium-air batteries.

Types	Cell reactions	Advantages	Disadvantages	References
Aprotic (nonaqueous)	$O_2 + 2e^- + 2Li+ \rightarrow Li_2O_2$ (3.10 V) $O_2 + 4e^- + 4Li+ \rightarrow 2Li_2O$ (2.90 V)	Extremely high theoretical energy density, rechargeability	Insoluble products, big material challenges (stable electrolytes, effective catalysts, etc.)	[20,22]
Aqueous	$4Li + O_2 + 2H_2O = 4LiOH$ (alkaline electrolyte) $4Li + O_2 + 4H+ = 4Li+ + 2H_2O$ (acid electrolyte)	No cathode clogging, no moisture effect (discharge products are soluble in aqueous system)	Lack of an effectively-ion conducting membrane Undetermined charging behavior. A lithium metal and water sable artificial SEIs	[24-26]
Hybrid (non-recycling and cycling batteries)	$4Li + O_2 + 2H_2O = 4LiOH$ (alkaline electrolyte) $4Li + O_2 + 4 H+ = 4Li+ + 2H_2O$ (acid electrolyte)	No cathode clogging, no moisture effect, natural SEI on lithium metal due to the application of aprotic electrolytes	Lack of an effective solid Li-ion conductive membrane. Undetermined charging behavior	[34,35]
Solid state	$O_2 + 2e^- + 2Li+ \rightarrow Li_2O_2$ (3.10 V)	May use air, good stability and rechargeability, avoid the undesirable lithium dendrite formation	Low Li-ion conductivity in solid-state electrolyte. Capacity and energy density are not desirable	[42,43]

Table 3 Electrolyte materials of aprotic lithium-air batteries.

Types	Typical examples	Advantages	Disadvantages	Refs.
Organic carbonates	Propylene carbonate, ethylene carbonate, diethyl carbonate, and dimethyl carbonate	A high oxidation potential (HOMO) at ca. 4.7 V relatively low viscosity	Electrolytes decomposition	[79,81]
Ethers	Dimethoxyethane (DME) tetraethylene glycol dimethyl ether crown ethers	Highly stable with Li metal, high oxidation potential over 4.5 V. Low volatility, relatively high stability to some Li_2O_2	Electrolyte decomposition	[77,82]
Ionic liquids	1-Ethyl-3-methylimidazolium bis-(triflouromethanesulfonyl)imide (EMITFSI)	A high oxidation potential (~5.3 V versus Li+/Li), nonflammability, a low vapour pressure, thermal stability, low toxicity, high boiling points, and a high Li-salt solubility	A high viscosity, low ion diffusion	[100,101]
Solid-state electrolyte	Lithium aluminum germanium phosphate glass-ceramic glass-ceramic $Li_{3-x}PO_{4-y}N_y$ (LiPON) lithium aluminum titanium phosphate ceramics, 1-ethyl-3-methylimidazolium bis(triflouromethanesulfonyl) imide	Act as a separator, good chemical stability	Low Li-ion conductivity	[42,43]

Table 4 Catalysts of aprotic lithium-air batteries.

Types	Electrochemical property (discharge)	Charge	Comment	Refs.
Carbon (carbon black, carbon nanotube, graphene)	Ketjen black exhibit the discharge capacity of 851 mA h/g. CNT electrode (590 mA h/g), N-CNT electrode (866 mA h/g). Graphene (doped grapheme) shows the highest discharge capacity (9000-12,000 mAh/g)	No obvious charging capacity	N-doping improve the ORR kinetics/discharge capacity, but no charging capacity, so only used for primary batteries	[121,128]
Metal oxides	Fe_2O_3 exhibits a high initial discharge capacity Fe_3O_4, CuO, and $CoFe_2O_4$ give a good capacity retention Co_3O_4 show the best compromise between the discharge capacity and the retention	MnO_2 exhibits a low charge potential of 3.8 V; $CoMn_2O_4$ exhibit a good bifunctional property in ORR and OER	Mn, Co-based metal oxides could be promising catalysis material considering the bifunctional property	[135]
Noble metal	Au can enhance the ORR during discharge PtAu alloy exhibit a high round-trip efficiency of 77%	Pt can facilitate OER during charge	The high cost is the main concern for this promising catalysis material	[71]
Others	N4-macrocycle complex and some transition metal nitrides exhibit a high ORR activity	No obvious charging capacity	Similar to carbon materials, these material could only be used in primary batteries	[153,155]

electrochemically reversible Li_2O_2, which will severely affect the rechargeability and cycle life of aprotic lithium-air batteries (Figure 5).

Ethers are also attractive for lithium-air batteries because they combine the following attributes: capable of operating with a lithium anode, stable to a high oxidation potential over 4.5 V versus Li/Li^+, safe, inexpensive and low volatility in the case of higher molecular weights, such as tetraglyme [77]. In contrast to carbonate-based electrolyte, studies by Read and Abraham showed that the discharge products were Li_2O_2 and Li_2O, depending on the applied discharging voltage. However, recent work by Bruce et al. indicated that although the ethers are more stable than organic carbonates [58,82], Li_2O_2 only forms on the first discharge and ethers electrolyte still undergoes decomposition, giving a mixture of Li_2CO_3, HCO_2Li, CH_3CO_2Li, polyethers/esters, CO_2, and H_2O. Especially after only five cycles, Li_2O_2 was almost not found and replaced by Li_2CO_3 and other products. Therefore, neither carbonate nor ether based electrolyte is suitable for Li-O_2 batteries and

Table 5 Main materials challenges facing aprotic Li-O_2 battery.

Facts	Status	Challenges	Possible solutions
Cathode materials	Various carbon materials	Discharge products clogging; low catalytic behavior; poor charging property; avoid humidification (air)	Porous network electrode structure; effective ORR catalysts; effective OER catalysts; membrane or hydrophic electrolytes
Electrolyte materials	Carbonates or ethers based electrolytes	The electrochemical instability (the decomposition); high volatility; low conductivity; low O_2 solubility	Novel electrolyte materials
Anode materials	Lithium metal	Dendrite formation; safety problems. or pre-coating; pre-lithiated Li alloy (such as Li_xSi)	Solid electrolyte interface layer via self-formation

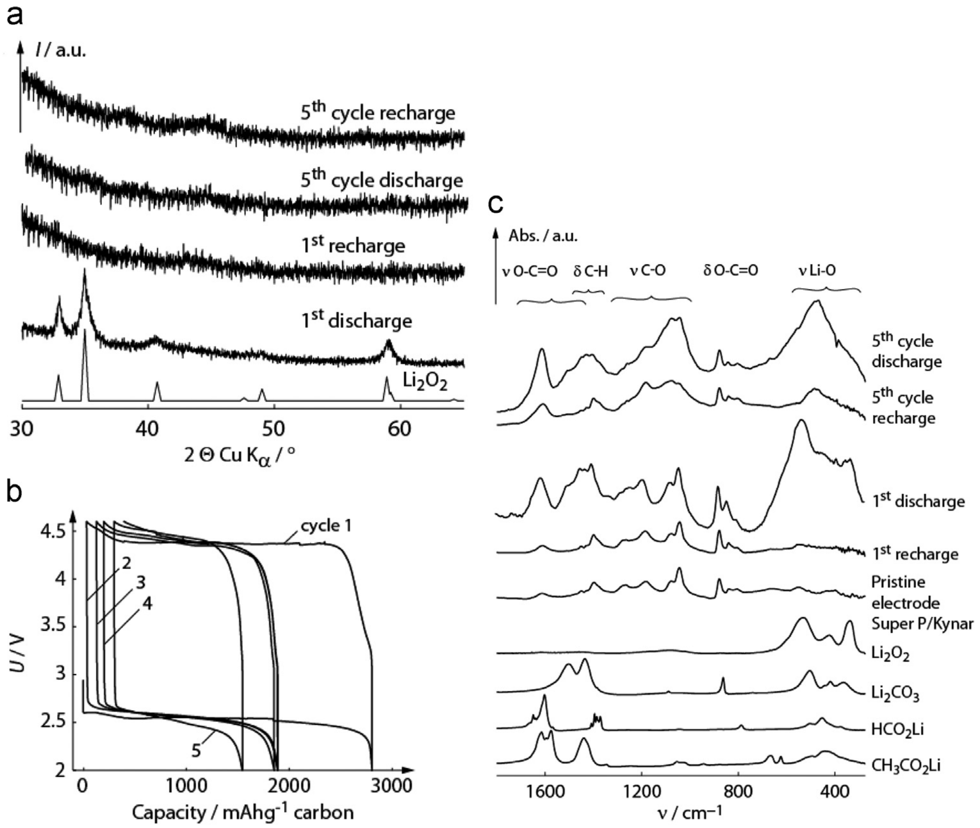


Figure 5 (a) Powder X-ray diffraction patterns of the composite cathode (Super P/Kynar) cycled in 1M $LiPF_6$ in tetraglyme under 1 atm O_2 between 2 and 4.6 V versus Li/Li+, rate = 70 m Ag^{-1}. (b) Load curves for the same cell. (c) FTIR spectra of the composite cathode (Super P/Kynar) cycled in 1 m LiPF6 in tetraglyme under 1 atm O_2 between 2 and 4.6 V versus Li/Li^+. Reproduced from Ref. [54] with permission. Copyright 2011 Wiley-VCH Verlag GmbH & Co.

identifying solvents resistant to attack by reduced O_2 species remains a major challenge.

Effect of electrolytes on performance

The influence of solvents on the kinetics of the ORR products and/or the nature of the oxidation reactions in the lithium-air batteries is now recognized [46,53,76,77,83,84]. Many physical and chemical properties of solvents including the evaporation rate, moisture absorption rate by solvents and electrolytes, chemical stability of solvents with Li metal, viscosity, ionic conductivity, O_2 solubility in the electrolytes, and contact angle of electrolyte on the air electrode can affect the electrode reaction kinetic and the resulting electrochemical performance of lithium-air batteries.

