# Electrocatalysts for Nonaqueous Lithium−Air Batteries: Status, Challenges, and Perspective

Yuyan Shao, Sehkyu Park, Jie Xiao, Ji-Guang Zhang,* Yong Wang,* and Jun Liu*

Pacific Northwest National Laboratory, Richland, Washington 99352, United States

ABSTRACT: The Li−air battery has recently emerged as a potentially transformational energy storage technology for both transportation and stationary energy storage applications because of its very high specific energy; however, its practical application is currently limited by the poor power capability (low current density), poor cyclability, and low energy efficiency. All of these are largely determined by interfacial reactions on oxygen electrocatalysts in the air electrode. In this article, we review the fundamental understanding of oxygen electrocatalysis in nonaqueous electrolytes and the status and challenges of oxygen electrocatalysts and provide a perspective on new electrocatalysts' design and development.
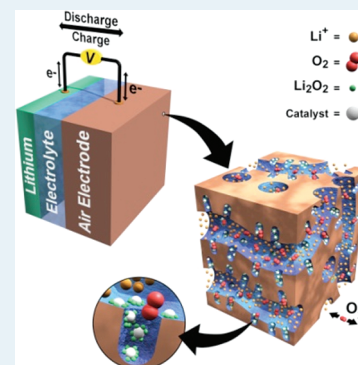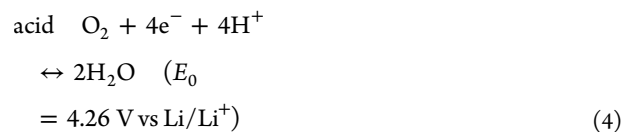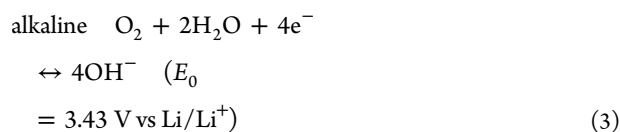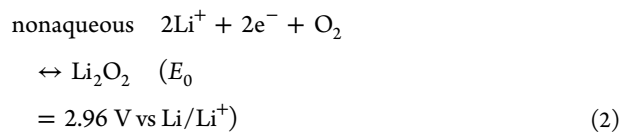
1. INTRODUCTION

The Li−air battery is an advanced energy storage and conversion technology. It converts the chemical energy in lithium (anode) and oxygen (cathode) into electric energy during discharge (like a fuel cell, but the fuel here is lithium instead of hydrogen), and it stores electric energy by splitting Li−O_2 discharge products (i.e., Li_2O_2 in nonaqueous systems and LiOH in aqueous systems) during charge using electricity (like an electrolysis device or a reversible fuel cell to generate hydrogen and oxygen by splitting water).

Generally, two types of Li−air batteries are being investigated: nonaqueous system[1] and aqueous system,[2] both of which have been shown to be electrically rechargeable. The fundamental electrochemical reactions are shown in the following:

Anode:

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

Cathode:

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

$$\text{alkaline} \quad O_2 + 2H_2O + 4e^-$$
$$\leftrightarrow 4OH^- \quad (E_0$$
$$= 3.43 \text{ V vs Li/Li}^+) \tag{3}$$

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

The lithium−air battery combines the advantages of fuel cells and batteries. It has no "fuel infrastructure issue", as do hydrogen fuel cells, and its energy density and specific energy are much higher than lithium ion batteries.[3−6] It is estimated that a practical Li−air battery could potentially provide a specific energy as high as around 800 Wh/kg,[3,4] which is about 4 times that of state-of-the-art Li ion batteries. Considering the reactions in eq 3 and 4, which involve water or acid as active reagents in aqueous systems, the preliminary modeling results[7] show that the theoretical energy density of a nonaqueous Li−air battery system is higher than that of an aqueous Li−air battery system, and the practical energy density depends on discharge/charge rates and, of course, the cell design, which is still an open question. Therefore, nonaqueous Li−air batteries have attracted much more attention around the world in recent years[4,5,8] and will be the focus of this review.

