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Making Li-Air Batteries Rechargeable: Material Challenges

Yuyan Shao, Fei Ding, Jie Xiao, Jian Zhang, Wu Xu, Sehkyu Park, Ji-Guang Zhang,* Yong Wang,* and Jun Liu**

A Li-air battery could potentially provide three to five times higher energy density/specific energy than conventional batteries and, thus, enable the driving range of an electric vehicle to be comparable to gasoline vehicles. However, making Li-air batteries rechargeable presents significant challenges, mostly related to the materials. Here, the key factors that influence the rechargeability of Li-air batteries are discussed with a focus on nonaqueous systems. The status and materials challenges for nonaqueous rechargeable Li-air batteries are reviewed. These include electrolytes, cathode (electrocatalysts), lithium metal anodes, and oxygen-selective membranes (oxygen supply from air). A perspective for the future of rechargeable Li-air batteries is provided.

1. Introduction

The electrification of transportation[1] and large-scale deployment of renewable energy (e.g., solar, wind)[1] have been the indispensable strategies to address the issues with global climate change, energy security, and sustainability. One of the most difficult challenges for this transformation is the unsatisfactory electrical energy storage (EES) systems.[1–3] Among various EES technologies, rechargeable batteries, especially lithium-ion batteries are attractive due to their high energy density and efficiency. However, the state-of-the-art batteries fall far behind the requirements for electric vehicles and grid energy storage. For example, current traction batteries in electric vehicles (e.g., Li-ion batteries) are still short of energy storage capacity, which severely limits the range of electric vehicles (<100 miles). After several decades of development, the energy density of Li-ion batteries increased ≈15% per year and may reach the theoretical limits soon.[4–8] In this context, in addition to the continuous investigations on advanced Li-ion batteries,[9–13] there have been great efforts in new transformational "beyond Li-ion" battery technologies[14–19] that can provide sufficient energy storage capacity for practical electric vehicles (without "range anxiety").[20] Lithium-air batteries seem to be one of the most promising battery technologies that could provide significantly enhanced energy storage capability that would be sufficient to drive electric vehicles of more than 300 miles (per charge), which is comparable to gasoline vehicles.[21] Therefore, there has been strong interest in Li-air battery technology around the world in recent years.[20,21]

The schematics of nonaqueous Li-air batteries[22] and aqueous Li-air batteries[23] are shown in **Figure 1**a,b, respectively.[24] Both of these systems have been reported to be electrically rechargeable. The fundamental electrochemical reaction at negative electrode is the same for both systems (Equation (1)). The electrochemical reactions at positive electrode depend on the environment (electrolyte) around it and so do the electrode potentials.[21,25] In the case of aqueous Li-air batteries,[21,26–31] the electrochemical reactions at positive electrodes are shown in Equation (2,3) for alkaline (neutral) and acidic systems, respectively. They are similar to cathode reactions of alkaline fuel cells (zinc-air batteries) and acidic fuel cells, respectively. In nonaqueous Li-air batteries, the desired electrochemical reaction on positive electrode is shown in Equation (4).[32–40] Here we use the term "desired electrochemical reaction" because there are other Li-O_2 reactions at oxygen electrode in nonaqueous systems that lead to various discharge products of Li-air battery,[37,40–42] but only the one in Equation (4) with Li_2O_2 as the discharge product could enable truly rechargeable Li-air batteries;[40,42] in other words, the successful formation/decomposition of Li_2O_2[38] is the prerequisite for a practical rechargeable Li-air batteries. This will be discussed in details in the Section 3.1.

Anode:

$$\text{Li} \leftrightarrow \text{Li}^+ + e^- \tag{1}$$

Cathode:

$$\text{Alkaline}\quad O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- (E_0 = 3.43\ \text{V vs Li/Li}^+) \tag{2}$$

$$\text{Acid}\quad O_2 + 4e^- + 4H^+ \leftrightarrow 2H_2O\ (E_0 = 4.26\ \text{V vs Li/Li}^+ \tag{3}$$

$$\text{Nonaqueous}\quad 2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2\ (E_0 = 2.96\ \text{V vs Li/Li}^+ \tag{4}$$

Dr. Y. Y. Shao, Dr. F. Ding, Dr. J. Xiao, Dr. J. Zhang,
Dr. W. Xu, Dr. S. Park, Dr. J.-G. Zhang,
Dr. Y. Wang, Dr. J. Liu
Pacific Northwest National Laboratory
Richland WA 99352, USA
E-mail: yuyan.shao@pnnl.gov;
jiguang.zhang@pnnl.gov; yong.wang@pnnl.gov;
jun.liu@pnnl.gov

Dr. F. Ding
National Key Laboratory of Power Sources
Tianjin Institute of Power Sources
Tianjin 300381, P. R. China

Prof. Y. Wang
The Gene and Linda Voiland School of Chemical Engineering
and Bioengineering
Washington State University
Pullman, WA 99164, USA

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The extremely high specific energy/energy density of Li-air batteries mainly comes from two factors. First, in contrast to most other batteries that must carry both the anode and cathode inside a storage system, Li-air batteries are unique in that the active cathode material (oxygen) is not stored in the battery. Instead, oxygen can be absorbed from the environment and reduced by catalytic surfaces inside the air electrode. In practical Li-air batteries, carbon-based air electrodes are sometimes also called the cathode for convenience. Its main function is to provide a triple phase region to facilitate the Li-O_2 reaction and host the reaction products.[43–45] Second, the anode material (lithium metal) of Li-air batteries has the highest specific capacity (3862 mAh/g) and the lowest electrochemcial potential (–3.04 V vs. SHE[46]), which corresponds to the highest voltage when reacting with oxygen. Recently, a team at the Pacific Northwest National Laboratory (PNNL) demonstrated a primary nonaqueous Li-air battery of 362 Wh/kg based on the whole cell weight and working for 33 days in ambient air with a humidity of 20% RH (there is still much room for improvement by the optimization of the cell structure and materials),[47] while the current well-developed Li-ion batteries have cell-based specific energies of only ≈200 Wh/kg. A hierarchically porous graphene oxygen electrode with a high capacity of 15 000 mAh/g has also been reported for primary nonaqueous Li-air battery from this team.[48] A well-developed nonaqueous Li-air battery could potentially provide a specific energy of 500–1000 Wh/kg, which is at least 2–5 times greater than the present Li-ion batteries.[49,50] However, in order to compete with Li-ion batteries, Li-air batteries need to be rechargeable. Therefore, intensive efforts have been made worldwide to explore the rechargeability of Li-air batteries. We want to point out that most Li-air batteries in research labs are tested in pure oxygen in order to avoid contaminants from air (especially water). Therefore, "Li-air" and "Li-oxygen", and, "air cathode" and "oxygen cathode" are usually used without differentiation unless specified.

Making a Li-air battery truely rechargeable presents significant challenges, especially for cell component materials. As we will discuss in the following sections, most of the key components still cannot meet the requirements for practical rechargeable Li-air batteries. These components include electrolytes (both solvents and lithium salts), cathodes/catalysts/binders, anodes and oxygen-selective membranes for oxygen supply from air. Furthermore, these components interplay with each other, which further complicates the investigation on individual components. For example, in a nonaqueous Li-air battery, some electrolytes are stable with the anode, but they are not stable with the cathode, especially in an oxygen-rich environment.

In the last a few years, several review articles on Li-air batteries have been published from different perspectives.[21,28,44,45,49–52] Here, we will focus on the critical issues that must be understood and addressed to make Li-air batteries truly rechargeable. Except for a briefly summary on the challenges in aqueous Li-air batteries (Section 2), most part of this review will discuss various issues related to the rechargeability of nonaqueous Li-air bateries. These issues include: 1) electrolytes, 2) air electrode material and strucure, 3) catalysts, 4) lithium metal anodes, and 5) oxygen selective membranes. We understand that other components such as seperators[53–55] and corrent collectors[56] are also important, but, at least at the present stage, they are not the core research activities in the field. Therefore, these are not included here. The last section of this review gives a perspecitive on the future challenges and opportunites for rechargeable Li-air batteries.

Dr. Ji-Guang (Jason) Zhang is a Laboratory Fellow at the Energy and Environment Directorate of the Pacific Northwest National Laboratory (PNNL). Currently, he is the group leader for PNNL's efforts in the area of Energy Storage for Mobil Applications. His research interests are in the development of energy storage and energy efficient devices, including lithium-air batteries, lithium-ion batteries, thin-film solid-state batteries, and electrochromic devices.

Dr. Jun Liu is a Laboratory Fellow at the Pacific Northwest National Laboratory and leader for the Transformational Materials Science Initiative. Dr. Liu's main research interest is the synthesis of functional nanomaterials for energy storage, catalysis, environmental separation, and health care.

Yong Wang graduated with PhD in Chemical Engineering at Washington State University (WSU) in 1993, and joined PNNL in 1994. He recently assumed a joint position at WSU and PNNL, continuing to be a Laboratory Fellow at PNNL and being the Voiland Distinguished Professor in Chemical Engineering at WSU. Dr. Wang is best known for his leadership in the development of novel catalytic materials and reaction engineering for the conversion of fossil and biomass feedstock.