First, it was found that electrolyte formulation has a dramatic influence on cell performance [74,85]. In a lithium-oxygen battery system, oxygen transport in the electrolyte is responsible for effective electrode reactions; those electrolytes having high oxygen solubility and high oxygen diffusivity result in high discharge capacity and good rate capability. The above factors such as oxygen solubility, dynamic viscosity, and ion conductivity were also found to be related with applied current density during lithium-air batteries operation. For example, a study with ether-based electrolytes containing four different electrolyte salts indicated that discharge capacity at a high current density (e.g. 0.5 mA/cm^2) was determined by dynamic viscosity alone, while discharge capacity at relatively low current densities (e.g. 0.2 and 0.05 mA/cm^2) shows no correlation with either oxygen solubility, dynamic viscosity, or conductivity [74]. Meanwhile, the result also indicated that once a certain level of oxygen solubility is reached, it is no longer an important factor in determining discharge capacity, and viscosity becomes the determining factor.

In addition to electrolyte formulation, co-solvent was also found to be helpful in electrochemical reaction in lithium-air system. Oxygen reduction reaction in lithium-air battery can be divided into three steps: (1) dissolution of gaseous oxygen into the electrolyte, (2) diffusion of dissolved oxygen into catalytic sites of the electrode surface, and (3) catalytic reduction of oxygen into Li_2O_2. Clearly, the first step of the dissolution of oxygen is critical for overall electrode reaction. Perfluoro solvents have been considered as a good liquid medium for oxygen due to fast dissolution kinetics and high solubility of oxygen in these compounds [86,87]. Zhang recently applied methyl nonafluorobutyl ether (MFE) and tris(2,2,2-trifluoroethyl) phosphite (TTFP) as a co-solvent for the aprotic electrolyte of lithium-air battery and it enhances discharge performance of lithium-air batteries, including both specific capacity and rate capability [88].

Furthermore, the improvement in ionic conductivity of electrolytes can enhance the lithium-air batteries performance. Crown ethers, especially 12-crown-4 and 15-crown-5, have the capability to coordinate with lithium ions, thus increasing the ionic conductivity of the electrolyte and improving battery performance [89-91]. For example, when the content of crown ether increases to 15 wt% in the electrolytes, both 12-crown-4 and 15-crown-5 largely increase the capacity of lithium-air batteries over the control electrolyte by 28% and 16%, respectively. Moreover, the content and types of crown ethers have a big influence on the performance of lithium-air batteries because the combined effects of the changes in the electrolyte's contact angle, oxygen solubility, viscosity, ionic conductivity, and the stability of complexes formed between the crown ether molecules and lithium ions [75]. For example, adding 18-crown-6 in the electrolytes was found to lead to a continuous decrease in cell capacity.

It has been confirmed that the insoluble reduction products lead to cell failure due to pore blocking in the cathode. Therefore, a solvent with high solubility of discharge products is more desirable for improvement of specific discharge capacity and cycle life. Recently methoxybenzene has been demonstrated an increased solubility of lithium oxide. The primary lithium-air batteries with electrolytes containing methoxybenzene demonstrate significantly higher discharge capacities than cells with electrolytes containing no methoxybenzene [92].

Reasons for instability of electrolyte

Organic carbonate-based electrolytes have been the most widely used in lithium-air batteries to date. However, as we discussed above, such electrolytes decompose during discharge process. Ethers are more stable than carbonates at the beginning cycles, however, still undergo the decomposition during cycling [93,94]. Understanding the decomposition mechanism and development of novel electrolytes with high stability is critical for the lithium-air batteries. Currently, some important progress has been made in understanding the instability and decomposition mechanism.

The true discharge products were determined and confirmed when electrolytes undergo decomposition. Recent work by Bruce indicated that the aprotic rechargeable lithium-air battery containing an alkyl carbonate electrolyte discharges by formation of $C_3H_6(OCO_2Li)_2$, Li_2CO_3, HCO_2Li, CH_3CO_2Li, CO_2, and H_2O at the cathode, due to electrolyte decomposition. Similar discharge products were also identified by other researchers [55,60,83,84,95-97]. For example, X-ray diffraction analysis by Zhang et al. showed that regardless of discharge depth lithium alkylcarbonates (lithium propylenedicarbonate (LPDC), or lithium ethylenedicarbonate (LEDC), with other related derivatives) and lithium carbonate (Li_2CO_3) are constantly the main discharge products, while lithium peroxide (Li_2O_2) or lithium oxide (Li_2O) is hardly detected.

Further, a charging process study indicated that the charging process reactions involves oxidation of $C_3H_6(OCO_2Li)_2$, Li_2CO_3, HCO_2Li, CH_3CO_2Li accompanied by CO_2 and H_2O evolution [58]. These discharge/charge reactions are found to be irreversible because the pathways for discharge are different from the charge process. In situ gas chromatography/mass spectroscopy analysis revealed that Li_2CO_3 and Li_2O cannot be oxidized even when charged to 4.6 V versus Li/Li^+, while Li_2O_2 easily oxidizes to form O_2 with high efficiency, but lithium alkylcarbonates (e.g. LEDC and LPDC) are oxidizable to release mainly CO_2 and CO [83]. The irreversible discharge/charge behavior correlates with the widely observed voltage gap in lithium-air batteries, which will seriously affect the columbic efficiency, rechargeability, and even cycle life. These electrochemically irreversible products (e.g. HCO_2Li, CH_3CO_2Li, Li_2CO_3, and $C_3H_6(OCO_2Li)_2$) will accumulate in the cathode on cycling, correlating with capacity fading and cell failure alongside electrolyte consumption. Such a failure mechanism is compounded by consumption of the electrolyte on each cycle, bringing big challenges for lithium-air battery.

The formation of these carbonate species has been hypothesized based on the reaction of Li_2O_2 with either carbonates or CO_2 gas in the presence of trace moisture, or the decomposition of the carbonate solvent through reactions with the O_2 radicals or superoxide anions that are formed during the initial O_2 reduction. There is increasing evidence that cyclic and linear carbonates, commonly used solvents in Li ion battery electrolytes, are unstable in the presence of superoxides. Density functional theory calculations also indicates that nucleophilic attack by O_2^- at the O-alkyl carbon is a common mechanism of decomposition of organic carbonates [59,98]. Furthermore, Li_2O_2 irreversibly decomposes the carbonate solvent, leading to alkyl carbonates (Figure 6) [99]. A stable electrolyte that does not lead to an irreversible by-product formation due to O_2^- attack in an organic electrolyte is necessary for truly rechargeable aprotic lithium-air batteries. Nevertheless,

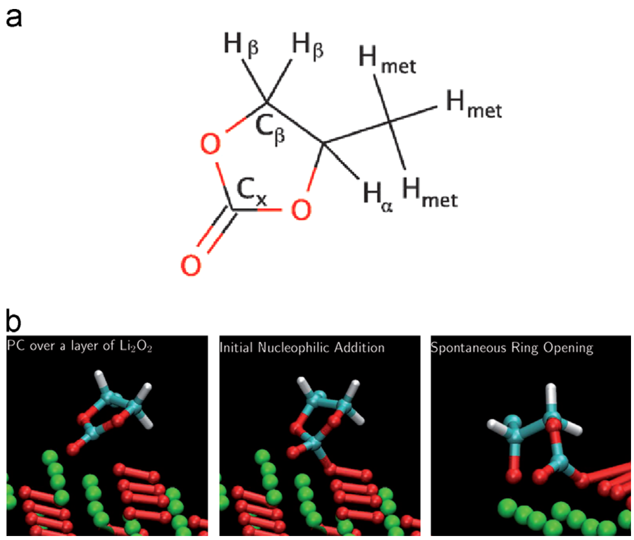


Figure 6 (a) Chemical structure of propylene carbonate (PC), with the relevant position when reacting with Li_2O_2 in evidence (Cx, Cb: carboxylic carbon and ester carbon, respectively, subject to nucleophilic attack, Ha, Hb, Hmet subject to hydrogen abstraction). (b) Representative snapshots for the reactivity of PC with a surface [100] of Li_2O_2. Lithium ions are shown in green, carbon in cyan, oxygen in red and hydrogen in white. Reproduced from Ref. [99] with permission. Copyright 2012 Wiley-VCH Verlag GmbH & Co. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

current understanding of this process is still in its infancy and more systematic work remains in order to reveal the underlying mechanism.

Several possible solutions

Both carbonates and ethers electrolytes decompose to Li-alkyl carbonates and Li_2CO_3 during the operation of lithium-air batteries, which compelled us to search for alternative electrolyte systems for lithium-air batteries.

Ionic liquids

The use of room temperature ionic liquids (RTILs) in aprotic lithium-air batteries is attractive due to their low flammability, hydrophobic nature, low vapor pressure, wide potential window, and high thermal stability. In particular, the extended anodic voltage window in RTILs is of interest as the presence of cathode catalysts, frequently employed in the lithium-air system, can shorten the potential window of many organic electrolytes (e.g. carbonate solvents) and affect cell performance. Some research efforts have already utilized ionic liquids as electrolyte systems [100,101]. Kuboki et al. [101] used 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide in lithium-air cells. The hydrophobicity and negligible vapor pressure of the ionic liquids make it a promising candidate as a waterproof electrolyte for lithium-air battery [102-104]. The authors reported high discharge capacities greater than 5000 mAh/g carbon when very low discharge currents (0.01 mA/cm^2) were applied. The compact structure and stable interface resistance are in favor of long-time durability when the cell tested in ambient atmosphere, which may be because the ionic liquid electrolyte can effectively stabilize the interface and diminish lithium corrosion by moisture thusly giving higher discharge capacity [100].

Abraham et al. investigated the oxygen electrode rechargeability in a room-temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis(triflouromethanesulfonyl) imide (EMITFSI). The result indicated that the nature of the electrode affects the reaction mechanism, with gold showing the ability for high efficiency recharging of the oxygen electrode, as evident in multiple cycles without passivation. Ionic liquids are therefore promising electrolytes for rechargeable lithium-air batteries, and the selection of an electrolyte stable to both the Li and oxygen electrode is recognized as a major future direction of research [105].