Lithium−air batteries, on the other hand, also present the challenges of both (reversible) fuel cells and batteries.[5,8−12] Therefore, significant efforts are needed to improve their power density (current density), cycling capability, and energy efficiency before their practical applications can become a reality.[4,5,10] An oxygen electrocatalyst, including the funda-

mental understanding of Li−O₂ reactions, is one of the most challenging tasks in developing lithium air batteries. Among other important challenges are the lithium metal anode (dendrite formation, incompatibility with electrolyte and air, etc.),[13] electrolytes (instability in oxygen-rich electrochemical conditions, conductivity, evaporation for nonaqueous electrolytes, etc.),[14−16] and the oxygen supply from air.

Great challenges exist in air electrode and oxygen electrocatalysts. An air electrode determines the power, energy density and energy efficiency of a Li−air battery. Current Li−air batteries can only be discharged/charged at a current density of 0.1−0.5 mA/cm² (in comparison, >10 mA/cm² for a Li ion battery, >1500 mA/cm² for polymer electrolyte membrane (PEM) fuel cells), and the voltage gap between the charge and discharge is larger than 1.0 V, which results in a low voltage efficiency of <60% (in comparison with >90% for a Li ion battery). These can be largely attributed to the poor performance of the air (oxygen) electrode because of the sluggish kinetics for oxygen reduction/evolution, the side Li−O₂ reactions, and the inefficient air electrode design.[17−19]

The electrocatalysts for the oxygen reduction reaction (ORR, $O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$) and oxygen evolution reaction (OER, $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$) play a key role in improving the power density,[20] cyclability,[21] and energy efficiency[22−24] and are key enablers for practical rechargeable Li−air batteries. Therefore, we focus on oxygen electrocatalysts in this work. Specifically, we will review the status and challenges and provide a perspective of oxygen electrocatalysts for nonaqueous Li−air batteries. The content is organized as follows: (1) fundamental understanding of oxygen electrocatalysis in nonaqueous electrolytes, (2) current electrocatalysts under investigation for Li−air batteries, (3) future a perspective on oxygen electrocatalysts for Li−air batteries, and (4) a summary.

The aqueous Li−air battery is not included here because (1) its theoretical energy density is predicted to be lower than a nonaqueous system if considering that water or acid is also involved in the reactions;[5,7,25] (2) for aqueous Li−air batteries, even though the oxygen electrocatalysts are critical, the most challenging problem lies in the anode, that is, the protection of the Li metal;[2,13,26−28] (3) the fundamental reaction at the 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 late systems can be used in aqueous Li−air batteries,[29−33] and there are already quite a few excellent reviews on this topic.[34−36]

2. OXYGEN ELECTROCATALYSIS IN NONAQUEOUS ELECTROLYTES

The understanding of oxygen electrocatalysis mechanisms (ORR and OER) is critical to a new electrocatalyst design for Li−air batteries; however, knowledge of oxygen electrochemistry in nonaqueous systems is quite limited as compared with that in aqueous systems. Significant work is needed to establish a solid foundation on oxygen electrocatalysis mechanisms in nonaqueous systems.

2.1. Oxygen Electrochemistry in Nonaqueous Liquid Electrolytes. Oxygen reaction mechanisms depend on both the electrode materials (e.g., electrocatalysts[37])[38,39] and electrolytes.[38,40−42] The supporting electrolytes, especially the cations, have significant influence, whereas the anions have little influence on ORR and OER.[40] It has been established[43,44] that in nonaqueous electrolytes with large cations, such as tetrabutylammonium (TBA⁺) and tetraethylammonium

(TEA⁺), oxygen reduction−oxidation is a reversible, one-electron transfer reaction near the equivalent potential.[43,45,46] In this case, the oxygen molecule (O_2) is first reduced to a superoxide radical (O_2^-), followed by its subsequent solvation by TBA⁺ or TEA⁺, and then O_2^- can be reversibly oxidized with small overpotentials (Figure 1). If the electrode potentials are
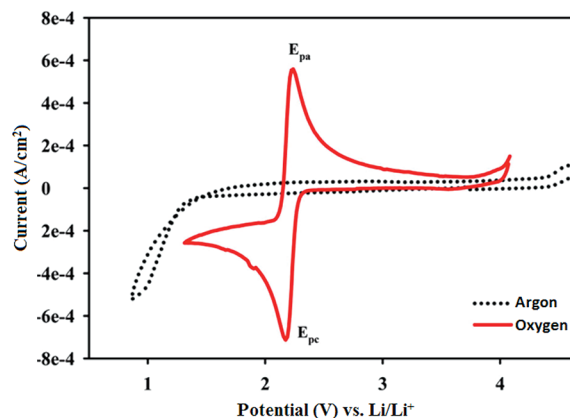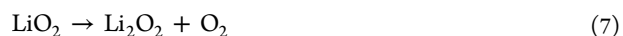