2. Challenges in Aqueous Li-air Batteries

In aqueous Li-air batteries, water and/or H^+/OH^- also participate in the reactions as shown in Equation (2,3). Considering all the reactants shown in the left side of the Equation (2–4),

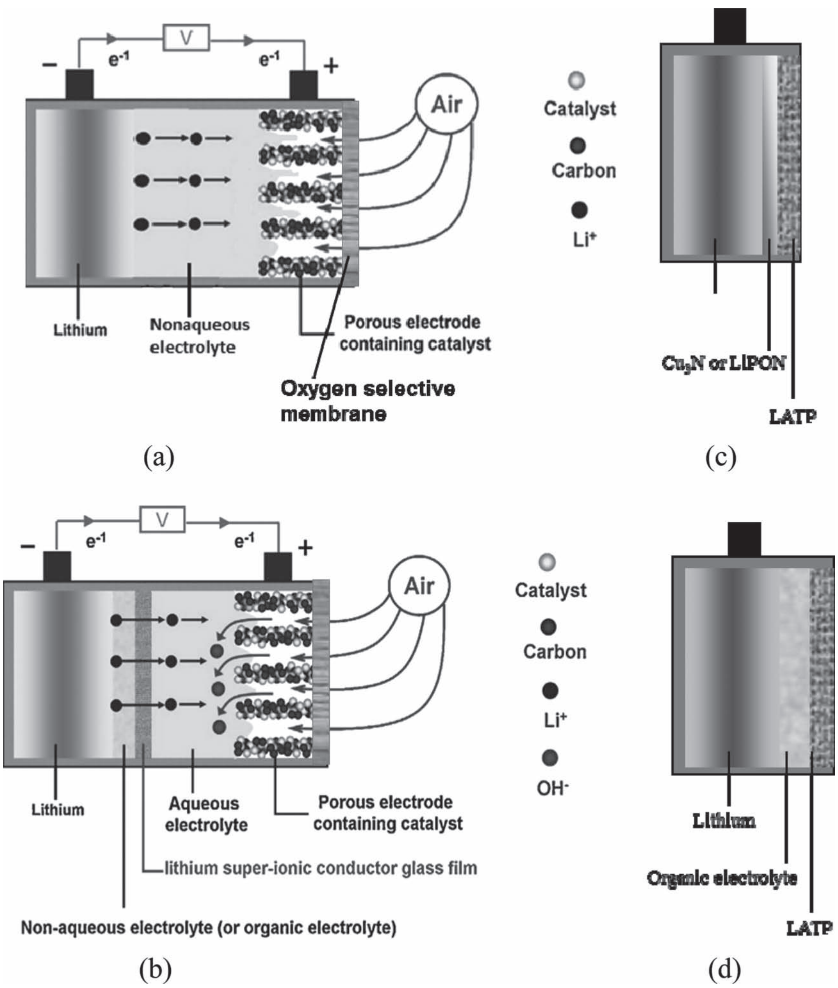


Figure 1. a) Structure scheme of a nonaqueous Li-air battery system. b) Structure scheme of an aqueous Li-air battery. c) Original Polyplus protected lithium electrode structure with solid thin film as interlayer. d) Protected lithium electrode with organic electrolytes as the interfacial layer. Reproduced with permission.[24] Copyright 2010, Elsevier.

nonaqueous Li-air batteries exhibit higher theoretical energy density than aqueous systems[29,57] and have attracted the most effort worldwide to date.[21,29,57] Therefore, in addition to the short discussion on the status and challenges of aqueous Li-air batteries in this section, we will focus on nonaqueous Li-air batteries in the following sections.

For aqueous Li-air batteries, great effort and progress have been made since the pioneering work by Visco and colleagues.[58] It is well known that lithium metal will react violently with water. Solid electrolytes, such as NASICON glass ($\mathrm{Li}_{1+x+y}\,\mathrm{Al}_x\mathrm{Ti}_{2-x}\,\mathrm{Si}_y\mathrm{P}_{3-y}\mathrm{O}_{12}$ or LATP) made by Ohara Inc. (Japan) have good lithium-ion conductivity (≈10^{-4} S cm^{-1}) and are impermeable to water. However, this material is not stable when in contact with lithium metal. Visco et al.[58] first solved this problem by depositing a solid-state interfacial layer ($\mathrm{Cu_3N}$, Lipon, etc.) between lithium metal and NASICON glass, thus forming a protected lithium electrode (PLE) as shown in Figure 1c. Imanishi's group also did extensive studies on the stability of such a lithium anode using LiPON as the interfacial layer.[59]

Based on the PLE concept, several groups[24,31,60] used an organic liquid or polymer electrolyte as the interfacial layer between lithium metal and LATP glass, forming a triple electrolyte structure (organic electrolyte/LATP glass/aqueous electrolyte) or hybrid electrolyte (Figure 1d). Both organic liquid electrolytes and polymer electrolytes have demonstrated similar performances to those with LiPON or $\mathrm{Cu_3N}$ films. Since the structure in Figure 1d is easier to prepare in research laboratories, this PLE architecture has been used in most aqueous Li-air battery studies.

For long-term cycling of a rechargeable Li-air battery, LATP glass (and other water-impermeable solid state electrolyte) needs to be highly stable in aqueous electrolytes with a large range of pH values. Therefore, the chemical stability of LATP glass in neutral (LiCl or $\mathrm{LiNO_3}$ electrolyte),[61] acidic (HCl, lithium acetate electrolyte and phosphate buffer electrolyte),[30,61–63] and alkaline electrolytes (LiOH electrolyte)[61,64] have been extensively investigated. It is found that LATP glass will be corroded rapidly in acidic or alkaline electrolytes, while this glass is more stable in the neutral electrolytes (pH value from 4 to 10). The buffer acid electrolyte and saturated alkaline electrolyte are both useful to protect the LATP glass.[62,64] Zhou and co-workers[60] suggested a fuel cell design to control the electrolyte pH value and to protect the LATP glass. Wolfenstine[65] tried to use potential-pH diagram to predict LATP glass stability in an aqueous electrolyte and it was discovered that a simple potential–pH diagram for water cannot accurately predict the stability of solid Li-ion conducting membranes in aqueous environments.

Since the naked proton ($\mathrm{H^+}$) is smaller than $\mathrm{Li^+}$ ion (the ion transfer in LATP does not involve solvation shell), there is a concern that a proton may transfer through LATP (although it may be slow) and be reduced by lithium metal to form hydrogen, which is detrimental for long term stability and presents safety issues in Li-air batteries. Our recent inveistigation indicated that the $\mathrm{H^+}$ ion cannot go through the LATP glass, and further confirmed the stability of the PLE structure in the neutral electrolytes.[66]

On the cathode side, Zhou's group studied several novel catalysts and cabon materials, including Cu catalyst,[67] titanium nitride catalyst,[68] and graphene.[26] Cu metal was first suggested as a catalyst in air electrode based on the copper-corrosion mechanism. They also reported that aqueous Li-$\mathrm{O_2}$ batteries using a graphene-based air electrode exhibit good discharge performances. Meanwhile, Zhou and co-workers also suggested a titanium electrode for the cathode charging process, which reduces the charge overpotential of the air cathode.[27] The fundamental reaction at an aqueous Li-air cathode is similar to that in a Zn-air battery (or a fuel cell). Therefore the widely developed oxygen electrocatalysts in the later systems can be used in aqueous Li-air batteries[26,60,69–71] and there are already several excellent reviews on this topic.[72–74]

Although aqueous Li-air batteries show good promise and much progress has been made, significant challenges still exist for their practical applications. The first challenge is the long-term stability of protected lithium anode in aqueous electrolytes. Several methods have been proposed to keep the electrolyte pH value stable (close to neutral) to minimize the corrosion of the LATP glass.[60,62,64] Since cation/anion exchange membranes can suppress the anion/cation going through the membrane, these membranes can be used to control the pH value on the LATP glass surface if such a film can be attached to the LATP glass. However, even in a neutral electrolyte, slight corrosion of LATP glass has already been observed.[61] The long-term (e.g., >1 year) stability of LATP glass has not been demonstrated.

The second challenge in aqueous Li-air batteries is the battery rate performance (this is also true or even worse for nonaqueous Li-air batteries). The limited conductivity of the LATP glass restricts the current densities of anodes to only a few mA per cm^2 at room temperatures. In addition to further improve the conductivity of the LATP glass by optimizing their composition and synthesis conditions, Yamamoto[31] proposed to operate Li-air batteries with LATP glass at elevated temperatures to increase the conductivity of the glass. However, the high temperature system has additional problems, such as electrolyte evaperation and quicker corrosion of LATP glass.

The third challenge in aqueous Li-air batteries is the precipitation of LiOH in cathode. During the discharge process, LiOH will become saturated in electrolyte and precipitate on the cathode. It will block the air channel and reduces the active area of cathodes. Novel cathode design that could minimize the electrode blocking is needed. More air channels, higher effective area and proper pore size of air cathodes are all very important.

Other challenges for rechargeable aqueous Li-air batteries include 1) water balance, 2) low discharge/charge efficiency, and 3) CO_2 contamination from air. As discussed in Section 3.5, oxygen-selective membranes might be applicable to address the issues with water evaporation and CO_2 contamination.

3. Challenges in Nonaqueous Li-Air Batteries

3.1. Electrolytes

Although various nonaqueous electrolytes have been widely investigated and used in lithium batteries in the past decades,[75] most of the these investigations are performed in a closed and oxygen-starving environment typical for Li-ion batteries. Several new barriers have to be overcome before application of nonaqueous electrolytes in Li-air batteries. First, the electrochemical stability of these electrolytes have to be re-examined in an oxygen-rich environment. Secondly, these electrolytes have to be less sensitive to moisture and other impurities. In other words, in addition to the typical requirements for electrolytes used in Li-ion batteries[75] (e.g., high ionic conductivity, electronic insulativity, wide electrochemical window, etc.), electrolytes used in Li-air batteries should have the following characteristics:[21,49] 1) high stability in oxygen-rich electrochemical conditions,[35,37,41,76–78] 2) high boiling point/low vapor pressure, and 3) high oxygen solubility and diffusivity.[79] Ideally, they also should be able to dissolve the Li-O_2 reaction products (such as Li_2O_2), at least partially.

Since the Li-air battery is still in its early stage of the development, there is still no perfect electrolyte that can meet all the requirements. However, it is possible to explore a proper electrolyte in several stages. First, we need to identify or synthesis the electrolytes that are electrochemically stable in an oxygen-rich environement. Once a stable electrolyte (which does not react with oxygen and its intermediates but facilitates elecrochemcial reaction between lithium and oxygen) is identified, and only after that, can a meaningful catalysts study for the formation and decomposition of Li_2O_2 be carried out; otherwise, high-performance catalysts may accelerate the electrolyte decomposition process as reported by Bruce and co-workers.[36] They demonstrated that the electrolyte (ether based) decomposition becomes more severe when a catalyst (α-MnO_2 nanowires) is used. Therefore, in the following of this section, we will focus on the stability of electrolytes in oxygen-rich electrochemical conditions, i.e., the decomposition of electrolytes by Li-O_2 reaction intermediates and products. The side reactions are affected not only by the selection of organic solvents, but also by the selection of lithium salts. At the end of this section, we will briefly disscuss other requirements for electrolytes.