Although ionic liquids may be employed as electrolyte solvents in lithium-air batteries cells, they have to be further modified in order to exhibit both higher electrochemical stability and lower viscosity for better ion diffusion. Currently, lower discharge capacities were found for lithium-air batteries using ionic liquids compared to carbonate-based solvents, which are attributed to their higher viscosity and hence inferior wetting of the oxygen electrode. For example, a low discharge voltage ranging from 2.0 to 2.5 V were observed for ionic liquids, while it was recorded at a higher potential range between 2.7 and 2.8 V for the carbonate-based electrolytes. Sometimes it is difficult to satisfy simultaneously requirements of electrochemical stability and low viscosity. For example, the pyrrolidinium-based ionic liquids were found to be more stable than the imidazolium-based ionic liquids, but lower discharge capacities were observed in the case of pyrrolidinium-based electrolyte systems [106]. Therefore, ionic liquids may be further modified prior to use. In addition to electrochemical performance and viscosity issues, the discharge mechanism might be different in the case of ionic liquids compared to carbonates. Furthermore, the stability and discharge product analysis also need further study.

Solid-state electrolyte

A totally solid-state lithium-air battery was demonstrated by Kumar et al., which used a highly Li-ion conductive solid electrolyte membrane laminate fabricated from glass- and polymer-ceramic materials as the electrolyte. This electrolyte has a high stability when exposed to moisture, a wide electrochemical window, and an excellent thermal stability, showing a good rechargeability in lithium-air battery systems at a wide operated temperature range. Nevertheless, the electrochemical stability study and product analysis are still scarce. The low electrochemical performance resulting from the low ion conductivity of the solid-state electrolyte need to be further improved. This solid-state lithium-air battery system with excellent reversibility deserves further development and study [42,43].

Oligoether-functionalized silane electrolytes

In contrast to carbonate-based electrolytes, ether-based ones indeed exhibit higher stability. By further functionalization and modifications, the stability of ether-based electrolytes may be enhanced. Recently, Amine et al. [107] combined experimental and computational study on an electrolyte based on tri(ethylene glycol)-substituted trimethylsilane (1NM3), and an oligoether-functionalized silane, thus providing a further evidence that the ethers are more stable toward oxygen reduction discharge species than propylene carbonate (PC). X-ray photoelectron spectroscopy (XPS) and FTIR experiments show that only lithium oxides and no carbonates are formed when 1NM3 electrolyte is used. This study provides a new direction to improve the stability of electrolytes by functionalization and modifications.

Polysiloxanes

Polysiloxanes containing oligo- (ethylene oxide) groups are good candidates for electrolytes, having desired properties such as low glass transition temperatures, effective ionic transport, low viscosity, and good conductivity in the presence of lithium ions, although the conductivity still needs improvement. Amine et al. recently employed quantum chemical method to study polysiloxanes oxidation potentials and decomposition reactions. These studies suggest that the Si–O group provides enhanced stability for siloxanes over their carbon analogs, and the siloxanes species are found to be more resistant to thermal decomposition compared to carbonates. Therefore, they hold potential as electrolytes in high energy density lithium–air batteries [108].

Nano cathode materials' status, challenges and opportunities

Nanostructured electrode

Currently, lithium–air batteries have been reported to have a higher specific capacity than most other batteries systems, but the rate capability, cycle life, and power performance of lithium–air batteries are still not satisfied for practical applications [109]. Some of the major obstacles are limiting oxygen solubility and diffusion, accumulation of reaction products, and the lack of effective 3-phase electrochemical interface, which are directly determined by electrode structure design [110]. A porous electrode with optimum porosity and effective catalysis site distribution for maximization of materials' utilization is desirable. In addition to optimizing the air electrode composition which may affect the cathode porosity, [111] more efforts should be devoted towards designing a novel porous air electrode (Figure 7).

Zhang simulated and analyzed several air electrode designs including single pore system, dual pore system in two dimensions, and dual pore system with multiple time-release catalysts. Some important parameters including the porosity distribution, pore connectivity, the tortuosity of the pore system, and the catalyst spatial distribution were studied in detail. The results indicated that the dual pore system offers advantages for improving oxygen transport into the inner regions of the air electrode. When coupled with multiple time-release catalysts, the system can substantially extend the duration at higher powers, and result in maximum utilization of air electrode materials [112]. Considering the requirement of porous structure and available void volume for discharge products, numerous efforts have been devoted to designing a novel porous air electrode with maximum void volume [113,114]. Shao-horn's group developed all-carbon-nanofiber porous electrode with highly efficient utilization of carbon material and void volume for lithium–air batteries which was found to yield high gravimetric energies of four times higher than lithium-ion batteries [113]. A similar freestanding carbon nanotube/nanofiber mixed buckypaper was also devepoped and applied in lithium–air batteries [115].

In addition to the void volume, oxygen diffusion in air electrode also plays an important role in battery performance. Recently, a porous carbon microstructure based on GNSs was developed by Zhang et al. With functionalization, the hierarchical arrangement of functional graphene

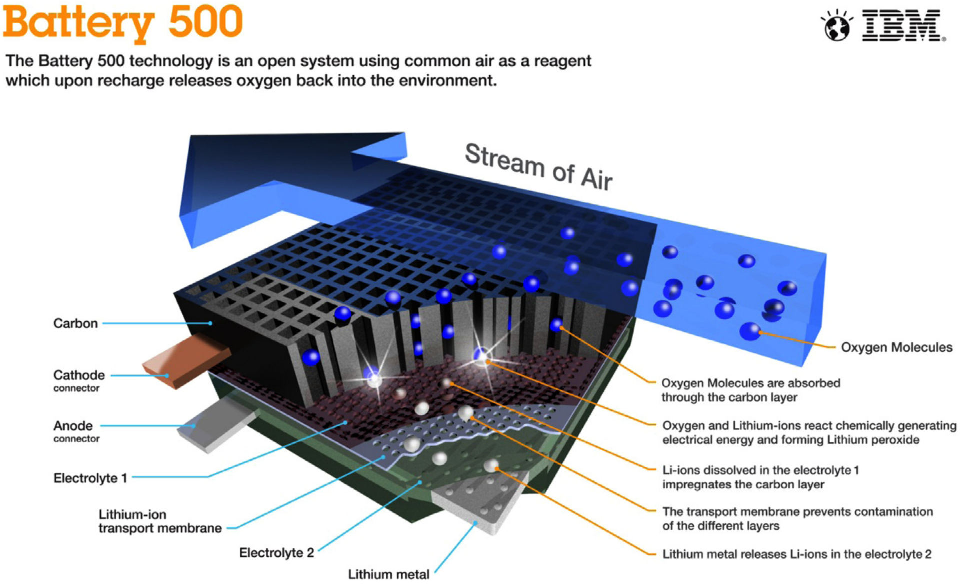


Figure 7 The structure design of an air-breathing lithium–air battery developed by IBM.

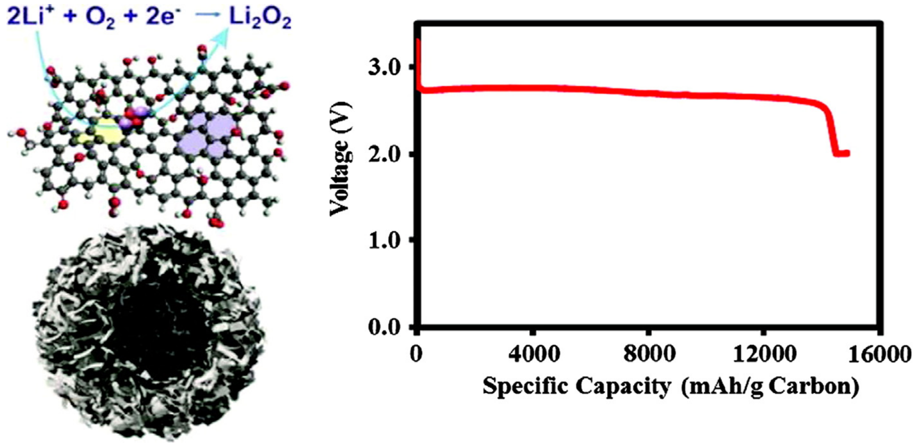


Figure 8 SEM images of as-prepared FGSs air electrodes at different magnifications. Reproduced with permission from Ref. [116]. Copyright 2011 American Chemical Society.

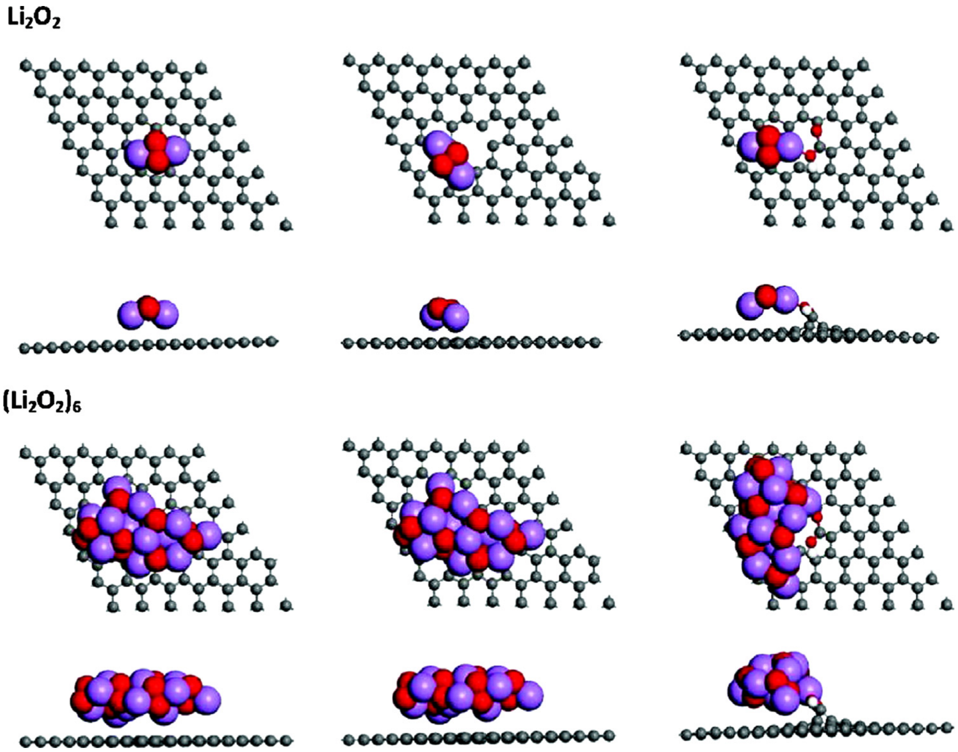


Figure 9 Top and side views of optimized structures of Li_2O_2 and $(Li_2O_2)_6$ clusters on perfect graphene (left column), the 5 8 5 defect graphene (middle column), and the 5 8 5 defect graphene with bound COOH group (right column). In each structure, the top and side views are shown in the upper and the lower panel, respectively. The color scheme is as follows: carbon atoms are in gray, lithium atoms are in purple, and oxygen atoms are in red. Reproduced with permission from Ref. [116]. Copyright 2011 American Chemical Society. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

nanosheets (FGSs) (Figures 8 and 9) [116] aggregated into loosely packed, "broken egg" structures with large interconnected tunnels which can function as numerous arteries that continuously supply oxygen into the interior of the electrode during the discharge process. Therefore, the lithium-air battery with this novel electrode delivers an exceptionally high capacity of 15,000 mAh g^{-1}, which is the highest value ever reported.