Figure 1. Cyclic voltammograms of oxygen reactions on glass carbon electrode in Ar- and O₂-saturated 0.1 M TBAPF₆ in DMSO.[41]

much lower, O_2^- can be further reduced to O_2^{2-}. O_2^{2-} can be oxidized only at much higher potentials, resulting in a reduction−oxidization potential gap of over 2 V (highly irreversible).[40] In nonaqueous electrolytes with large cations, oxygen reduction is a catalytically insensitive reaction, which means that nearly identical ORR activities are observed on Pt, Au, Hg, and carbon electrodes.[38,39] This might be explained by the following: (1) there is no cleaveage of the O−O bond involved, which is a notoriously sluggish process that usually requires precious metal catalysts such as Pt;[27] (2) O_2^- is a weakly adsorbed radical[37] and highly soluble in electrolyte, and the electrode may just work as an electron transfer media; (3) the thermodynamic reason, which will be discussed later.[37]

In contrast, oxygen electrochemistry in nonaqueous electrolytes with small cations such as Li⁺ and Na⁺ is quite different:[40,41] (1) the onset potential for ORR is positively shifted; (2) the ORR/OER becomes much less reversible. Bruce and coworks[42] studied ORR/OER in Li⁺-containing acetonitrile. Figure 2 clearly shows the transition from reversible reaction of ORR/OER in TBAClO₄−CH₃CN to a nonreversible reaction with the addition of Li⁺.[42] On the basis of the experimental observation, they concluded that ORR and OER in Li⁺-containing nonaqueous electrolyte follow the following pathways:[42]

ORR:

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

$$O_2^- + Li^+ \rightarrow LiO_2 \tag{6}$$

$$LiO_2 \rightarrow Li_2O_2 + O_2 \tag{7}$$

OER:

$$Li_2O_2 \rightarrow 2Li^+ + O_2 + e^- \tag{8}$$

Their in situ surface-enhanced Raman spectroscopy (SERS) (Figure 3) provided direct evidence that oxygen reduction in Li⁺-containing nonaqueous electrolyte first forms O_2^-, which then binds to Li⁺, forming LiO_2 on the surface of the
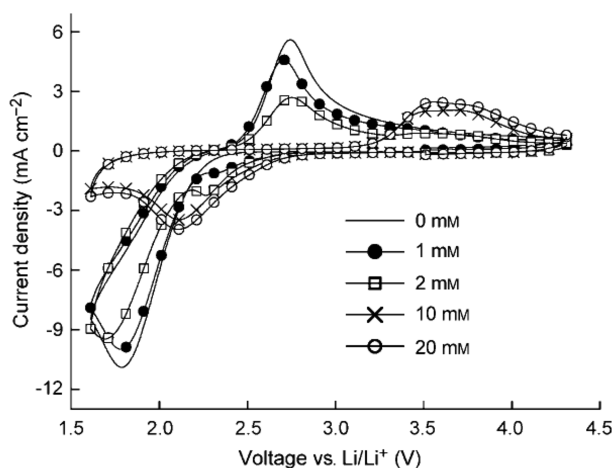
Figure 2. Cyclic voltammograms (1.0 V/s) at a Au electrode in O_2-saturated 0.1 M TBAClO$_4$–CH$_3$CN containing various concentrations of LiClO$_4$.[42].
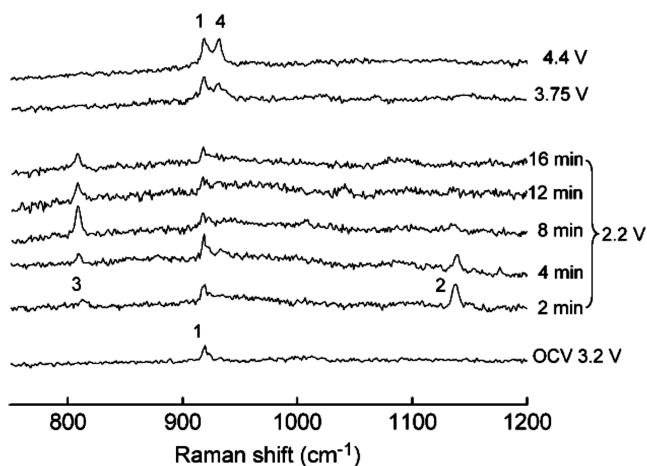