3.1.1. Instability of Organic Carbonate Solvents

Carbonate-based organic electrolytes such as propylene carbonate (PC) have been widely studied in Li-air batteries, mostly because carbonate mixtures are the dominating electrolyte solvents in Li-ion batteries and PC has a wide liquid-temperature range from –50 to 240 °C and a low volatility. Li_2O_2 was assumed or claimed to be the discharge product in previous publications.[80–82] However, in 2010, Mizuno et al. reported that the discharge products of Li-O_2 cells using PC-based electrolytes were mainly lithium carbonates, instead of the desired Li_2O_2.[41,77] Since then several groups have confirmed this result and reported that the carbonate-based solvents that were widely used in Li-air batteries before are not stable in oxygen-rich electrochemical conditions.[33,35,37,39–41,83] In fact, the issue of the possible instability of this kind of solvents in Li-air battery has been pointed out by Read almost a decade before,[84,85] and later experimentally observed by Kuboki et al.[86] (unfortunately, Kuboki et al.[86] attributed the observed Li_2CO_3 in the Li-O_2 discharge product only to the side reaction with CO_2 in air). Before that, the decomposition of organic solvents (e.g., PC, γ-butyrolactone) by intermediates/products of electrochemical reduction of oxygen (with/without Li^+) had been reported by Aurbach et al. in the 1980s and 1990s.[87,88]

The intermediates during oxygen reduction (Li-O_2 reactions), e.g., O_2^-, O_2^{2-}, LiO_2/LiO_2^-,[89] can react with other chemicals in many different ways, e.g., as a strong nucleophile, a Brønsted base, a one-electron reductant, and an oxidant.[90–95] They can easily decompose most organic solvents. Therefore, the main discharge products of a Li-air battery are Li_2CO_3, lithium alkyl carbonates, and/or LiOH when the carbonate based electrolytes

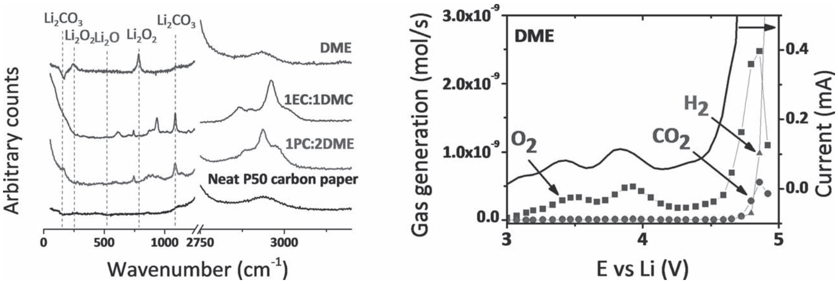


Figure 2. Raman spectra of discharged carbon cathodes in Li-O_2 cell based on DME, 1EC:1DMC, and 1PC:2DME. Gas evolution and current vs. cell voltage curves during a 0.075 mV/s linear oxidative potential scan of a discharged DME-based cell. Reproduced with permission.[35] Copyright 2011, American Chemical Society.

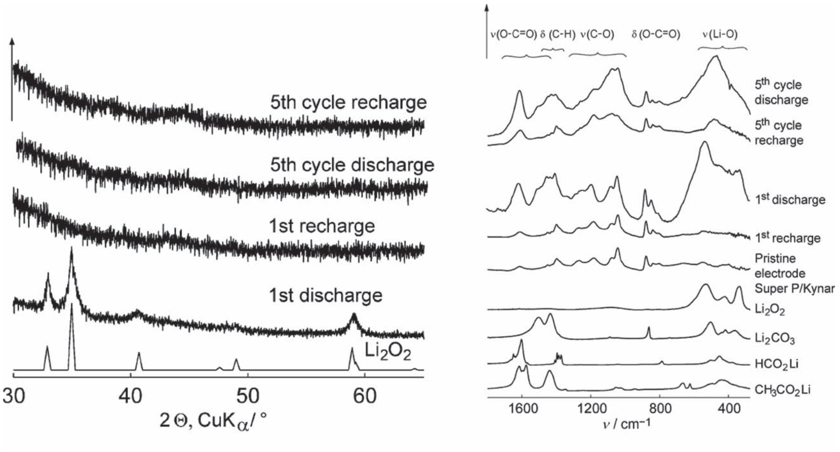
are used in the batteries. In contrast, the desired rechargeable compound, Li_2O_2, is not the main product in these reactions.[37,96] The decomposition of solvents and the resultant formation of lithium carbonates/LiOH are the main reasons for the low energy efficiency of a Li-air battery. A Li-O_2 cell with a relatively stable electrolyte, which is expected to produce Li_2O_2 as the main discharge product, has shown much lower charge voltages.[78,97] Furthermore, the side reactions lead to the contineous and irreversible consumption of electrolytes and therefore the battery is fundamentally nonrechargeable.

3.1.2. Higher Stability of Ethers Based Solvents

After realizing the instability issue of carbonates based electrolytes, alternative solvents have been investigated both experimentally[33,35,78,98–105] and theoretically.[83,106,107] Various ether based solvents have been investigated. McCloskey et al[35] studied the discharge-charge behavior of DME-based Li-air cell using multiple tools such as XRD, Raman and differential electrochemical mass spectrometry (DEMS) with isotope labeled oxygen atoms (^{18}O), which allowed them to analyze the discharge products and gas evolution during charge. The main discharge product was observed to be Li_2O_2 (**Figure 2**). However, the coulombic efficiency for oxygen evolution over oxygen reduction was only about 60%, which means the reversibility is very low. It is worthy noting that they only reported the results of the first discharge-charge cycle. They argued that the low coulombic efficiency could be due to a slow thermochemical or electrochemical reaction between Li_2O_2 and DME, but the true reasons remain illusive (according to the results of Xu et al., the reaction between commercial Li_2O_2 and solvents, even carbonates, is very little[76]). Here, we want to point out that the characterization tools have their own limitations, especially XRD and Raman. Some side-reaction products might not be detectable using these techniques. This can be seen from the report of Bruce and co-workers[99] in which XRD shows Li_2O_2 as the only discharge product, but FTIR, NMR, and mass spectroscopy show the presence of side reaction products such as lithium carbonates. This indicates that the multiple characterization tools are required to get the conclusive results on the reaction products in Li-air batteries.

Bruce and co-workers[99] studied a series of ether-based electrolytes (tetraglyme, triglyme, diglyme, 1,3-dioxolane, and 2-methyl-THF). Li_2O_2 was observed as the main products in the 1st-cycle discharge, but the percentage of Li_2O_2 in total products was found to decrease significantly during cycling; at the 5th discharge, no Li_2O_2 was observed (but other lithium compounds were observed in discharge products) (**Figure 3**). This is due to the accumulation of side-reaction products. We think this might also be true for DME-based Li-O_2 cells because of similarity of DME molecular and other ethers.

Recent reports from Amine, Curtiss, and co-workers[101] showed that oligoether substituted silanes such as tri(ethylene glycol)-substituted trimethylsilane (1NM3) were resistant to Li-O_2 reaction products. Based on their XPS characterization, the authors claimed that only lithium oxides were formed during discharge, and no lithium carbonates. The theoretical calculations on the stability of oligoether substituted silanes also support the experimental observation. The computed energy barriers for the reactions between Li-O_2 reaction products/intermediates and 1NM3 were always positive and much higher than those for PC. Interestingly, they found that LiO_2^- was the most reactive species, even more reactive than O_2^-, which is believed to be the first discharged species of O_2 and one intermediate in Li-O_2 reactions.[100] However no experimental evidence shows if LiO_2^- exists or not. On the other hand, the reversibility and cycling stability of 1NM3-based Li-air cells were still very poor. They attributed this to the failure to decompose all of the lithium oxide on charge since some of the lithium oxide might require a higher potential for decomposition.



(a) (b)

Figure 3. XRD patterns (a) and FTIR spectra (b) of air electrodes cycled in 1 M $LiPF_6$/Tetraglyme. Reproduced with permission.[99]

3.1.3. Other Organic Solvents

Other organic solvents have also been investigated, including acetonitrile (ACN),[100,108] dimethyl sulfoxide (DMSO),[109] and ionic liquids[110] such as *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI),[78] 1-ethyl-3-methylimidazolium bis(triflouromethanesulfonyl)imide (EMI-TFSI),[111] and *N*-butyl-*N*-methyl pyrrolidiniumbis(trifluoromet hanesulfonyl)imide (PYR_{14}-TFSI).[112] These chemicals showed relatively high stability toward Li-O_2 intemediates and products. Bruce and co-workers[38] reported the successful formation/decomposition of Li_2O_2 (i.e., ORR/OER) in acetonitrile. Our new results also show that the cycling stability of ACN- and DMSO-based electrolytes is higher than other solvents. PP13-TFSI seems very stable and a PP13-TFSI based Li-air cell shows much lower charge voltage.[78] Our mass spectroscopy analysis of the discharge products in PP13-TFSI based Li-O_2 cell show exclusive evolution of oxygen and no CO_2 evolved during charge and this cell also show good cyclibility and round-trip efficiency (unpublished results).

Some of the above solvents show promise and the knowledge from these studies will definitely benefit the investigation on stable solvents (both commerical solvents and molecular design for new solvent development). However, the exclusive formation of Li_2O_2 has yet to be established.

3.1.4. Lithium Salts

The active intermediates of Li-O_2 electrochemistry (O_2^-, O_2^{2-}, LiO_2/LiO_2^-) might also react with lithium salts.[89,90,113–116] The most widely used lithium salt in Li-ion batteries, i.e., $LiPF_6$, was found to react with Li_2O_2.[114] The spectroscopic characterization of Li-O_2 cell discharge products also shows evidence of the decomposition of $LiPF_6$ during discharge.[101,117] Theoretical calculations show the possible decomposition of lithium bis(oxalato)borate (LiBOB) by oxygen reduction intemediates.[118] This has been confirmed by Nazar and co-workers,[116] who identified the discharge products of a LiBOB-based Li-O_2 cell as lithium oxalate through ex situ X-ray diffraction and infrared spectroscopic observations. They attributed this to the nucleophilic substitution reaction at the boron centre by superoxide radicals. Scheiba et al.[115] indeed showed the high stability of $LiClO_4$ in the presence of Li_2O_2. However, our studies on the cycling stability of lithium salts in oxygen-rich electrochemical conditions show that neither $LiClO_4$, $LiPF_6$, nor $LiBF_4$, LiCl are stable (unpublished results). This indicates that the instability of lithium salts (i.e., the anions of the salts) can be a problem for rechargeable Li-air batteries. However, this has not received much attention.

Since lithium salts need to be dissolved in a proper solvent, the challenge in studying the stability of lithium salts is the absence of a stable solvent which can dissolve a certain amount of vairous lithium salts. Therefore, the investigation on a stable solvent should be the first priority in the current stage. Once stable solvents are available, the stability of lithium salts should be further investigated. Ironically, on the other hand, in order to study the stability of solvents in oxygen-rich electrochemical condition (preferably in Li^+-containing condition), a lithium salt is indispensable. The chicken-egg dilemma tells that the advance in electrolytes can only be made step by step.