Another strategy to enhance the accessible void volume and oxygen diffusion rate is decreasing the additive carbon and binders' amount. For example, a novel free-standing type cathode was designed by a simple chemical deposition method, and the new air electrode exhibited a noticeably higher specific capacity and improved cycle efficiency compared to the conventional carbon-supported electrode (Figure 10) [117]. Without additional carbon and binders,

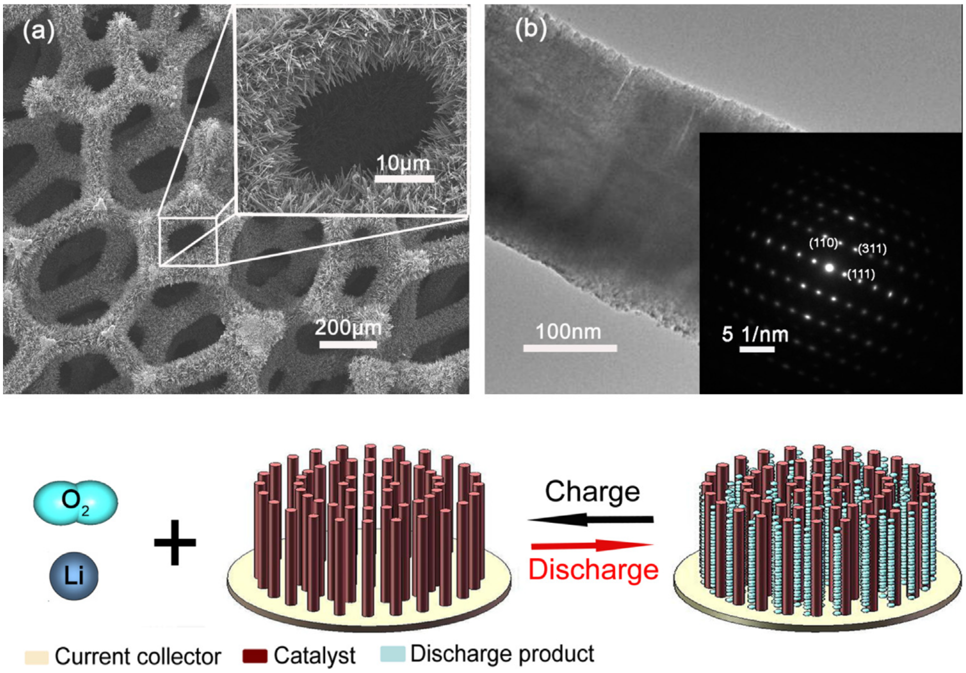


Figure 10 (a) The schematic diagram of the free-standing-catalyst based electrode during cycling in the Li-O_2 battery. SEM images of Co_3O_4@Ni. (b) TEM image and SAED patterns of the Co_3O_4 nanorods. Reproduced with permission from Ref. [117]. Copyright Royal Society of Chemistry 2011.

this 3D electrode provides abundant catalytic sites, intimate electronic contact and open pore system for unrestricted access of the reactant oxygen molecules.

Nano catalysis materials

One of the big challenges for the lithium-air battery is the limited electrical efficiency which is due to the overpotential or polarization losses at the cathode during discharge and charge. A high potential is needed for charging (~4.5 V) the porous carbon electrode whereas the discharge potential is around 2.5 V; the big difference between these two values leads to a low efficiency. The improvement of this efficiency may be expected by applying effective catalysts. Although recent reports doubt the efficacy of electrocatalysis in nonaqueous lithium-air batteries considering the electrolyte solvent decomposition [118], most reports indicate that by applying catalysts, which are both good for oxygen reduction reaction during discharge and oxygen evolution during charge, the round-trip efficiency will be dramatically increased, thus increasing the battery performance [119,120]. Therefore, we also reviewed here current catalyst development in lithium-air battery system including carbon-based material, metal oxides, noble metal, etc. (Table 4) (Figure 11).

Carbon nanomaterials

Various carbon materials have been applied as the air electrode for lithium-air batteries and systematic studies have been performed. Commercial carbon powders were first studied as cathode materials for lithium-air batteries by Xiao et al. [66,121,122] and the results indicated that the uniformity of the pore sizes also plays an important role in determining the electrochemical performances of the lithium-air batteries. The large volume expansion in the Ketjen black (KB)-based electrode led to extra triphase regions to facilitate the reaction in the electrode and extra volume to hold the reaction product. Consequently, batteries using KB-based air electrode exhibited the highest specific capacity (851 mAh/g) among all samples.

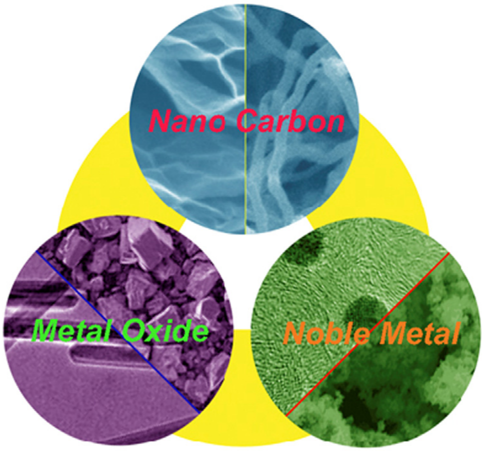


Figure 11 The category of catalysis materials in current aprotic lithium-air batteries.

Further, the porosity is also an important factor. It is reported that mesopores carbon material is more desirable for lithium-air battery application. Xia et al. synthesized mesocellular carbon foam (MCF-C) with narrow pore size distribution (30 nm) through a nanocasting method by using mesocellular foam silica as a template [123]. The MCF-C delivered a discharge capacity of 2500 mAh/g, about 40% higher than that of Super P at current density of 0.1 mA/cm^2. Compared to commercial carbon powder materials, MCF-C has a hollow structure that possesses much larger mesopores, which is beneficial on accommodating discharge product. Similar conclusions were also reached by other reports. Hall et al. [122] recently prepared mesoporous carbon aerogels with tunable porosity by the polycondensation of resorcinol with formaldehyde. The discharge capacity of the porous carbons showed that the appropriate pore volume and pore diameter are the key factors contributing to high capacity.

In addition to the carbon porosity and structure, the carbon nature also affects the catalysis in lithium-air battery system. The doping of the carbon with nitrogen atoms has drawn much attention because conjugation between the nitrogen lone-pair electrons and graphene π-systems may create nanostructures with desired properties such as improved oxygen reduction reaction activity [124,125]. Furthermore, recent studies also indicate that the nitrogen functionality on carbon is responsible for the electrocatalytic activity of cathode and enhancement in cell capacity of lithium-air battery [126,127].

1D carbon nanomaterials (nanotube, nanofibres) have been widely studied in various electrochemical energy systems such as fuel cells, supercapacitors, and batteries due to their superior properties. For the same reason, these 1D carbon nanomaterials also exhibit good performance in lithium-air battery applications. For example, aligned carbon nanofibers (CNFs) electrodes were fabricated using atmospheric pressure chemical vapor deposition (CVD) on porous anodized aluminum oxide (AAO) substrates coated with thin layers of Ta and Fe [113]. It was found that the unique properties of the CNF electrodes, including high electronic conductivity, high void volume, and an interconnected, well-developed pore structure play significant roles in determining the battery performance.

Similar to doping in common carbon materials discussed above, doping also moderates some advanced carbon nanomaterials such as carbon nanotubes. Sun et al. compared pristine carbon nanotubes (CNTs) and nitrogen-doped carbon nanotubes (N-CNTs) as cathode materials in aprotic lithium-air batteries (Figure 12) [128]. Interestingly, the N-CNTs electrodes exhibited significantly enhanced performance relative to the pristine CNTs. The N-CNTs electrode delivers an initial discharge capacity of 866 mAh/g, which is about 1.5 times that of the CNTs electrode (590 mAh g^{-}1). In addition, the discharge average voltage plateau of N-CNTs is about 0.1 V higher than that of CNTs, indicating a higher oxygen reduction reaction activity on the N-CNTs electrode [126-130]. Therefore, these nitrogen-doped carbon nanotubes have more potential in future lithium-air battery applications.