Figure 3. In situ surface-enhanced Raman spectroscopy (SERS) during ORR/OER on Au in O_2-saturated 0.1 M LiClO$_4$–CH$_3$CN. Peak assignments: (1) C–C stretch of CH$_3$CN at 918 cm^{-1}, (2) O–O stretch of LiO$_2$ at 1137 cm^{-1}, (3) O–O stretch of Li$_2$O$_2$ at 808 cm^{-1}, (4) Cl–O stretch of ClO$_4^-$ at 931 cm^{-1}.[42]

electrode.[42] LiO$_2$ is unstable and disproportionates to more stable Li$_2$O$_2$.[42] As in the electrolyte with large cations, on extending the voltage range to much more cathodic potentials (<1.8 V vs Li/Li$^+$), further electrochemical reduction of LiO$_2$ to Li$_2$O$_2$ occurs, but these potentials are out of the range of Li–air battery test voltages (usually ≥2.0 V vs Li/Li$^+$); therefore, in Li–air batteries that are tested in laboratories, the ORR process follows eqs 5–7, and usually, no LiO$_2$ is observed in Li–air discharge products because Li–O$_2$ cells are discharged over a much longer time, and hence, all the LiO$_2$ will have disproportionated to Li$_2$O$_2$ by the end of discharge (in fact, Li$_2$O$_2$ is not observed in most Li–air batteries, either, because of the side reactions between Li–O$_2$ reaction intermediates/products and electrolytes;[16,47−49] this will be discussed later). Upon charge, that is, the OER process, the reactions do not involve LiO$_2$; instead, Li$_2$O$_2$ is directly decomposed to Li$^+$ and O$_2$.[42] In other words, the pathways for ORR and OER are different. This might explain the different overpotentials for charge and discharge[50,51] and helps in designing new electrocatalysts for ORR and OER, respectively.

2.2. Complexity of Oxygen Electrochemistry in Li−air Battery.

2.2.1. Li−O$_2$ Electrochemistry Is a Complicated Process. Oxygen electrochemistry in Li−air batteries is a very complicated process. This complexity includes the following aspects: (1) Li−O$_2$ electrochemistry involves more than one elementary reaction, as shown in Bruce and co-workers' work.[52] Scrosati and co-workers[53] used potentiodynamic cycling with galvanostatic acceleration analysis (corresponding to a very slow discharge/charge rate) to study Li−O$_2$ redox electrochemistry in a Li−air cell with a solid electrolyte; three reaction peaks can be observed during ORR and OER (Figure 4). They
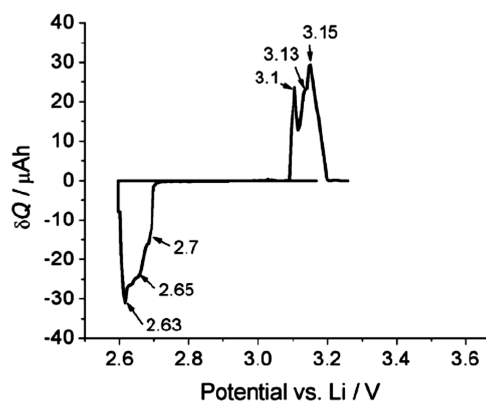

Figure 4. Incremental charge (dQ) vs potential profiles of the potentiodynamic cycling with galvanostatic acceleration analysis performed on the cell with the configuration Li/PCE/SuperP-O$_2$. The peaks correspond to the reactions O$_2$ + e$^-$ + Li$^+$ ↔ LiO$_2$ (2.7/3.1 V), LiO$_2$ + e$^-$ + Li$^+$ ↔ Li$_2$O$_2$ (2.65/3.13 V), and Li$_2$O$_2$ + 2e$^-$ + 2Li$^+$ ↔ Li$_2$O (2.63/3.15 V). PCE: ZrO$_2$-added PEO-based polymer composite electrolyte.[53].