3.1.5. Solid Electrolytes

Solid electrolytes have been widely used in Li-ion batteries due to the advantages of safety, cost and energy density.[119,120] Recently, breakthroughs have been made to improve the conductivity of solid electrolytes to be even higher than that of liquid nonaqueous electrolytes.[121] For rechargeable Li-air batteries, solid electrolytes may provide additional advantages of high stability in oxygen-rich electrochemical conditions and low volatility.[90] Recently, there have been some efforts on investigating solid electrolytes for Li-air batteries.[90,122–126] It is worth noting that the first rechargeable Li-air battery built by Abraham and Jiang was based on a solid state electrolyte (polyacrylonitrile-based polymer electrolyte).[22] Recently, Scrosati and co-workers[90] demonstrated high reversibility of Li-O_2 reaction (low redox voltage gap and the "close to 100%" charge ratio between OER and ORR) at low currents in PEO-$LiSO_3CF_3$-based solid state electrolyte. They attributed this to the high stability of solid electrolyte and, probably, the stabilization of triplet oxygen intermediate (Li_2O_3*): the triplet oxygen has much lower potential than singlet oxygen (2.91 V vs. ≈3.9 V).[90] Kumar et al.[122] reported a Li-ion conductive solid electrolyte membrane laminate fabricated from glass–ceramic ($18.5Li_2O:6.07Al_2O_3:37.05GeO_2:37.05P_2O_5$, LAGP) and polymer–ceramic (PEO-$LiN(SO_2CF_2CF_3)_2$-Li_2O-boron nitride) materials for rechargeable Li-air batteries.[122] The solid electrolyte LAGP, when used in cathode, can also improve the cathode kinetics, which in turn improves the capacity and rate capability.[124,127] Yu and co-workers[125] used hydrophobic ionic liquid in their polymer composite electrolyte and significantly improved Li-air cell discharge capacity in ambient atmosphere.

The above reports show the promises of solid electrolytes in rechargeable Li-air batteries. However, the sustainable rechargeability of a Li-air battery has never been demonstrated (usually the cell fails or the capacity fades significantly within a few cycles). Great efforts in fundamental understanding of the capacity fading are needed. Meanwhile, the challenges associated with solid state electrolytes should be kept in mind: 1) when the electrolyte is switched from liquid to solid, it is more difficult to manage the huge volume change between discharge and charge due to its rigidity and 2) the Li-O_2 electrochemical reaction interfaces are significantly changed with solid electrolytes in liquid electrolyte. The Li-O_2 reaction takes place at the three phase region composed of gas(O_2)-solid (electrode)-liquid (electrolyte), while in solid electrolyte, Li-O_2 reaction takes place at the three phase region composed of gas(O_2)-solid (electrode)-solid (electrolyte), which may make the Li-O_2 reactions more difficult.

3.1.6. Other Factors

Above we have focused on the stability issues of electrolytes (solvents and salts) in oxygen-rich electrochemical conditions, which is currently the research priority in the field. However, as we stated above, a practical electrolyte must meet multiple requirements, among which the following two are also very critical for rechargeable Li-air batteries: the Li metal anode stability and oxygen solubility.

Lithium metal has been proposed as a battery anode for decades.[128–133] The stability of lithium metal when cycled in nonaqueous electrolytes has always been one of the main concerns in this field, which has been reviewed elsewhere.[75,134] Electrolytes play a key role in managing the interface of Li/electrolyte so that the cycling efficiency can be improved and the dendrite can be suppressed or even eliminated in prolonged cycling.[75] Since the Li-compatible electrolytes have been closely associated with lithium metal anode development, this will be discussed in Section 3.4.

Oxygen solubility and transport in the electrolyte is critical for the rate capability and discharge capacity of a Li-air battery[79,85,135,136] and it might also influence the nature of the Li-O_2 discharge products.[84,137,138] Read and co-workers[84,85,138] studied the effects of oxygen solubility and diffusion (electrolyte viscosity) in electrolytes on the performance (discharge capacity and rate capability) of Li-air batteries. They found[85] that in ether based electrolytes, once a certain level of oxygen solubility is reached, it is no longer a capacity-determining factor and the electrolyte viscosity becomes the determining factor, depending on the discharge rates. For example, the discharge capacity is determined by dynamic viscosity alone at medium rate (0.5 mA/cm^2), while discharge capacity at low rates (0.05-0.2 mA/cm^2) shows no correlation with either oxygen solubility, dynamic viscosity, or conductivity. This is reasonable since the discharge rates are so low that the diffusion of oxygen to the Li-O_2 reaction sites is not limiting. However, at higher discharge rates, both oxygen solubility and electrolyte viscosity matter. Qu and co-workers[135] successfully increased the discharge current density to 5–10 mA/cm^2 in mixed solvents (PC/ACN) by adding perfluorinated compounds (perfluorotributylamine in PC) in a flow cell design.[79] This discharge rates are close to the practical requirement. The significantly improved discharge rate is due to the enhanced oxygen solubility[79] and diffusion coefficient, as well as the flow cell design.[135] Zhang et al.[139] also observed performance improvement in fluorinated solvent containing electrolytes. These findings may provide guidance for the investigation on electrolytes for rechargeable Li-air batteries. However, only after the electrolyte stability issue in oxygen-rich electrochemical conditions is addressed, can the investigation on oxygen solubility and transportation in electrolytes produce truly meaningful results for the development of rechargeable Li-air batteries.

In summary, the electrolyte plays the most important role in making Li-air batteries rechargeable (at least at the first stage of Li-air battery development). It determines if a truly rechargeable nonaqueous Li-air battery could be built or not. Currently, stable electrolytes in oxygen-rich electrochemical condition are the research priority. Recent results have shown that electrolytes could change the Li-O_2 electrochemistry significantly. A Li-air battery with relatively stable nonaqueous electrolytes (Li_2O_2 as the main discharge product) presents surprisingly low charge overvoltage (**Figure 4**).[78,101] This not only shows the great promise of rechargeable nonaqeous Li-air batteries, but also presents significant challenges in understanding Li_2O_2 electrochemistry and designing electrode materials that are active for Li_2O_2 electrocatalysis (ORR and OER) (see discussion in Section 3.3).

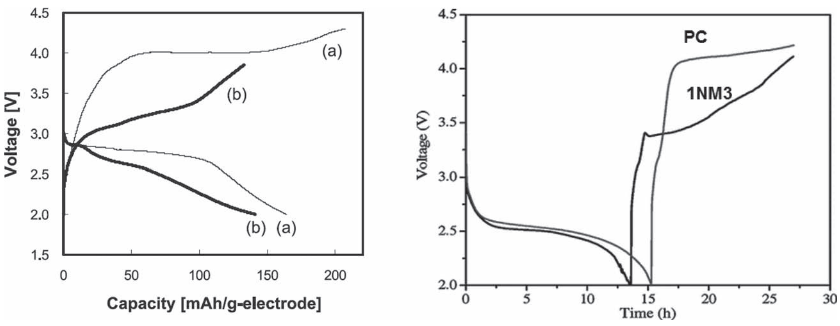


Figure 4. Left) First discharge-charge curves (0.02 mA/cm^2) of Li-O_2 cells with a) PC-LiTFSI and b) PP13TFSI-LiTFSI electrolytes. Reproduced with permission.[78] Copyright 2011, Electrochemical Society of Japan. Right) First discharge-charge cycles of a Li-air cell with propylene carbonate (PC) and 1NM3. Reproduced with permission.[101] Copyright 2011, American Chemical Society.

3.2. Air Electrode Material and Structure

It has been shown that the energy storage capacity and power capability of Li-air batteries are strongly determined by air electrodes which contributes to most voltage drop of Li-air battery.[44,140,141] Both materials and architecture of air electrodes influence its performance significantly.[43,48,140] Currently, air electrodes in most Li-air batteries consist of porous carbon materials.

In Li-air batteries, all of the Li-O_2 reactions (ORR and OER) occur on the carbon substrate, therefore it is critical to first build an ideal host structure for Li-air batteries by using appropriate carbons. At first glance, high surface area carbon is preferred for constructing air electrodes simply because a larger surface area means more active sites for electrochemical reactions and also more catalysts can be loaded. A further study revealed that the discharge capacity of Li-air batteries is more determined by the volume of the pores residing in the mesopore (2–50 nm) range.[86,142] For example, Super P with a low surface area (62 m^2/g) demonstrated a high capacity of more than 3000 mAh/g carbon;[143] however, at the same oxygen pressure, the activated carbon (AC) with the highest surface area (2100 m^2/g) shows much lower capacity than Super P. The latter has a large pore diameter of 50 nm. This suggests that the main factor that influences the capacity is related to the pore size and pore volume of carbon.[43,86,144] Based on this assumption, Ketjen black was tested and identified as the best carbon candidate for air electrode construction because Ketjen black has the highest total pore volume of 7.6 cc/g, most of which was contributed from mesopores (2–50 nm). Based on the pouch cell data reported by Zhang et al.,[47] the specific capacity from Ketjen black-based air electrode reaches 2340 mAh/g carbon with a high carbon loading of 15 mg/cm^2 in the ambient environment, further confirming the importance of mesopore volume in a carbon electrode. Because the formation of Li_2O_2 only occurs on the triple junctions where electrolyte, carbon, and oxygen coexist, the more triphase regions the more Li_2O_2 will be produced and therefore the higher capacity delivered from the cell. Too small or too large pore size will not benefit the oxygen reduction process because the former will be easily blocked by Li_2O_2 deposition on the pore entrance preventing further oxygen diffusion while the latter is usually flooded by the electrolyte forming two-phase instead of three-phase regions.[28,57]

In addition to the properties of carbon material itself, the pore sizes/volume and porosity of the electrode can be further tuned by various synthesis/preparation approaches.[145] The final pore volume and porosity of an air electrode can vary significantly using the same starting carbon materials because of the lamination process and the addition of binder.[47] The appropriate manipulation of air electrode can greatly increase the mesopore volume and porosity of the air electrode compared with their carbon precursors. For example, freestanding carbon nanotube/nanofiber mixed buckypaper has been used as an air electrode without any binder.[146] The discharge capacity is found to be strongly dependent on the thickness (carbon loading) as well as the current density. This is consistent with other reports on Li-air batteries using different carbons. The higher current density leads to the faster deposition of discharge product (which is insulating) on the carbon electrode surface that is exposed to the air. The formation of this insulating layer not only increases the resistance of the whole cell but more importantly it blocks the oxygen diffusion path to the interior carbon, thus leading to the incomplete utilization of the electrode. This also explains why a thinner air electrode or a lower carbon loading has higher specific capacity since the specific capacity is calculated on the weight of the total carbon material on the electrode. A more recent work uses hollow carbon fibers grown on a ceramic porous substrate as the oxygen electrode.[105] The energy density from this Li-air battery is four times greater than that of the state-of-art lithium intercalation materials. The low carbon packing in the grown carbon-fiber electrodes has highly efficient utilization of the available carbon and the void volume for Li_2O_2 formation. The interesting design of the nanofiber structure allows the direct observation of Li_2O_2 growth and disappearance on the sidewalls of the aligned carbon fibers providing valuable information for understanding the intrinsic challenges that exist in $Li\text{-}O_2$ batteries.