As the hottest carbon material currently, graphene nanosheets also exhibit superior property in lithium-air batteries field [131]. Sun et al. prepared graphene nanosheets (GNSs) with a thin, wrinkled structure by the oxidation of graphite powder using modified Hummers' method [132]. The GNSs electrode delivers a capacity of 8705.9 mAh/g, which is due to its unique morphology and structure. This electrode increases the electrochemically accessible site and provides a large diffusion path for the oxygen, therefore, significantly improving the discharge capacity. After discharge, the products deposit on both sides of the GNSs (Figure 13), and at the edges of the GNSs, a relatively darker/thicker color is observed (marked by arrows), suggesting more products on the edge sites. This is because the edge sites of GNSs contain a large amount

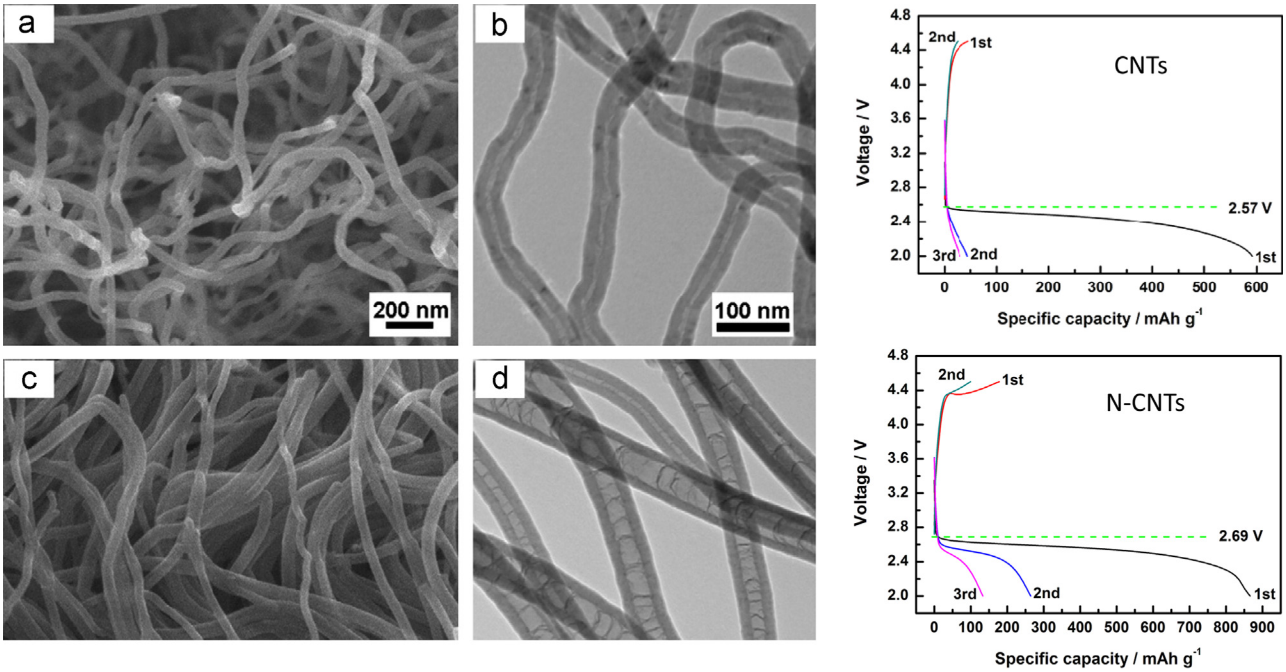


Figure 12 The SEM images and voltage profiles of CNTs (a and b) and N-CNTs (c and d) electrodes cycled in a voltage range of 2.0-4.5 V at a current density of 75 mA g^{-1} in the first three cycles. Reprinted from Ref. [128] with permission. Copyright 2011 Elsevier.

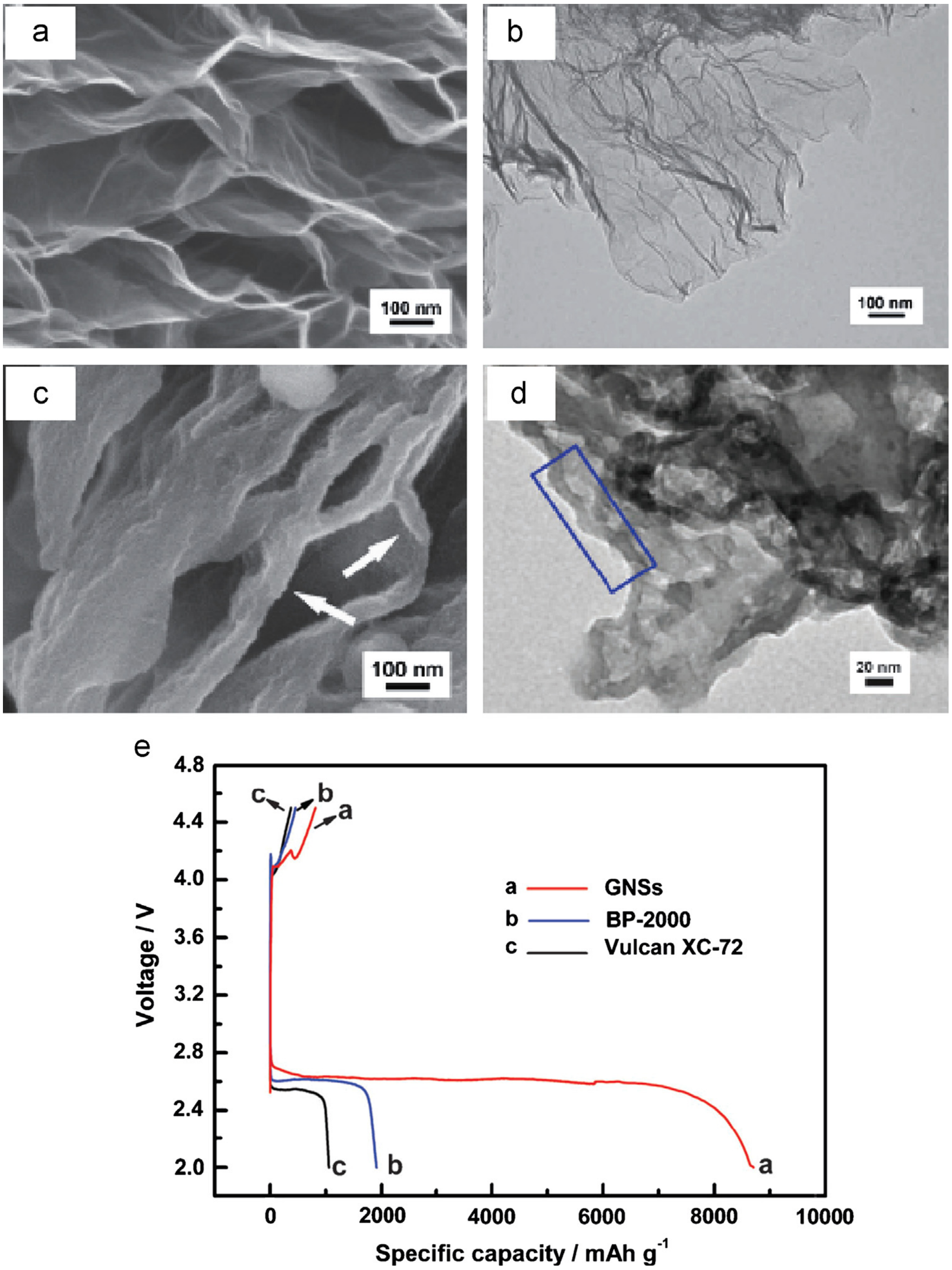


Figure 13 SEM and TEM images of GNSs electrodes before (a and b) and after (c and d) discharge; (e) discharge/charge performance of lithium-oxygen batteries with different carbon cathodes at a current density of 75 mA g^{-1}. Reprinted from Ref. [132] with permission. Copyright Royal Society of Chemistry 2011.

unsaturated carbon atoms which are very active to oxygen, improving activity for oxygen reduction reaction [133]. They further increased the battery performance by employing nitrogen-doped graphene nanosheets (N-GNSs) as cathode materials (Figure 14). Interestingly, the size of the discharge product on N-GNSs is much smaller than those on GNSs which is due to the introduced defective sites by nitrogen doping [134]. More recently, X. Sun employed sulfur-doped graphene nanosheets as cathode materials for lithium-oxygen batteries and found that the morphology of the discharge product was significantly different (nanorods) from the pristine graphene electrode (particles). An improved charging performance was obtained in sulfur-doped graphene. The morphology and distribution of discharge products Li_2O_2 is critical to further catalytic effects, and toward the goal of tailoring the Li_2O_2 properties to battery performance, it is important to select or design optimal growth of Li_2O_2 via substrate control, and therefore improve the discharge and charge properties of the batteries (Figure 15) [135].

Metal oxide nanocatalysts

Transition metal oxides, including Fe_2O_3, Fe_3O_4, NiO, CuO, Co_3O_4, $CoFe_2O_4$, etc., have been employed as catalysts in lithium-air batteries by Bruce [136]. Among them, Fe_2O_3

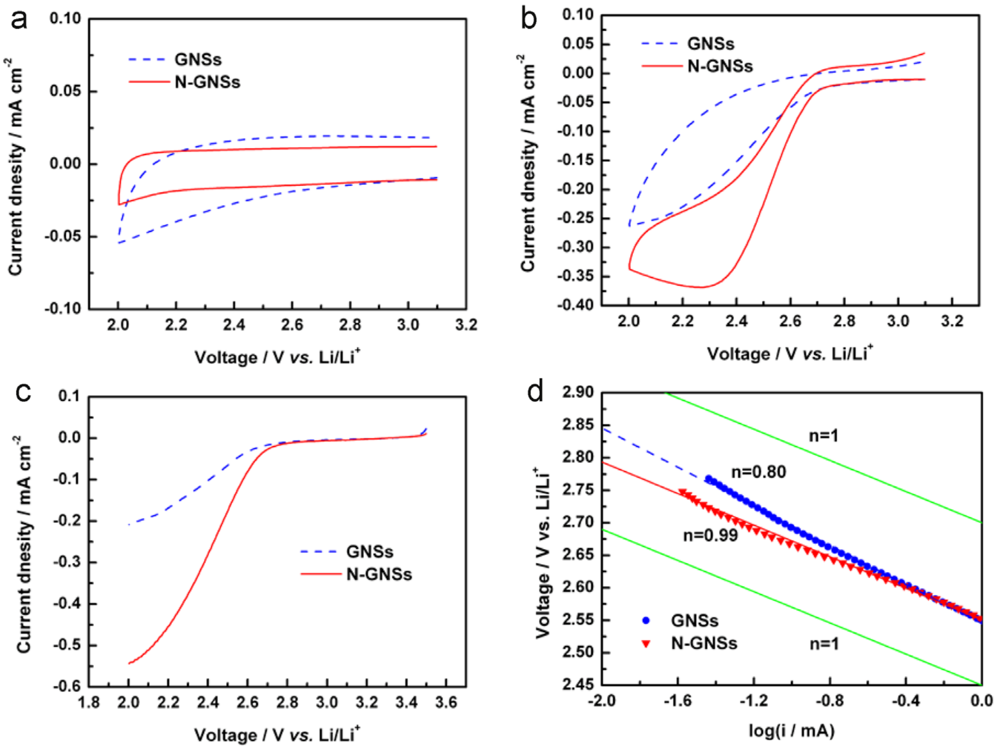


Figure 14 (a) Voltage profiles of GNSs and N-GNSs electrodes at various current densities; (b) CVs of GNSs and N-GNSs electrodes in O_2-saturated 0.1 mol dm^{-3} LiPF6 in TEGDME solution at a scan rate of 5 mV s^{-1}, inset is the CVs in Ar-saturated solution; (c) rotating-disk electrode voltamograms recorded for GNSs and N-GNSs electrodes for ORR at a rotating speed of 100 rpm in O_2-saturated 0.1 mol dm^{-3} $LiPF_6$ in TEGDME solution at a scan rate of 5 mV s^{-1}; (d) Tafel-slops for the ORR on the GNSs and N-GNSs electrodes. Reprinted from Ref. [134] with permission. Copyright 2011 Elsevier.