attributed these current peaks to (1) O$_2$ + e$^-$ + Li$^+$ ↔ LiO$_2$, (2) LiO$_2$ + e$^-$ + Li$^+$ ↔ Li$_2$O$_2$, (3) Li$_2$O$_2$ + 2e$^-$ + 2Li$^+$ ↔ Li$_2$O, respectively. This is different from that in Bruce and co-workers' work.[52] (2) ORR and OER processes might be influenced by electrolytes, electrode materials, oxygen pressure,[54,55] and even electrochemical stressing (i.e., charge/discharge profile in a Li−air battery).[56−58] (3) Li−O$_2$ electrochemistry is further complicated by the nonsoluble, nonconductive Li−O$_2$ products. These Li−O$_2$ products, once deposited on an electrode, block the surface and prevent further ORR reactions, and especially for OER reaction, the electrocatalysts might be completely deactivated.[9,20] (4) The intermediates in Li−O$_2$ electrochemical reactions, for example, O$_2^-$, O$_2^{2-}$, and LiO$_2$/LiO$_2^-$,[59] are very reactive.[46,53,60−63] They can easily decompose most organic solvents. This leads to Li−air battery discharge products of Li$_2$CO$_3$, LiOH, and lithium alkyl carbonates,[14,16,48,49,64−66] instead of only the desired product (Li$_2$O$_2$), which can make a Li−air battery truly rechargeable.[16,67] (therefore, we use "Li−O$_2$ products" instead of a specific chemical name such as Li$_2$O$_2$, Li$_2$O, or Li$_2$CO$_3$ because different discharge products are generated in Li−air batteries, depending on electrolyte, air electrode, even discharge conditions[16,47,68]).

Recently, more studies on oxygen electrocatalysis (ORR/OER) have been carried out in Li−air batteries to understand this complicated process and to establish scientific fundamentals for oxygen electrocatalyst design and development; however, because of the poor understanding of Li−O$_2$

electrochemistry, there is still significant disagreement on the electrocatalyst role for Li−O$_2$ reactions in Li−air batteries.

2.2.2. Disagreement on Oxygen Reduction. For ORR process, several groups have reported that the discharge voltages of a Li−air battery with/without electrocatalysts are almost identical;[23,58,69,70] therefore, they assume that ORR in a Li−air cathode is independent of electrocatalyst materials, and even carbon itself can provide high enough catalytic activity. In fact, the "catalytic insensitivity" of oxygen electrochemistry is widely recognized in nonaqueous liquid electrolyte with large cations (TBA$^+$, TEA$^+$).[38] On the other hand, the discharge voltage, rate capability and ORR kinetics have been observed by other research groups to be significantly improved by proper electrocatalysts.[1,20,22,24] Even though the discrepancies might arise from the difference in their test conditions or air electrode structures, which might lead to different limiting factors in their Li−air batteries,[9,10,71] it is worthy of significant efforts since this will determine if an electrocatalyst is needed for Li−air battery discharge.

Here, we want to have a short discussion on this complexity based on the available experimental results and hypothesis. The observation in some reports that the discharge voltages of a Li−air battery with/without electrocatalysts are almost identical can be explained using the Pourbaix diagram of Li$_2$O$_2$/O$_2$ (Figure 5). This diagram was proposed by the Shao-Horn group[37] and
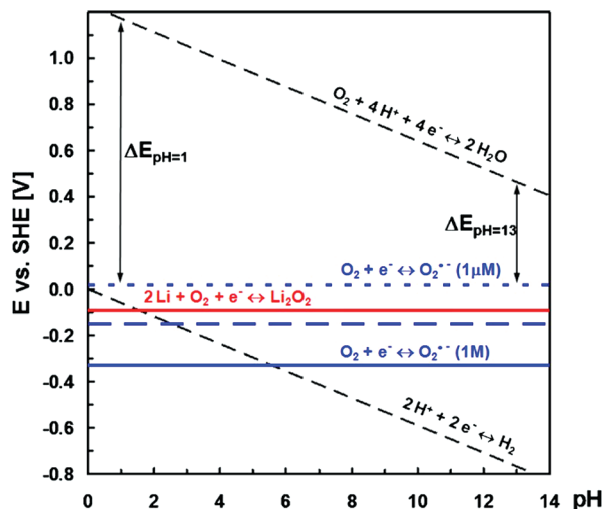
Figure 5. Modified Pourbaix diagram for Li$_2$O$_2$−O$_2$ with the equilibria for the O$_2^-$/O$_2$ reaction.[37]