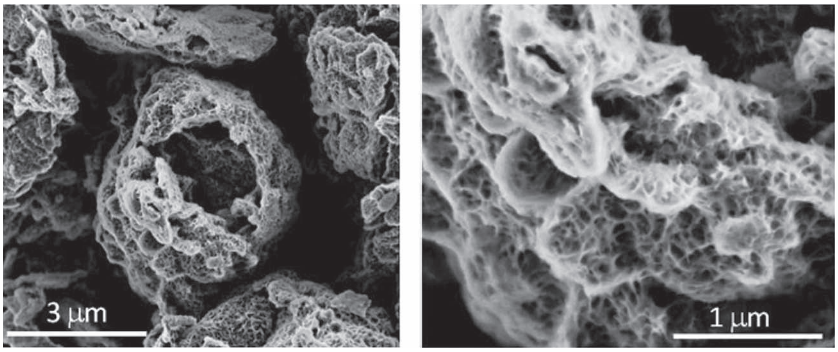


Figure 5. SEM images of a graphene air electrode at different magnifications. Reproduced with permission.[48] Copyright 2011, American Chemical Society.

In general, the ideal microstructures for the air electrode should be a bimodal design.[147] That is, during discharge, the large tunnels can function as "highways" to supply the oxygen continuously to the interior parts of air electrode while the small pores on the walls are the "exits", which provide tri-phase (solid-liquid-gas) regions required for oxygen reduction.[147] The recent discovery on graphene-based air electrode provide an excellent example that satisfies the aforementioned requirements as shown in **Figure 5**.[48] Xiao et al. used a colloidal microemulsion approach and demonstrated, for the first time, the construction of hierarchically porous air electrodes with functionalized graphene sheets (FGSs) that contain lattice defects and hydroxyl, epoxy, and carboxyl groups. The 3D air electrodes developed in their work consist of interconnected pore channels on both the micro- and nanometer length scales. Extremely high capacities (≈15 000 mAh/g) of these air electrodes have been correlated with their bimodal pore structures that can be used potentially for many other energy applications as well.

In summary, a good carbon candidate for Li-air batteries should have the characters of accurately controlled pore sizes/volume which can be further modulated during synthesis. The surface area of the carbon should also be tailored to reduce the side reactions but reach a balance for the active sites for the battery. It is also feasible to produce "porous" carbon from non-porous, 2D forms such as graphene sheets. The tunable morphologies of different carbon can be combined to satisfy various energy application requirements.

3.3. Catalysts for Rechargeable Li-Air Batteries

As we have discussed in the Section 3.1, in 2010 Mizuno first reported[77] that the discharge products of carbonates-based $Li\text{-}O_2$ battery are lithium carbonates instead of Li_2O_2. Before that, significant efforts had been made in developing electrocatalysts for rechargeable Li-air batteries. However, these electrocatalysts were later proved to catalyze the formation/decomposition of lithium carbonates and/or decompostion of electrolytes, not Li_2O_2. Recently, more efforts are focused on catalyzing Li_2O_2 reactions in relatively stable electrolytes. Here we will discuss the catalyst efforts and challenges in two subsections: before and after positive identification of Li_2O_2 as the main discharge products. As we will show below, even though Li_2O_2 was not positively identified as main discharge products in some cases, the findings from these researches can still provide guidance for future electrocatalysts investigation, especially for discharge processes (ORR).

3.3.1. Catalysts Development Without Positive Identification of Li_2O_2

The voltage gap between discharge and charge of a Li-air battery (carbonates-based) was usually higher than 1 V, thus the round-trip efficiency is significantly lower than that of Li-ion battery. Due to the similarity of Li-air battery and fuel cell/zinc-air battery (all have an oxygen cathode) in which electrocatalysts have an significant effect on the reaction kinetics and efficiency, it is reasonable to assume that electrocatalysts also play a key role for ORR and OER thus improve the kinetics and effiency in Li-air batteries. Therefore, great effort has been devoted to designing and developing electrocatalysts for Li-air batteries, even before the systematic fundamental studies and clear understanding on $Li\text{-}O_2$ electrochemistry have been carried out. As is known now, the electrocatalytic effect reported in those publications is in fact toward the decomposition of electrolytes and other lithium compounds (e.g., carbonates, hydroxide) instead of Li_2O_2. These electrocatalysts are roughly classified into the four categories.

1) Porous carbon materials, including carbon black,[43] nanostructured carbon,[105,142,146,148] functionalized carbon,[123,149] nanostructured diamond-like carbon,[82] and graphene.[48,150,151] Porous carbon is the critical material for the architecture design of air electrode. This was discussed in the Section 3.2. Carbon can function as both a substrate (for electrocatalysts) and a catalytic material. It is worth mentioning that carbon with defects or dopants improves ORR kinetics in aqueous solution. Recently, it has also been observed that graphene with more defects sites exhibited high performance in a nonaqueous Li-air battery.[48] This indicates the correlation between nonaqeous and aqeous electrocatalysis. Therefore, abundant knowledge in aqueous oxygen electrochemistry is beneficial for Li-air electrocatalysts development. Based on the fact that functionalized carbon improves ORR kinetics, it is expected to improve the rate capability of Li-air batteries. Obviously, more effort is needed in this aspect.
2) Transition metal oxides, mainly manganese oxides[42,70,125,138,152–156] and their composites,[149,157,158,159] cobalt oxides.[160,161] Among these, MnO_2 nanostructures[81] and Co_3O_4[161] show high performance for the "charge" process. Bruce and co-workers[81] claimed that the capacity and cyclablity of an air cathode that utilized transition metal oxides could be further improved by i) increasing surface area of catalyst with differnt aspect ratios, ii) adopting unique crystal structure that incorporates Li-O_2 products (i.e., Li_2O) inside, iii) adjusting the maximum capacity during discharge, which prevents the pores from being clogged and modified by Li-O_2 products (possibly Li_2O_2), and iv) further controlling porous structure such as porosity and pore size distribution.
3) Non-precious metals.[22,162] Ren et al.[162] studied non-precious metal electrocatalysts (CuFe supported on Ketjenblack carbon) for Li-air battery. These catalysts were originally developed for aqueous alkaline fuel cells.[163,164] The CuFe/C catalysts could significantly improve the discharge voltage and rate capability. But they did not present the charge performance. The enhanced ORR activity was attributed to the higher level of free catalytically active site density in CuFe/C, which decreases the ORR polarization.[162] In contrast to the mechanism of the clogging of pores at the cathode that are proposed by other researchers,[44,57,103,140,152] they argued that the termination of the cell discharge process is due to the rapid build-up of Li-O_2 products covering the active sites. The deactivated catalytic sites can be regenerated only by removing the Li-O_2 products into electrolyte or other nonactive sites in air electrode. Therefore, the sustainable discharge rate of a Li-air battery depends on the initial number of accessible catalytic sites and the balance of the production and the removal of Li-O_2 products in maintaining a sufficient number of accessible catalytic sites to sustain the ORR.
4) Precious metals (alloys), e.g., Pt,[165,166] Au,[104,166,167] Ag,[168,169] and Pd.[80,170,171] Shao-Horn and co-workers[167] reported a bifunctional electrocatalyst PtAu by combining Pt, which is beneficial for charge process, and Au, which is beneficial for discharge process.[165,166] The new bifunctional Pt-Au electrocatalyst significantly decreases the overvoltage especially for the charge process, thus increasing the round-trip efficiency. However, the use of precious metals will significantly increase the cost of Li-air batteries.[172] Other bifunctional catalysts might present more promise.[173]

As is known now that the Li-O_2 discharge products in above researches are very likely to be lithium carbonates instead of Li_2O_2,[35–37,40,41,96] i.e., the electrocatalysts improve the kinetics of lithium carbonates formation and decomposition (and/or decomposition of electrolytes), not Li_2O_2. However, the findings from the above researches can still provide guidances for future electrocatalysts investigation. For example, bulk lithium carbonates and Li_2O_2 are all nonconductive and form an insulating layer on electrode surface that is very critical for Li-air capacity and rate capability,[174,175] therefore if the electrocatalysts work well for lithium carbonate formation, they should be also beneficial for Li_2O_2 formation during discharge, i.e., ORR.

Interestingly, for the ORR process, there has been a discrepancy on the role of electrocatalysts. On one hand, the discharge voltages of a Li-air battery with/without electrocatalysts are observed to be almost identical;[138,143,161,176] therefore, ORR in a Li–air cathode is sometimes assumed to be independent of the type of electrocatalyst materials or carbon itself can provide high enough catalytic activity. In fact, this has also been observed for oxygen electrochemistry in nonaqueous liquid electrolytes with large cations (TBA^+, TEA^+) in which one-electron transfer reaction takes place ($O_2 + e^- \leftrightarrow O_2^-$).[177] On the other hand, the discharge voltage, rate capability, and ORR kinetics can also be significantly improved by proper electrocatalysts or even functionalized carbon.[22,162,166,167] The discrepancies might arise from the difference in their test conditions and/or air electrode structures that might lead to different limiting factors in their Li-air batteries.[44,45,174] This needs fruther investigation. Most importantly, more effort is needed to identify limiting factors that are responsible for capacity and rate capability.[174]

3.3.2. Catalysts for Li_2O_2 Formation and Decomposition

It was generally believed that electrocatalysts are critical in improving the power, cycling capability and round-trip energy efficiency of Li-air batteries.[81,161,166,167] However, as we will show below, Li-O_2 electrochemistry is unique, quite diferent from traditional electrocatalysis. Therefore, novel understanding and vision about Li-O_2 electrocatalysis and electrocatalysts design/development are needed.

The successful formation of Li_2O_2 is the prerequisite for the investigation on true electrocatalysis and its materials for the reaction $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$. In the Section 3.1, we have shown how critical the electrolyte is for Li_2O_2 formation. In fact, the electrode material (electrocatalyst) also matters. Bruce and co-workers[99] studied Li-O_2 reaction on three different carbons (Super P, Ketjen Black, and Black Pearls) in ether based electrolyte in which Li_2O_2 is to be formed as the main product during the 1st discharge while the decomposition of electrolyte also occurs. The FTIR results show greater presence of polyethers/esters (ν(C–O) bands) in Black Pearls than in Super P and Ketjen Black (Ketjen Black and Black Pearls present the same surface area). No direct evidence confirms whether polyethers/esters are from the decomposition of electrolyte which is catalyzed by Black Pearls or they are from Black Pearls itself (reacting with Li-O_2 reaction intermediates or other chemicals); Bruce and co-workers attributed polyethers/esters compounds to the decomposition of the ethers on discharge.[99] The nature of the electrode substrate (material) does influence the discharge products thus the rechargeability to some extent. Abraham and co-workers[111] also observed a similar effect on electrodes, with higher cycling capability on Au electrode than glass carbon electrode. This is reasonable since Au is a well-known inert electrode material. However, Au is not a practical electrode material because of its high density and prohibitive cost. Searching for a low-cost and light electrode material that has a balanced properties (i.e., high activity for ORR and inertness to electrolytes) is a challenging task. It is worth noting that as a key component in air electrodes, binders also seem to have significant influence on Li-O_2 discharge products. Wu et al.[40] reported that the solution changed from light yellow to brown when Li_2O_2 was added to the PVDF-NMP solution and then formed a dark gel when stored for a longer time. They attributed this to the reaction between Li_2O_2 and PVDF/NMP leading to PVDF crosslinking. Nazar and co-workers[178] recently reported that superoxide readily dehydrofluorinated polyvinylidene fluoride to give byproducts which then react with catalysts to produce LiOH.