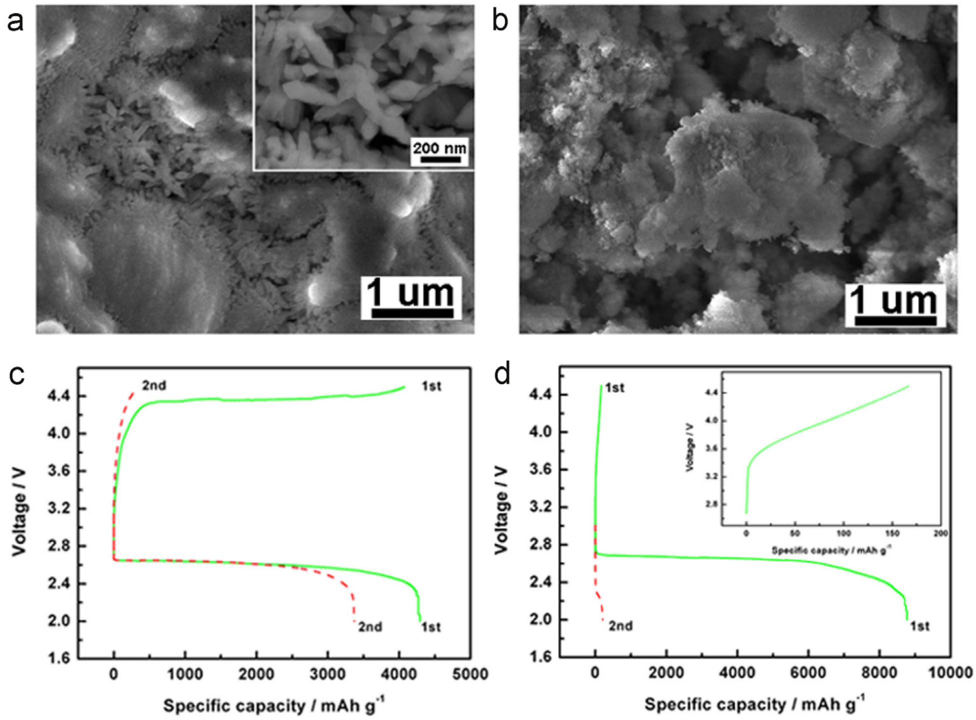


Figure 15 SEM images of (a) sulfur-doped and (b) pristine graphene discharged electrodes and the discharge/charge curves for (c) sulfur-doped and (d) pristine graphene. Reprinted from Ref. [135] with permission. Copyright Royal Society of Chemistry 2012.

exhibits the highest initial discharge capacity, while Fe_3O_4, CuO and $CoFe_2O_4$ give the best capacity retention. Co_3O_4 shows the best compromise between the discharge capacity and the retention [137,138]. However, the reaction mechanism for these findings is still unclear and more detailed investigations are required.

Introduced by Bruce et al., manganese oxides are the most studied catalysts for lithium-air battery [139]. They compared several types of MnO_x, including α-MnO_2 nanowires, β-MnO_2 nanowires, bulk MnO_2 (α, β, γ, λ), and commercial Mn_2O_3 and Mn_3O_4 and found that α-MnO_2 nanowires are the most effective catalysts for rechargeable lithium-air battery due to their special crystal structure and high surface area (Figure 16). Zheng et al. prepared a composite electrode by mixing α-MnO_2 nanorods with carbon nanotubes/nanofibers and demonstrated that the charge capacity and cyclability of the battery were largely increased with the catalyst [69]. The reason is that the α-MnO_2 reacts with discharge product Li_2O to form Li_2MnO_3 during discharge, while the Li_2O could be electrochemically removed from $LiMnO_3$ during charge. Guan et al. synthesized α-MnO_2 nanoflakes coated on multi-walled carbon nanotubes (MWNTs) and used this composite as cathode for lithium-air batteries [140]. The MnO_2/MWNTs cathode exhibits a low charge potential of 3.8 V, dramatically improving the energy efficiency and cyclic ability. The MnO_2 catalysts with different morphologies were also applied for lithium-oxygen batteries [141-143].

In addition to MnO_2, considering the side reactions and instability of propylene carbonate electrolytes, Bruce et al. explored lithium-metal oxides with a high formal Li_2O content such as Li_5FeO_4 ($5Li_2O \cdot Fe_2O_3$), Li_2MnO_3, and $LiFeO_2$ composite ($Li_2O \cdot MnO_2$) ($Li_2O \cdot Fe_2O_3$) as electrocatalysts for lithium-oxygen cells, resulting in very high discharge capacities [144].

In addition to oxygen reduction reaction, an effective charging process reaction is even more important for the reversibility of lithium-air batteries. Thus, a bifunctional catalyst with high catalytic behavior for both ORR and OER is vital. Amongst metal oxides materials, a recent report indicated $CoMn_2O_4$ nanoparticles to have good ORR and OER catalytic activities [145]. Goodenough also further improved its electron transport ability by applying graphene as supports and growth substrate for $CoMn_2O_4$ spinel nanoparticles obtaining for lithium-air batteries with high energy density [70,146].

Noble metal nanocatalysts

An important breakthrough to improve the charging efficiency of lithium-air batteries was made by Shao-Horn et al. who reported that gold (Au) can enhance the ORR during discharge, and Pt can facilitate OER during charge (Figure 17) [72,147-151]. They further demonstrated that the Pt-Au alloy particles can serve as bifunctional catalysts, leading to a high round-trip efficiency of 77%. The discharge voltage of electrode with PtAu/C is higher than that of Vulcan XC-72 carbon electrode, while the average charge voltage of PtAu/C is 3.6 V which is 900 mV lower than that of carbon (~4.5 V). This finding evoked ample research interests on noble catalysts for lithium-air batteries. For example, Tatsumi et al. investigated the catalysis of noble Pd, mixed noble Pd and several metal oxides or metals for cost reduction as well as the improvement of discharge performance [152,153]. It was found that by adding MnO_2 to the electrode, the discharge plateau of the battery increases to 2.9-2.7 V, while the charge potential decreases to 3.6 V, leading to a high specific energy efficiency of 82%.

Similar to fuel cell field, noble catalyst may exhibit superior catalytic activity for ORR and OER, deserving further study to improve the electrochemical performance of lithium-air batteries. However, the high cost and limited source of noble metal have to be considered in future application in lithium-air batteries system.

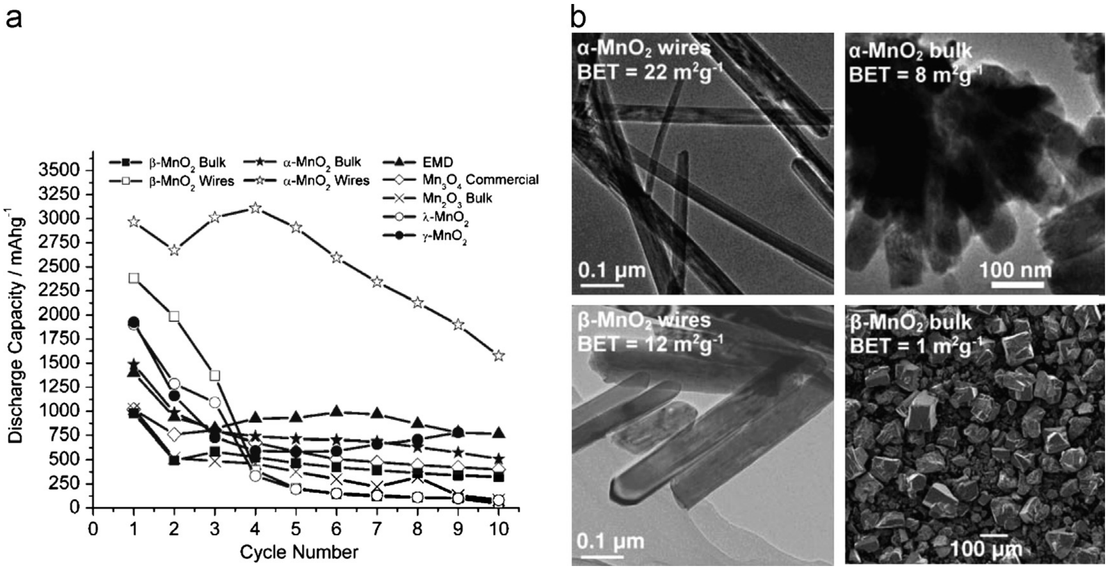


Figure 16 (a) Variation of discharge capacity with cycle number for several electrodes containing different manganese oxides as catalysts; (b) SEM and TEM images of various MnO_2 materials. Reproduced from Ref. [139] with permission. Copyright 2008 Wiley-VCH Verlag GmbH & Co.