is based on the Pourbaix diagram of H$_2$O/O$_2$.[72] The first electron transfer process (O$_2$ + e$^-$ → O$_2^-$) is considered to be the rate determining step (rds),[37,43] the reversible potential for which (−0.30 V vs SHE[72]) is much lower than that for the reduction of oxygen with Li ions to form Li$_2$O$_2$ (2.96 V vs Li/Li$^+$, −0.07 V vs SHE). In fact, the first electron transfer process (O$_2$ + e$^-$ → O$_2^-$) may also be the potential-determining step (pds), which is "the step with the least favorable equilibrium potential".[73−78] From the thermodynamic viewpoint, the reaction 2Li$^+$ + O$_2$ + 2e$^-$ → Li$_2$O$_2$ is downhill at potentials ← 0.30 V (SHE) (i.e., 2.73 V vs Li/Li$^+$). This is also true if Li−air battery discharge products are not Li$_2$O$_2$[16,47,68] because the discharge voltage of Li−air battery is usually around 2.5−2.6 V, which is much lower than that required for the pds. The overpotential should be able to provide driving force high enough to make the reaction take place on any electrode

surface, especially at such low current densities (0.1−0.5 mA/cm^2).

However, as we have discussed above, Li−O$_2$ reactions are really complicated ones. There are many possible reaction pathways.[42,53] Some of the elementary steps in Li−O$_2$ reactions are nonelectrochemical processes.[50,71] Furthermore, Li−O$_2$ products (namely, Li$_2$O$_2$, Li$_2$O, and other lithium compounds) are not soluble and are not conductive. They form a solid film on the surface of an electrode that prevents further reaction. Other processes such as mass transfer in an air electrode also contribute to this complexity.[58] In such a complicated situation, the whole Li−O$_2$ reaction process might be electrochemically controlled, for which the electrocatalysts might function well and the enhanced kinetics can be observed with electrocatalysts; however, it might be controlled by nonelectrochemical (or even nonchemical) processes. In this case, electrocatalysts, if used, have no effect on the reaction process from the sense of "catalysis". However, as we will discuss in Section 4, electrocatalysts may influence the particle size, morphology, surface chemistry/physics of Li−O$_2$ discharge products, which in turn influences the discharge behavior (e.g., to increase the conductivity of Li−O$_2$ discharge products). In either case, the effect of electrocatalysts is important, but the whole picture of Li−O$_2$ electrode processes, especially passivation of electrocatalysts in Li−air batteries, needs to be considered carefully.[71,79]

2.2.3. Complex Oxgyen Evolution Reaction Process. For rechargeable Li−air batteries, the OER reaction (i.e., the charge process), is of greater significance. The electrochemical decomposition of Li$_2$O$_2$ plays a key role in this process. Bruce and co-workers[23,80] first demonstrated the rechargeability of Li$_2$O$_2$ using an artificially packed Li$_2$O$_2$ electrode. Zhang and co-workers[68] later demonstrated that the rechargeability of artificially packed Li$_2$O$_2$ electrode is not sustainable in organic carbonate electrolytes because of the decomposition of electrolyte. McCloskey et al.[49] made a detailed study of the electrochemical decomposition of Li$_2$O$_2$ in dimethoxyethane (DME), which seems stable under oxygen-rich Li−air cathode conditions (but its long-term cyclability still needs more investigation).