For a rechargeable Li-air battery, the charge process (OER) is more critical. Significant efforts are needed for the electrochemical decomposition of Li_2O_2. Since the cycling of exclusive formation/decomposition of Li_2O_2 has yet to be established and the stable electrolytes are still under investigation, an alternative way to study Li_2O_2 electrocatalysis is to artificially pack Li_2O_2 and electrocatalysts in a composite electrode. It is known that during the charge process the Li_2O_2 proceeds only through the decomposition of Li_2O_2 ($Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$).[37,40] Therefore, the complicated Li-O_2 reactions can be avoided, in particular the side reactions with nonaqueous electrolytes, and the electrochemical decomposition of Li_2O_2 can be focused on. In fact, it is this method that originally provides the scientific fundamentals about the rechargeability of Li_2O_2,[42,76] not other compounds (Li_2O, Li_2CO_3, lithium alkylcarbonates, etc.).[76] In order to study the effect of various catalysts on Li_2O_2 decomposition during charge, Giordani et al.[179] packed various metal oxides electrocatalysts with Li_2O_2. Their results[179] show that MnO_2 is the best among the studied metal oxides and the structures and morphologies of MnO_2 influence its performance with the nanowires showing the lowest charge voltage (highest activity). This is consistent with Bruce and co-workers' results[81,161] even though for the later there were significant side reactions of Li-O_2 with electrolytes which forms lithium carbonates. This also indicates the correlation between the electrocatalysis of the decomposition of lithium carbonates and Li_2O_2.

The other way, of course, is to study Li-O_2 electrochemistry in stable electrolytes. There have been advances on stable electrolytes for Li_2O_2 formation in the past two years. Therefore, the investigation of "true" electrocatalysis and electrocatalysts for Li_2O_2 become possible. However, contradictory results on the catalyst effects have been reported and this seems to challenge the traditional electrocatalysis concept. Wen and co-workers[180] presented the promise of Co_3O_4 as electrocatalysts, which decreases the discharge/charge overvoltage of their DME-based lithium-air cell (Li_2O_2 as the main discharge product) depending on the structure of Co_3O_4. McCloskey et al.[97] reported that the most widely used electrocatalysts (Pt, Au, MnO_2) did not change the charge voltage in a Li-air cell using DME as electrolyte solvent (**Figure 6**). They explaned this observation as: true electrocatalysis requires that both the reactants and products of the rate-limiting step be mobile so that the reactants can diffuse to the catalytically active site and the products can diffuse away from it, which keeps the catalyst active; however, for Li-O_2 reactions in Li-air cells, the intermediates and products (LiO_2/Li_2O_2) are not soluable/mobile, or their surface diffusion is not sufficiently fast over macroscopic distances to let electrocatalysis to proceed (i.e., not electrochemically controlled); furthermore, the catalytically active sites if existing would be deactivated (or poisoned) by the insoluble Li_2O_2 during discharge.

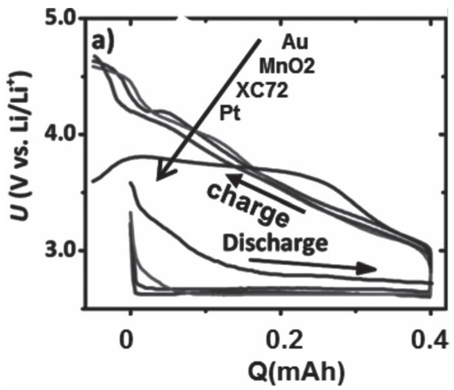


Figure 6. Discharge–charge voltage curves of a Li-air cell with DME as electrolyte solvent (Li_2O_2 is the main discharge product). Reproduced with permission.[97] Copyright 2011, American Chemical Society.

Most interestingly, the onset potential of decomposition of electrochemically formed Li_2O_2 (Li_2O_2 formed in battery discharge process) can be as low as around 3.0 V (Li/Li^+).[35,97] This is very close to the equivalent potential ($E_0 = 2.96$ V vs. Li/Li^+) of $2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$. The charge voltage for a Li-air cell with relatively stable electrolytes is also significantly lower than carbonate-based Li-air cell even though high voltage (≈4.5 V) is still needed at the last stage of charge.[78,97,101] McCloskey et al.[35] reported several oxidation peaks during the linear potential scan of a discharged Li-O_2 electrode (DME-based electrolyte), in accordance with various charge plateaus. There are probably several reasons for this as described in the following.

Various discharge products other than Li_2O_2 are still possible even in relatively stable electrolytes. The OER/ORR coulombic efficiency is only about 60% in McCloskey et al.'s cell;[35] no direct evidence yet shows that Li_2O_2 is the sole discharge product in Zhang et al.'s cell[101] or Mizuno's cell.[78] The decomposition voltages for various discharge products are quite different. Theoretical calculations have shown that the electronic resistivity of Li_2O_2 is orders of magnitude smaller than that of Li_2O or Li_2CO_3.[174] This influences the charge voltage significantly. In fact, there has been experimental evidence for this.[37,40,76]

The nature of Li_2O_2 influences its charge behavior. This includes the morphology/particle size and surface/bulk chemistry/physics (defect/vacancies): 1) Morphology/particle size of Li_2O_2. The OER potential for artificially packed Li_2O_2 electrode (4.65 V) is significantly higher than that for electrochemically deposited Li_2O_2 (3.2–4.6 V).[35] Ball-milling decreases the charge voltage of Li_2O_2 electrode.[40,76] This is mainly due to the different particle sizes of Li_2O_2 (tens of nanometers for electrochemically deposited Li_2O_2 vs. tens of micrometers for artificially packed Li_2O_2).[35] 2) Surface chemistry and physics of Li_2O_2. The presence of vacancies, dopants, and amorphous structures may result in a lower electronic resistivity of Li_2O_2.[34,181] This is advantageous for the discharge/charge of Li-air battery. Recent theoretical calculation results[182] show that Li_2O_2 surfaces are metallic because Li_2O_2 forms an oxygen-rich thin layer. If we assume that the oxygen-rich surface of Li_2O_2 has similar structure as LiO_2, the decomposition potential at the beginning should be similar to that of LiO_2. Bruce and co-workers' results show that the onset decomposition potential of LiO_2 is around 3.0 V, much less than that of Li_2O_2.[100] That is exactly the onset potential of O_2 evolution in McCloskey's cell.[97] We can even further assume that more than one charge potential plateau for a Li-O_2 cell with relatively stable electrolytes probably comes from the nature of electrochemically formed Li_2O_2.[35,78,97,101] The first charge plateau might be due to the decomposition of conductive and less stable surface Li_2O_2 (e.g., oxygen rich, LiO_2-like structure) and the remaining are due to the decomposition of bulk Li_2O_2. If this is true, to form more oxygen-rich Li_2O_2 becomes meaningful. Several factors are worth of investigation: 1) the particle size of Li_2O_2 does matter: the smaller particles have higher specific surface areas so that the surface oxygen-rich Li_2O_2 content is higher and 2) the electrocatalyst might help to form oxygen-rich Li_2O_2 as shown in the work of Shao-Horn and co-workers.[104] Therefore, electrocatalysts might work in such a novel way that a desired surface chemistry/physics/morphology of the discharge product Li_2O_2 can be obtained. This is completely a new concept of electrocatalysis and is worth further investigation.

3.4. Lithium Metal Anodes

Among all the anode materials, lithium metal is the most promising candidate for Li-air battery anode due to its extremely high specific energy (3860 mAh/g) and the lowest negative potential (–3.04 V vs. SHE).

However, even after decades of extensive research, the development of rechargeable batteries with a lithium metal anode is still hindered by two important problems. The first is the growth of lithium dendrites during repeated charge-discharge cycles,[131,183] which leads to internal short-circuit of the batteries and thus severe safety issues. The second is the low charge/discharge efficiency.[184] It comes from several aspects for example, the continuous growth of solid electrolyte interface (SEI) layer and the formation of irreversible "dead lithium".[131] There have been great efforts in understanding the growth mechanisms of lithium dendrites. Generally, three mechanisms are proposed to explain the dendrite formation. The most widley recognized one is the SEI film theory as shown in **Figure 7**.[185,186] According to this theory, lithium metal growth/deposition is quicker at the points where Li^+ ion conductivity is higher because of some intrinsic and

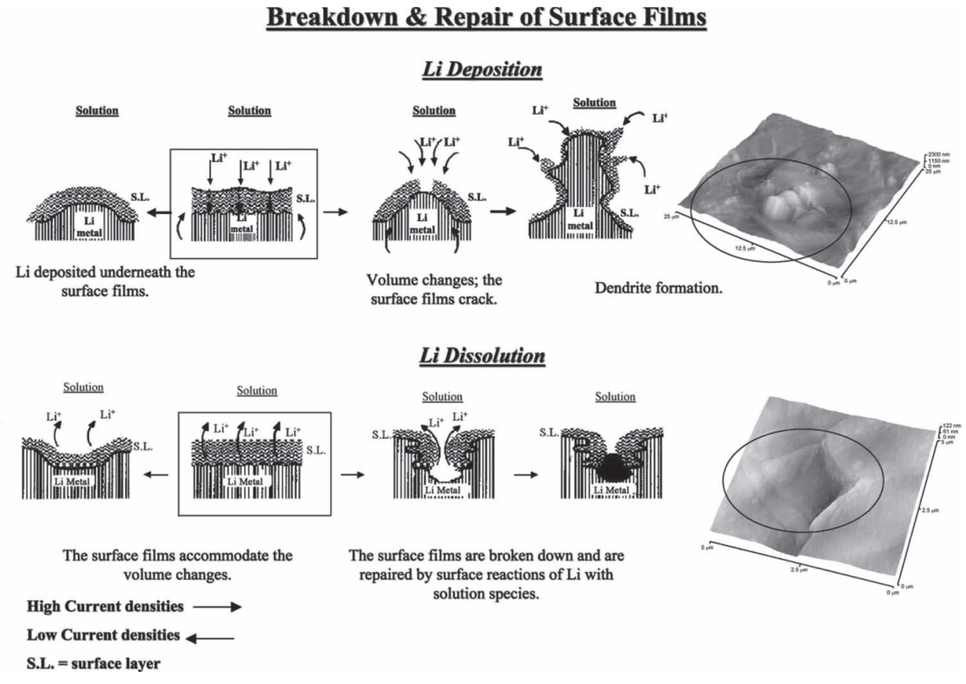


Figure 7. A description of the morphology and failure mechanisms of lithium electrodes during Li deposition and Li dissolution. Reproduced with permission.[131] Copyright 2002, Elsevier.

uncontrollable unhomogeneity. If the current density at a certain site is high enough, the growth speed difference between different sites will produce enough strength to break the SEI film on lithium metal. It results in an even higher growth speed at the SEI broken site to form lithium dendrites. The second dendrite growth mechanism is based on lithium metal material drawback.[187] Lithium deposition is easy to take place on the defect sites, ridge-lines and the grain boundaries, which results in the ununiform surface morphology and dendrites. The third mechanism suggested that the dendrite is induced by the ion concentration variation on the lithium anode surface as indicated in Chazalviel's physical model,[188] which is caused by high current density or local inhomogeneities.