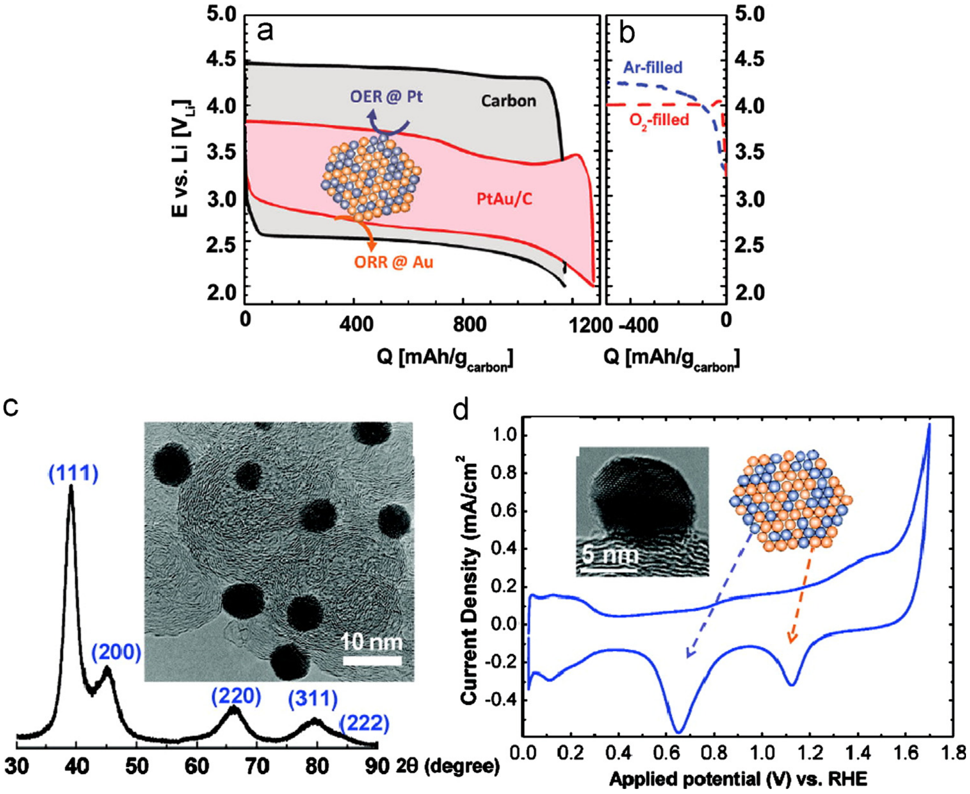


Figure 17 (a) Lithium-air cell discharge/charge profiles of carbon and PtAu/C in the third cycle at 0.04 mA cm^{-2} electrode. (b) Background measurement during charging at 100 mA g^{-1} carbon of Ar- and O_2-filled cells for PtAu/C. (c) XRD and TEM of PtAu/C. (d) CV of PtAu/C. Reproduced with permission from Ref. [71]. Copyright 2010 American Chemical Society.

Others nanocatalysts

Transition metal N4-macrocycle complexes have long been known to be highly active for the catalytic reduction of oxygen. The heat-treated transition metal N4-macrocycle complexes have been considered as an excellent catalyst for the oxygen reduction in lithium-air batteries [154]. Some conductive polymer and composites also exhibit good catalytic activity for oxygen reduction in lithium-oxygen system [155,156]. Furthermore, some transition metal nitrides with high activities in fuel cell system have also attracted extensive attention for lithium-oxygen batteries field. Molybdenum nitride/nitrogen-doped graphene nanosheets (MoN/NGS) were synthesized and used as an alternative O_2 electrode for Li-O_2 batteries. This hybrid cathode exhibits a high discharge potential (around 3.1 V) and a considerable specific capacity of 1490 mAh/g [157]. Nano-sized $La_{0.8}Sr_{0.2}MnO_3$ was recently reported as an effective catalyst for oxygen reduction reaction in Li-oxygen batteries [158].

Catalysts supporting nanomaterials

In order to achieve high utilization and stabilization of nano catalytic sites for ORR and OER, catalyst supporting strategies, as those widely applied in fuel cell systems, should be systematically investigated. Generally, the requirements for catalyst support materials can be summarized as: (1) a high specific surface area, which provides high dispersion and high utilization of nano catalysts, (2) high conductivity, (3) high chemical and electrochemical stability under lithium-air operating process, and (4) low reactivity with electrolytes in lithium-air batteries system. Currently, the most popular support material in lithium-air system is carbon material due to its high conductivity, high surface area, and low cost. In the future research, efforts should be devoted to developing some novel supporting materials including oxides, carbides, nitrides, etc., to further improve the battery performance and life time. Here, we focus on two most promising categories: (1) novel carbon nanomaterial and nanostructure, including carbon nanotubes, doped carbon nanomaterial, graphene, 3D structured carbon material, etc., and (2) metal oxides including SnO_2, WO_3, and their composites.

Novel carbon supporting nanomaterials

Novel nanostructured carbon materials have been receiving attention for a long time as catalyst supports for fuel cells because of their unique structure and properties. For example, carbon nanotubes have provided overwhelming advantages such as higher conductivity and high stability in fuel cells, compared with common carbon black [154-163]. Further surface modification of carbon nanotubes by heteroatoms doping (B, N) or graphitized treatment improve its corrosion resistance and metal-support interaction, therefore contributing to higher electrochemical stability in fuel cells. Such strategies are also significant for lithium-air system [164-167]. More recently, graphene, a novel carbon nanomaterial, has attracted much interest for energy environmental application such as lithium-air batteries and fuel cells. This material exhibits a high stability due to high graphitization. Furthermore, doped graphene without any metal catalysts has shown a high catalytic activity for ORR, thus could be a more promising electrode material for lithium-air batteries [168–173]. In addition to these novel carbon materials, novel carbon structure such as 3D vertically aligned CNTs grown on carbon paper may also act as a promising electrode support for lithium-air batteries application due to the regular pore structure and conductive paths, allowing faster electron transfer and oxygen diffusion [174–177].

Metal and metal nanooxides

Although carbon is generally considered as a good electrode material in lithium-air batteries, it may undergo corrosion/oxidation at high potentials and result in some possible side reactions in discharge/charge process in lithium-air batteries. As a result, seeking alternative support materials is important for the development of lithium-air batteries. Some metal oxides have also attracted significant attention as catalysts supporting materials due to the improved electrochemical kinetics and effective electron transport paths. For example, growth of various nanowires (TiO_x, ZrO_2, WO_3, SnO_2, Sn) directly on carbon paper may considerably improve electrical contact with the external electrical circuit and the supported catalysts' utilization in fuel cell systems [178,179]. Our group reported superior electrochemical properties of Pt and PtRu nanoparticles supported by SnO_2 nanowires directly grown on carbon paper for anodes in fuel cell applications [180]. This enhanced catalytic activity can be attributed to the unique microstructure and metal-support interaction. The strong "metal-support interaction" between SnO_2 and Pt was also reported to contribute to the improvement of ORR and possible electrochemical stability [181,182]. In addition to SnO_2, titanium oxide was also considered as a good catalyst supporting material for fuel cell applications due to its high electric conductivity and electrochemical stability [183]. For example, Ti_4O_7 in particular exhibits a high electrical conductivity of around 1000 S/cm at room temperature, which is even higher than that of some carbon materials [184]. Some other metal oxides such as WO_x and ZrO_2 have also been widely studied as catalyst supporting materials [185,186]. By designing 3D structured electrodes with directly grown metal oxides on carbon paper, one may make full use of the unique properties for fuel cells and lithium-air battery because the high gas permeability at the 3D structure can improve mass transport and oxygen accessibility. Furthermore, these metal or metal oxides themselves process certain catalytic activity for ORR, which also applies for the electrochemical reaction in lithium-air batteries. Therefore, such superior merits could also allow us to apply these metal oxide supports for lithium-air batteries system.

Anode nanomaterials

There are many challenges in the practical applications of lithium-air batteries including safety issues and their fast degradation due to decomposition and unwanted moisture issues. In particular, the highly reactive lithium must somehow be isolated from water moisture permeating to the anode part of the cell from the surrounding atmosphere. This is the main reason that recent aprotic lithium-air batteries still widely use highly pure oxygen as the active material. Considering future applications for electrical vehicles, applications of atmosphere air is necessary for reducing volume.

The perfect exclusion of water in air on the air electrode is difficult and the electrolyte may be contaminated with water in the long-term operation. Therefore, the stability of lithium anode in the electrolyte containing trace water is the most critical point for a long period operation. Currently, efforts have been made to protect the Li anode from moisture corrosion. The protection strategy for lithium metal anode in aprotic lithium-air system follows the same method as the aqueous lithium-air system. Various water-stable solid state electrolytes such as widely used NASICON-type lithium conductors and their composites with PEO-based polymers and lithium phosphorous oxynitride (LIPON) were applied and exhibit a high stability in water-containing electrolyte system [28,187,188]. However, the lithium conductivity in this solid-state electrolyte still needs to be further improved.

In addition, development of hydrophobic electrolytes is also a feasible methods. Kuboki et al. [101] found that a hydrophobic ionic liquid electrolyte, 1-ethyl-3-methylimidazolium bistrifluoromethylsulfonylamide, could prevent vaporization of the electrolyte and hydrolysis of the anode. A lithium-air battery using this electrolyte was able to discharge for 56 days at a low current rate of 0.01 mA/cm^2 in air with 60% relative humidity RH.

In addition to electrolytes, the anode lithium metal itself may be replaced by other anode material used in lithium-ion batteries such as Si or Sn [16,17], which may be pre-lithiated or lithiated in situ prior to use in lithium-air batteries. This method may improve the anode stability, but sacrifice the accessible lithium amount and decrease the actual energy density in lithium-air batteries.

Air dehydration membranes

For ambient air operation of a lithium-air battery, the most urgent problem to be solved is to prevent the side reaction of the Li anode with moisture from environmental air. Currently, lithium-air batteries under research are mainly operated in a pure O_2 environment or dry air condition [47,189–192]. Continuous supply of dry O_2 from ambient air is still a big problem in practical operation. Even trace amounts of water may induce fast corrosion of the Li anode resulting in poor battery performance and serious safety risks. Thus the development of effective air dehydration membranes is urgent for future application of this novel battery system.