Figure 6 shows the results from a combination study of linear electrochemical potential scan and differential electrochemical mass spectrometry on Li$_2$O$_2$ decomposition in Li−air battery.[49] Four distinct peaks (at 3.2, 3.4, 3.8, and >4.5 V) are observed in the potential scan, with the first three evolving exclusively O$_2$ and the last coincident to O$_2$ and CO$_2$ evolution, which are
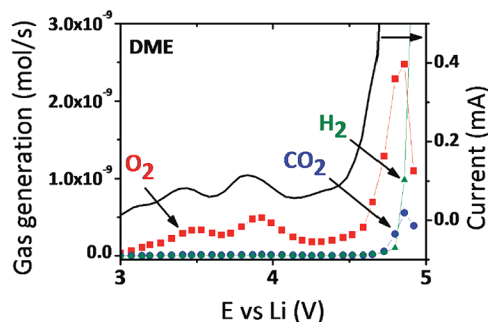
Figure 6. Gas evolution and current vs cell voltage during a 0.075 mV/s linear potential scan under Ar of a discharged DME-based Li−air cell (discharge at 0.09 mA/cm^2 for 10 h under ^{16}O$_2$ prior to the potential scan).[49]

attributed to the decomposition of Li_2O_2 (and the decomposition of solvent for the last peak). This indicates a wide distribution of Li_2O_2 decomposition overpotentials. The overpotential distribution is considered the origin of the several charge stage of the Li−air battery. No information about the sources of the overpotential distribution is available in their report.[49] We speculate that the particle size of Li_2O_2, the contact interface between Li_2O_2 and catalyst, the defects/vacancies in Li_2O_2 must influence this process, which are worthy of further investigations.

It was believed that the OER process is catalytically sensitive, which means that electrocatalysts decrease the overpotential for charge process (i.e., OER).[69,81] However, McCloskey et al.[82] recently reported that, in a Li−air cell using DME as electrolyte solvent in which Li_2O_2 is the main discharge product, the investigated electrocatalysts (Pt, Au, MnO_2) do not change the charge voltage. They suggested[82] that true electrocatalysis requires that both the reactant and product of the rate-limiting step be mobile so that the reactant can diffuse to the catalytically active site and the product can diffuse away from it, allowing it to be used again; however, for Li−O_2 reactions in Li−air cells, the intermediates and product (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. In other words, it is not electrochemically controlled. Furthermore, the catalytically active sites if existing would be blocked by the insoluble nonconductive Li_2O_2 during discharge. However, it can be seen from Figure 7 that, even under such a
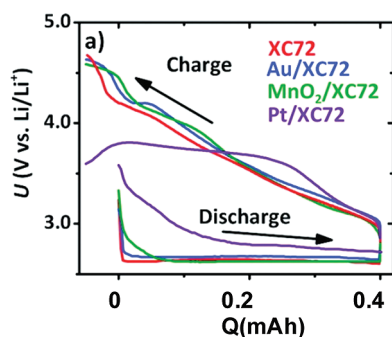

Figure 7. Discharge−charge voltage curves of a Li−air cell with DME as electrolyte solvent (Li_2O_2 is the main discharge product).[82].

low degree of discharge (DOD, 65−135 mAh/g), the charge potential can be as high as 4.5 V during the last stage of charge.[82] Therefore, strategies that can significantly decrease the charge voltage are needed to make a practical rechargeable Li−air battery. This indicates that new concepts of electrocatalysis theory and electrocatalyst design are needed.

In summary, oxygen electrochemistry in Li−air battery-related nonaqueous electrolyte conditions involves complicated processes and needs further careful study, especially the formation/decomposition of Li_2O_2. It is important to identify the limiting factors in the Li−O_2 reaction processes, both electrochemical and nonelectrochemical, because this is the prerequisite for the design and development of advanced bifunctional electrocatalysts for rechargeable Li−air batteries.