However, no single mechanisms by itself could explain all the phenomena of lithium dendrite growth. This indicates the complex of lithium dendrite formation which needs a holistic consideration of influencing factors.

The SEI film on lithium metal shows a profound influence on electrode characteristics.[186] The SEI film is of a double-layer structure with a thickness of 50 Å. The inner layer is a dense layer of Li_2O, and the outer layer is a porous layer that is formed by LiF, LiOH, Li_2CO_3, and other electrolyte reduction products. A uniform composition and structure of the SEI film is beneficial for better surface morphology and cycleability. Until now, almost every effective method to improve lithium anode performance is related to the modification of the SEI film characteristics.

During the past 30 years, many ideas have been proposed to suppress the formation of lithium dendrite and push the practical application of lithium metal anode. Electrolyte solvents and salts are the most important factors that influence lithium dendrite formation. They can influence the components and structure of SEI film greatly. There have been extensive studies on different electrolyte solvents, including ethers,[189,190] alkyl carbonates,[191–193] and their derivants. Among all the solvents studied, Aurbach and co-workers suggested 1,3-dioxolane is the best solvent.[194,195] It acts as an oligomeric species on the lithium anode surface and makes the surface films elastic. Such an elastic film can suppress dendrite formation effectively. Wang et al.[190] also found that the ether electrolytes showed great effects on the lithium metal anode. Another promising solvent is ethylene carbonate (EC), which was found to open its chain and form $(CH_2OCO_2Li)_2$, which is the best protective agent among all the other alkyl carbonate reduction products, such as $ROCO_2Li$ or ROLi species.[131,186]

Different lithium salts also affect the lithium anode performances greatly. Most lithium salts for nonaqueous electrolytes have been tested for the lithium anode,[196,197] including $LiPF_6$,[184] $LiBF_4$, $LiAsF_6$,[198] $LiClO_4$,[199] LiI, LiTFSI, and $LiSO_3CF_3$. The correlation between lithium surface chemistry, morphology, cycling efficiency, and interfacial properties in different lithium salt electrolytes has been extensively studied. Among these salts, $LiPF_6$, LiTFSI, and $LiAsF_6$ lead to better surface morphology and higher cycling efficiency. The probable reason is that these salts contain fluorine and LiF is formed as one of the main decomposition products,[184] which helps to protect lithium electrode and improve its morphology and cycleability. This has been verified by different work.[186,199]

Polymer electrolytes are believed to suppress lithium dendrite growth because of their high mechanical strength. Various polymer electrolyte systems have been studied, including the PEO (poly(ethylene oxide)) system,[200] the PVDF (poly(vinylidenefluoride)) system,[201] the PMMA (poly(methyl methacrylate)) system,[202] and the PEM (poly[oxymethylene oligo-(oxyethylene)]) system.[203] Unfortunately, lithium dendrites can still penetrate the polymer film and lead to the failure of the battery. Significant effort is still needed to develop highly ion-conductive polymer electrolytes that can effectively suppress lithium dendrites.

Electrolyte additives have also been studied to prohibit lithium dendrite growth and enhance lithium anode performances. HF[130,204] and CO_2[205,206] are the two well-known effective inorganic additives. HF leads to the formation of a dense LiF layer on lithium electrode, which can effectively suppress dendrite formation. CO_2 turns to Li_2CO_3 in the presence of lithium, which is beneficial for a smoother lithium morphology and better rechargeability. SO_2 was also reported as a good electrolyte additive. Metal ions (Mg^{2+},[207] Ca^{2+}, Al^{3+}[208]) in electrolytes were also reported to show positive effects on a smooth lithium morphology because of the alloying effect. Many organic materials have also been studied as additives in electrolyte. PVP, VC, and FEC show promising effects, probably because they can polymerize on the lithium surface and form a better SEI film similar to 1,3-dioxolane and EC.

In addition to the above work on electrolytes, significant work has also been done on the lithium anode itself. Lithium alloys such as Li-Al alloy, Li-Na,[209] and Li-Mg alloy have shown some advantages to enhance the lithium anode performance because of the higher interface stability of the lithium alloy and lesser dendrite formation on lithium alloy. Recently, a Li-Ga alloy as the anode in a lithium battery has been demonstrated.[210] This is an interesting anode material since Ga is liquid above 30° C, which might help to address the dentrite issues. Surface modification is also used to passivate the lithium surface. Some inorganic material,[211] organic surfactants, or silane material[212] show positive effects to improve lithium deposition morphology.

Non-chemical approaches have also been tested. Based on the fact that low current density leads to less dendrites, the high surface lithium electrode was proposed as anode, including lithium powder[213] and high surface carbon hosted lithium.[214] Higher battery assembling pressure leads to less dendrites, so higher assembling pressure is preferred.[131] The battery operation temperature was also found to influence the lithium anode performance.[215] Low temperature would decrease interface reactions and reduce dendrite growth. Comparing all the efforts to improve lithium anode performance, the proper electrolyte (including solvents, salts, and additives) with good lithium anode compatibility shows the greatest positive effect because it changes the SEI film more directly and more significantly. Therefore, finding an ideal electrolyte for lithium metal anode is the most important.

Meanwhile, as we can see from the effects of electrolytes and additives on the SEI structure and component, it is obvious that the inorganic additives always influence the inner layer of SEI film, while the organic components more probably influence the outer layer of SEI film. We believe that the inner layer of

SEI film is more important to enable the lithium metal anode. Therefore, the inorganic additives and lithium salts deserve more efforts in future research activities.

Solid electrolytes, both solid organic electrolytes and solid inorganic electrolytes, should be an alternative and promising strategy for lithium metal anodes due to their strong mechanical strength.[121]

The above research on lithium metal anodes mainly targets Li-ion batteries. Few efforts have been made for rechargeable Li-air batteries. Lithium metal anodes present new and more challenging problems in rechargeable Li-air batteries. It is known that electrolytes are critical to enable Li metal anode. As we have discussed in the Section 3.1, the electrolytes that are effective in suppressing lithium dendrites and improving cycling efficiency also need to be stable in oxygen-rich electrochemical conditions for rechargeable Li-air batteries.

3.5. Oxygen Selective Membrane and Oxygen Supply

As we have discussed above, the unique advantage of Li-air batteries is that the reactant for cathode, O_2, is not stored inside the battery but is acquired from ambient air. However, the "free" oxygen from air comes with impurities, such as H_2O, CO_2, and N_2 (an oxygen tank can be used but with a great energy density penalty[50]). These impurities, especially H_2O, which reacts with the Li anode, may cause fast battery failure and severe safety issues due to the generation of H_2. CO_2 may damage the rechargability of Li-air battery due to the difficulty of electrochemical decomposition of discharge product Li_2CO_3 in the cathode.[216] Therefore, currently most Li-air batteries are run in pure O_2 or a dry air environment.[84,138,217] Continuous supply of uncontaminated O_2 from ambient air is a significant challenge for long-term operation of Li-air batteries, especially rechargeable Li-air batteries.

A promising solution to remove H_2O from ambient air is to use an O_2-selective water barrier membrane that can selectively let a sufficient amount of O_2 permeate through while blocking the permeation of H_2O. However, the development of such a membrane is very challenging. As we know, O_2 and H_2O cannot be separated by porous membranes with bulk or Knudsen diffusion due to the higher diffusivity and smaller kinetic diameter of H_2O molecule than O_2 molecule. The Knudsen separation factor of O_2 over H_2O ($K_{\frac{O_2}{H_2O}} = \sqrt{\frac{18}{32}} = 0.75$) is smaller than 1, which means H_2O molecules diffuse faster than O_2 molecules in porous membranes if the diffusion is based on Knudsen mechanism.[218]

Current porous and nonporous O_2-selective membranes are mainly developed for O_2/N_2 separation.[219–221] Reports on the development of O_2-selective water barrier membranes are rare. Reynolds et al.[222] soaked polyperfluoropropylene oxide co-perfluoroformaldehyde (PFPO) liquid into a polymer Celgard 2500 porous substrate and obtained O_2 permeance of 1.7×10^{-10} mol m^{-2} s^{-1} Pa^{-1} and O_2/H_2O selectivity of 3.9 at 50 °C. However, no data was available about application of this membrane in a real Li-air battery for ambient operation. The compatibility of this membrane with the electrolyte was also unknown. Zhang et al.[223] developed an O_2-selective immobilized liquid membrane for operation of nonaqueous Li-air battery in ambient air of 20–30% relative humidity (RH). The membrane was prepared by soaking high viscosity polydimethylsiloxane liquid (silicone oil) into porous metal or Teflon substrates (**Figure 8**). The membrane was selective to O_2 over H_2O (with a selectivity of ≈3.6) due to the higher solubility and/or diffusivity of O_2 than that of H_2O in the silicone oil. The membrane enabled a Li-air battery to operate in ambient air (at 20% RH) for 16.3 days with a specific capacity of 789 mAh/g$_{\text{carbon}}$ and a specific energy of 2182 Wh/kg$_{\text{carbon}}$. Its performance was much better than a reference battery assembled with a commercial PTFE membrane, which only had a discharge time of 5.5 days corresponding to a specific capacity of 267 mAh/g$_{\text{carbon}}$ and a specific energy of 704 Wh/kg$_{\text{carbon}}$. This kind of immobilized membrane is very easy to make and is of low cost. Permeation measurement showed that the membrane had high air permeance of 1.62×10^{-6}mol m^{-2} s^{-1} Pa^{-1}, indicating a high O_2 permeation rate for high current density discharge. The same group[224] also reported the hydrophobic zeolite membrane and poly(tetrafluoroethylene) (PTFE) membrane as O_2-selective water barriers. A dense-phase PTFE membrane enabled a Li-air battery to operate in ambient air with 20% RH for 21 days with a specific capacity of 1022 mAh/g$_{\text{carbon}}$ and a specific energy of 2792 Wh/kg$_{\text{carbon}}$.