Presently, commercially available air electrodes for metal-air batteries are usually laminated with a layer of porous polytetrafluoroethylene (PTFE) membrane as a water barrier [193]. The surface hydrophobicity of PTFE is necessary to prevent water vapor condensation from ambient air and its subsequent penetration into the membrane, but is not sufficient to obtain a selective permeation of O_2 over H_2O molecules [194].

Recently, an O_2-selective hydrophobic membrane was developed by introducing an O_2-selective coating layer on hydrophobic membrane. Such an O_2-selective membrane allows O_2

or N_2 to diffuse through the lithium-air battery while rejecting moisture from ambient air [195]. The lithium-air battery equipped with the selective membrane showed a much better performance in ambient air operation(20% RH) than the reference battery tested in a dry air box (1% RH). The similar O_2-selective membrane was also developed by loading O_2-selective silicone oils into porous supports such as porous metal sheets and Teflon (PTFE) films. The immobilized silicone oil membrane in the porous PTFE film enabled the lithium-air batteries with carbon black air electrodes to operate in ambient air (at 20% RH) for 16.3 days with a specific capacity of 789 mA hg^{-1} carbon and a specific energy of 2182 Wh/kg carbon. Its performance is much better than a reference battery assembled with a commercial, porous PTFE diffusion membranes as the moisture barrier layer on the cathode, which only had a discharge time of 5.5 days corresponding to a specific capacity of 267 mAh/g carbon and a specific energy of 704 Wh/kg carbon [10]. Although this selective membrane shows a good selectivity, the oxygen permeation is usually low. For example, Reynolds et al. [196] prepared immobilized polyperflurocarbon liquid into a polymer Celgard 2500 porous substrate and obtained an O_2/H_2O selectivity of 3.9, but the O_2 permeance was low. This will prevent the battery from discharging at high current density due to limited O_2 supply.

Although it is a promising method for future lithium-air batteries to use a membrane that is selective to O_2 while preventing moisture from entering the battery, it is challenging because O_2 and H_2O cannot be easily separated due to the higher diffusivity of H_2O than O_2 and smaller kinetic diameter of H_2O than O_2. Current air dehydration membranes are far away from practical applications in lithium-air batteries system, and await future development of lithium-air batteries which use surrounding air.

Collectors materials

Currently the majority of lithium-air studies have used Ni current collectors [197], which were recently found to promote the decomposition of $LiPF_6$-organic carbonate electrolytes under normal charging conditions reported for rechargeable lithium-air cells and conceivably for other electrolytes as well. The degradation of the electrolyte will directly impact the capacity, rechargeability, and the lifetime of a rechargeable lithium-air battery. Ni in contact with the electrolyte should be used with caution at potentials greater than 3.5 V. Partially coating the Ni and Ni-free porous carbon supports can reduce the extent of electrolyte decomposition, so they will be more appropriate cathode current collectors. An alternative choice may be Al or a graphitic carbon structure [198].

Recent breakthroughs

The performance of non-aqueous lithium-air battery has been limited by poor cycle life, which is mainly due to the instability (decomposition and side-reactions) of electrolyte systems such as organic carbonates and ethers. As a result, the choice of a stable electrolyte is the key for developing lithium-air battery. Recently, important breakthroughs have been made in improving the cycle and rate performance in lithium-air batteries just before this review was submitted. Y.-K. Sun and B. Scrosati applied a tetra(ethylene) glycol dimethyl ether-lithium triflate (TEGDME-$1LiCF_3SO_3$) electrolyte (a glymes-based electrolyte mainly for use in lithium-sulfur cells) in an advanced oxygen electrode [199]. It was demonstrated that the lithium-air battery was capable of operating 100 cycles with capacity and rate values as high as 5000 mAh/g_{carbon} and 3 A/g_{carbon}, respectively. Importantly, the lithium diffusion coefficient is comparable to the values commonly reported for most cathodes presently used in lithium-ion batteries, which contributes to a high rate capability for lithium-air batteries. The authors suggested that the unique behavior originates from the stable electrolyte and oxygen electrode design.

More recently, P.G. Bruce reported a reversible and higher-rate lithium-oxygen battery (Figure 18) [200]. In the battery, a 0.1 M $LiClO_4$ in dimethyl sulfoxide electrolyte and a nanoporous gold electrode were applied. Nanoporous gold electrode lowers the charging potential and more effectively promotes Li_2O_2 oxidation than carbon electrode. The kinetics of Li_2O_2 oxidation on charge is approximately 10 times faster than on carbon electrodes. The battery can exhibit 300 mA h/g (based on the mass of Au) at a current density of 500 mA h/g, corresponding to ~3000 mA h/g (based on the mass of carbon), and sustain superior reversible cycling, retaining 95% of its capacity after 100 cycles. The discharge product analysis confirmed 99% purity of Li_2O_2 formation at the cathode, even on the 100th cycle. These big breakthroughs will evoke more studies in non-aqueous lithium-air batteries. In addition, as to the analysis of electrochemical reaction products, a recent report by C.P. Gray and P.G. Bruce demonstrated that solid-state NMR

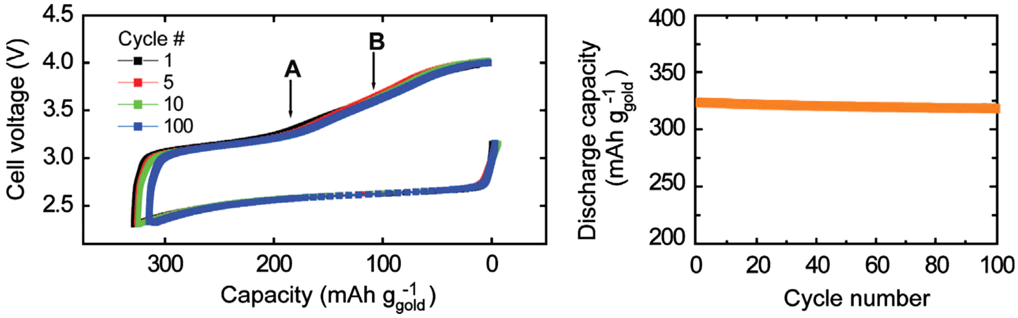


Figure 18 Charge/discharge curves (left) and cycling profile (right) for a Li-O_2 cell with a 0.1 M $LiClO_4$-DMSO electrolyte and a NPG cathode, at a current density of 500 mAg^{-1} (based on the mass of Au). Reproduced with permission from Ref. [200]. Copyright 2012 by the American Association for the Advancement of Science.

(ssNMR) spectroscopy (especially ^{17}O NMR spectroscopy) is an effective tool to study the electrochemical products formed in lithium-air batteries because ^{17}O NMR spectra provides clear information for the major discharge products such as Li_2O_2 and Li_2CO_3 [201].

Conclusions and perspective

Aprotic lithium-air batteries have received much attention as potential energy system for future electric vehicle applications. Although this technology has the potential to provide higher energy density than current lithium-ion system, it is still in the developmental stages, and far away from its practical application due to many challenges reviewed here. Understanding of this novel electrochemical energy system is still largely incomplete. Numerous systematic and detailed studies especially in material research direction are still required to promote the progress of this technique. In our opinion, some key aspects are urgent for the development and eventual commercialization of the rechargeable aprotic lithium-air battery.

Further fundamental studies about the electrochemical reaction process and mechanism in various electrolytes systems (e.g. aprotic, aqueous and hybrid electrolytes) are required to better understand this novel energy system, which will guide us on developing novel electrode materials including electrolytes, cathode materials, separator, and anode (Table 5).

Development of novel electrolyte materials with high electrochemical stability, high oxygen solubility/diffusivity, high ion conductivity and low volatility are urgent because electrolyte issues especially the electrolyte decomposition problem have been one of the big challenges inhibiting current lithium-air battery advancement. In addition, an ideal electrolyte system also needs to be hydrophobic to prohibit moisture permeation especially when surrounding air is used. Moreover, the desirable electrolyte system should maintain stable with contact with lithium metal anode. Currently most of the widely used electrolyte systems in lithium-ion batteries cannot meet all the above requirements. Therefore, the modifications of existing electrolytes and search for novel electrolyte systems present new challenges for chemists and materials scientists.

Design of cathode materials/structures with improved and optimized porosity for facilitating high oxygen diffusivity and Li ion transport toward the active surface of the electrode is critical for the overall electrochemical reaction and the resulting discharge/charge capacity of the battery. In addition, research on catalysis and development of effective catalysts that facilitate both oxygen reduction reaction and oxygen evolution reaction are also important for lithium-air batteries to reduce the gap between discharging and charging potential and improve columbic efficiency. However, the practical role of catalysts in the discharge/charge process in an aprotic lithium-air battery has been doubted because the presence of highly active catalyst may catalyze the electrolyte solvent decomposition, and the catalysis contribution to oxygen evolution may be overestimated. The heterogeneous electrocatalysis in an aprotic rechargeable lithium-air battery may be more complex than conventional catalysis in fuel cells, although both cathode structures are similar. More studies are therefore necessary to truly understand it. In addition, the material stability will also be an important issue in the application of lithium-air batteries in the near future. Similar to carbon corrosion in fuel cells, carbon materials may undergo corrosion challenges as well considering the high operation potential and high oxygen circumstance in lithium-air batteries. Therefore, the development of non-carbon supporting materials such as various stable metal oxides with novel nanostructures (nanowire, nanorods, and nanotubes) will be important research directions in lithium-air batteries.

Some other issues are still needed to be studied, considering future practical applications in electric vehicles. Safety is always the most important factor for battery systems application in EV. One potential safety problem in an aprotic lithium-air battery comes from lithium metal anode. Dendrite may form at lithium metal that will cause serious safety problems and poor cycle performance. A possible solution is to introduce or create a stable solid electrolyte interphase film by the additives in electrolytes. Considering to battery weight and cost, ambient air should also be considered in the future practical battery. Moisture issue opens up new challenges for the aprotic lithium-air battery. Development of a highly selective separator is required to protect electrolytes and anode from contact eliminating possible reaction with water.

Although many challenges need to be overcome before production of a commercially available lithium-air battery, the enormous advantages with ultrahigh theoretical energy density far exceed other conventional rechargeable battery systems. More intensive research especially in material aspects deserves to devote to this promising power source.

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