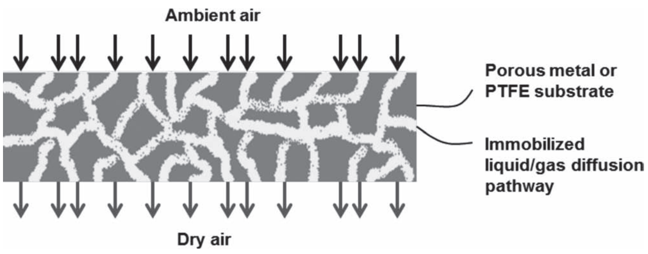


Figure 8. Schematic of immobilized liquid membrane structure. Reproduced with permission.[223] Copyright 2010, Elsevier.

Zhang et al.[47,225,226] investigated the ambient operation of Li-air batteries based on nonaqueous electrolytes. A heat-sealable polymer membrane (Melinex 301H, Dupont Teijin Films, Wilmington, DE) was used as both an O_2-diffusion membrane and as a moisture barrier for Li-air batteries. The membrane could also minimize the evaporation of electrolyte from the battery. A Li-air battery packaged with this membrane could operate in ambient air (with an oxygen partial pressure of 0.21 atm and RH of ≈20%) for more than one month with a specific energy of 362 Wh/kg, based on the total weight of the battery including its packaging. The membrane also enabled a Li-air battery with a graphene air electrode to operate in ambient air (RH of 20%) with a specific capacity exceeded 5000 mAh/g graphene.[48] Crowther et al.[227] used silicone rubbers (polysiloxane and methacrylate-polysiloxane copolymers) as oxygen selective membranes for optimizing the performances of primary organic-based Li-air cells. The hydrophobic silicone rubber membranes were coated directly onto the surface of the air electrodes. When discharged in air at 0.2 mA/cm^2 and a relative humidity of 42.9%, Li-air cells (capacity of 570 mAh/g) protected with the thin silicon rubber membrane prepared from Semicosil 964 performed much better than unprotected cells (capacity of 151 mAh/g). The same group[228,229] also used commercial Teflon/coated fiberglass cloth (TCFC) membranes (McMaster Carr) as the O_2 diffusion membrane. They found that these membranes can transfer O_2 sufficienct to support a discharge rate of ≈0.2 mA/cm^2 if the air window is the same size as the cathode. Approximately 2% of the electrolyte evaporated out of the TCFC membrane pouch over 40 days.

In previous research, both porous and nonporous membranes have been investigated for O_2/H_2O separation. So far, approaches using porous membranes were not very successful. All the porous membranes tested,[224] including microporous or macroporous PTFE or silicalite zeolite materials, were ineffective for the battery operation in ambient air, although the exterior surface of these membranes appeared to be hydrophobic based on contact angle measurements. It is worthwhile to make further effort for the development of porous O_2-selective membrane due to the high oxygen flux that can be obtained through porous membrane. For future Li-air powered electrical vehicle application, an alternative approach is to use highly H_2O-selective membrane module as an air dehumidifier to generate dry oxygen supply. However, the dehumidifier will consume certain power generated by the Li-air battery. The feasibility of this approach needs to be further evaluated.

Nonporous membranes, including dense polymer membranes and immobilized liquid membranes, exhibited promising performance for ambient air operation of Li-air batteries. For nonporous membranes, there are two possible mechanisms to prevent or reduce the moisture impact on the Li-air batteries. First is to reduce the permeability of both O_2 and H_2O, which would also reduce the electrolyte evaporation. This mechanism is suitable for a low discharge rate discharge battery because the O_2 supply is very limited. The second is to use membrane that is selective to O_2 over H_2O. However, it is hard to obtain membranes with high O_2/H_2O selectivity. Practically, a balanced approach between the diffusivity reduction and O_2/H_2O selectivity enhancement can be sought for ambient operation of Li-air batteries. Several criteria need to be considered in the development of O_2-selective water barrier membranes: 1) good O_2 selectivity; 2) high O_2 permeation rate, which requires either high O_2 solubility/diffusivity or small membrane thickness; 3) good compatibility with electrolyte, chemically and mechanically stable; 4) easy integration into the Li-air cell; and 5) low cost.

4. Perspective: Challenges and Opportunities

Li-air battery technology (both nonaqueous and aqueous system) is still in its early development stage. Nonaqueous Li-air battery presents potentially greater advantages over aqueous systems in terms of energy density, safety, and probably cost. We have reviewed the cirtical factors that influence the sustainable rechargeability of nonaqueous Li-air batteries. These include electrolytes, air cathodes (electrode architecture and electrocatalysts), lithium metal anodes, oxygen-selective membranes for oxygen supply from air. Significant challenges exist for each one and, of course, for the system.

A stable electrolyte in oxygen-rich electrochemical conditions (i.e., Li-air battery operating condition) is the current research priority in the field. Fundamentally, it determines whether a truely rechargeable Li-air battery can be built or not. Progress has been made in the past years. However, the high-efficiency formation and decomposition of Li_2O_2 has yet to be established (99.9% coulombic efficiency corresponds to 74% capacity retention after 300 cycles, an estimated number that is probably high enough for a vehicle with a 150, 000 mile lifetime and a 500 mile range per charge).[21] Here, we want to emphasize the research tools for stable electrolyte study, both experimental and theorectical modeling. 1) Tools that are able to accurately characterize the coulombic efficiency for oxygen reduction (discharge) and oxygen evolution (charge) are extremely important to establish the true reversibility and thus rechargeability of a Li-air battery. The integration of multiple tools (mass spectroscopy,[35,40] NMR,[37,102] Raman,[35,100] XRD,[99] XPS,[101,117] etc.) is necessary. A single tool sometimes gives misleading results. For example, FTIR tells the existence of side reactions products while XRD may reveal the sole discharge product of Li_2O_2;[99] XRD and Raman may show the sole discharge product of Li_2O_2 while DEMS still may show a relatively low coulombic efficiency.[35] 2) Theoretical modeling has been effective for studying the decomposition mechnisms[83] and predicting stability of solvents.[101,107] Keeping in mind that various active species (O_2, O_2^-, O_2^{2-}, LiO_2, LiO_2^-, Li_2O_2) are prabably involved in Li-O_2 electrochemistry,[101] among which LiO_2^- seems to be the most active one.[83,101] This is very helpful for selecting solvents and provides guidance for design stable molecules as solvents. 3) Fast experimental screening strategy of stable electrolytes is desired. Electrolyte stability test in a real Li-air cell is complicated and time-consuming. An ex situ electrochemical method through checking the reversibility and cycling stability of Li-O_2 electrochemistry in certain electrolytes[33] and chemical method by reacting KO_2 with certain solvents provides alternative and time-efficient approaches.[178,230]

The cathode determines the capacity, rate capability, and cycling efficiency. High-capacity cathodes have been demonstrated but at low rates.[48] Metal air and fuel cells all have an oxygen electrode. But why is the rate capability of Li-air battery orders of magnitude lower than zinc-air batteries and fuel cells? What are the key rate-limiting factors? Identifying the rate and capacity limiting factors is an important topic for air electrode design and development. Recent results show the passivation of electrode by Li-O_2 reaction products plays a key role in this aspect.[174] A monolayer carbonates at the carbon–Li_2O_2 interface causes a 10 to 100 fold decrease in the exchange current density and significantly increases the overvoltage.[175] The dual pore system air electrode architecture is beneficial for capacity and rate capability[147] but high-capacity air electrodes at practical rates (e.g., 10 mA/cm^2) have yet to be demonstrated. We believe more challenges for developing Li-air batteries will be revealed as progresses proceed. For examples, surface chemistry of carbon electrode materials influences the discharge products probably through catalyzing the decomposition of electrolytes;[99] the conventional electrocatalyst role is questioned since they did not catalyze the charge process of a DME-based Li-air cell;[97] and the so-called twin problems of interfacial carbonate formation (between Li_2O_2-electorlyte and Li_2O_2-carbon) increase the overpotentials significantly.[175] More and more surprises and difficult tasks may arise with fundamental understanding of Li-O_2 reaction processes. Recent results[78,101] indicate low charge voltages of Li-air cells with relatively stable electrolytes, which are expected to yield Li_2O_2 as the main discharge products. Conventional electrocatalysis concept and theory might not work for Li_2O_2 electrochemistry. The product Li_2O_2 forms a nonconductive layer on air electrode. This significantly decreases the conductivity of electrode; most importantly, it covers the electrocatalytically active sites and deactivates them. This is completely different from conventional electrocatalysis in which mobile or soluble reactants and products are involved so that the catalytic sites can function continuously. Therefore, more effort is needed for understanding Li_2O_2 electrochemistry, especially the non-electrochemical factors in Li_2O_2 reactions. Material selection and design for an air cathode needs a comprehensive vision that combines its activity for Li-O_2 reaction, its inertness for electrolytes and Li-O_2 reaction intermediates/products, and its catalytic role in the formation of desired Li_2O_2 structure and morphology.

The lithium metal anode has been a historic challenge in the battery field. The dendrite and the low cycling effiency are the two main obstacles for the practical applications of lithium metal anodes. Various strategies have been developed. Electrolytes that help to form desired SEI structures seem most promising to suppress dendrite formation and improve the cycling effiency. However, the long-term cycling of lithium metal anodes has yet to be demonstrated.

Oxygen selective membranes for oxygen supply are important especially for rechargeable Li-air batteries. Impurities in ambient air such as water moisture and CO_2 are detrimental for Li metal anodes and air cathodes, which lead to the Li-O_2 products that are not rechargeable. Progress has been made to remove moisture from air. However, the oxygen selectivity needs to be improved; furthermore, oxygen flux needs to be significantly improved in order to support high rates.

In summary, Li-air batteries present extremely high theoretical specific energy and energy density. In the early stages of development, Li-air batteries have already shown several times higher practical energy density/specific energy than Li-ion batteries. Therefore, this is a transformational energy technology that deserves significant effort. However, making Li-air batteries rechargeable is also extremely challenging, especially for nonaqueous Li-air batteries, which have higher theoretical energy density/specific energy than their aqueous counterparts. Extensive fundamental studies on Li-O_2 electrochemistry in nonaqueous systems and novel functional materials including electrolytes, cathode/catalysts, anodes, and oxygen-selective membranes for oxygen supply from air are needed to enable truely rechargeable nonaqueous Li-air batteries without large energy penalty.

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