3. CURRENT ELECTROCATALYSTS FOR LI−AIR BATTERY

It is generally believed that electrocatalysts are critical to improving the power density, cycling capability, and round-trip

energy efficiency of Li−air batteries.[21−24] It has been shown that the energy storage capacity and power capability of Li−air batteries are determined mainly by the air electrode, which contributes to most voltage drops of Li−air batteries.[9,19,56]

In recent years, great efforts have been made in the development of electrocatalysts for both primary and rechargeable Li−air batteries. Even though recent reports have questioned the true electrocatalytic effect of these catalysts,[16,82,83] the research results can still provide some guidance for future investigation on Li−O_2 electrocatalysts, as we will discuss at the end of this section. The electrocatalysts can be roughly classified into the following four categories: (1) porous carbon materials, including carbon black,[84] nanostructured carbon,[85−88] functionalized carbon,[89,90] nanostructured diamond-like carbon,[91] and graphene;[92−94] (2) transition metal oxides, mainly manganese-based oxides[31,58,80,95−100] and composites,[89,101,102] and cobalt oxides;[23,103] (3) nonprecious metals;[1,20] (4) precious metals (alloys), for example, Pt,[22,37] Au,[22,24,104] Ag,[105,106] and Pd.[107−109]

3.1. Porous Carbon. Strictly speaking, carbon is not an electrocatalyst. However, carbon is the most widely used material in the air electrode of Li−air batteries, either by itself or as an electrocatalyst support or as an electrically conductive additives. An air electrode in a Li−air battery is a gas diffusion electrode (GDE), like that in PEM fuel cells.[34,110−112] It is well-known that the porosity is extremely important for GDE. Carbon is the best material that can provide the desired porosity and electronic conductivity. In fact, carbon is the critical material for the architecture design of an air electrode. There have been many studies on the influence of carbon properties on Li−air performance. It is generally believed[9,56,58] that the pore volume, especially the mesopores,[84,113,114] instead of specific the surface area[70] is the most important factor that determines the capacity and rate capability of a Li−air battery. Optimization of mesopores is also important because too large or too small pores lead to a less efficient use of mesopore volumes.[84,115,116]

Li−O_2 reaction products in nonaqueous electrolyte are not soluble and are nonconductive. Deposition of these products on the surface of the air electrode may have significant effects on subsequent reactions; however, it is still difficult to determine the most critical factors that terminate Li−air discharge process (i.e, the capacity, which is usually characterized using "mAh/g carbon" or "mAh/cm²").[4,11] These factors may include the clogging of pores in the air electrode,[9] the blockage of catalytically active sites on the (carbon) surface,[117] or the loss of electrode conductivity (i.e., electrical passivation of the electrode[71]) by the nonsoluble, nonconductive Li−O_2 products.

In fact, all of these mechanisms will influence the discharge and charge processes of Li−air batteries. Their relative contributions might be dependent on the air electrode design (which is out of the scope of this article but worthy of a brief discussion). For a thin-layer air electrode with highly efficient gas transfer pathways, the passivation mechanism might control the process; for a thick air electrode with poor gas transfer pathways, the clogging of pores (usually at the side facing the air/oxygen[55,58,85]) should be responsible for deteriorating performances, especially at high current densities. This can be seen from the large influence of carbon loading (i.e., electrode thickness) on the specific capacity of the air electrode.[19,85] Therefore, it is very important to develop new concepts of air electrode design.

Williford and Zhang[18] proposed an interconnected dual pore system in air electrode (one catalyzed and one noncatalyzed, or one macroporous and one mesoprous/microporous systems). On the basis of their modeling results,[18] it is expected that dual pore system electrodes (materials) are the most promising one in terms of energy density and power density: the first pore system (mesopores) serves for the storage of Li−O$_2$ products, and the second pore system (macropores) allows oxygen transport; the products do not clog the second pore system, and this secures oxygen transport into the inner regions of the electrode and improves the utilization efficiency of the pores.[9] In fact, this concept was successfully used in fuel cells.[110,111] For instance, the air electrode in PEM fuel cells typically comprises microporous agglomerates of the catalyst (Pt or Pt alloy nanoparticles on the support), the solid electrolyte (Nafion ionomer), and the macropores between microporous agglomerates. Hence, the microporous agglomerates contain a triple phase boundary at which the oxygen reduction reaction takes place, whereas the macropores provide paths for the reactant and product flow into and out of catalytically active sites.[118−120]

Recently, the concept of dual pore system electrodes has been demonstrated by Xiao et al. in a Li−air battery using a hierarchically porous graphene air electrode.[92] In their air electrode, graphene aggregates into loosely packed, "broken egg" structures with large interconnected tunnels; the "shells" of the "broken eggs" consist of numerous smaller nanoscale pores in direct communication with the large tunnels. During discharge, the robust large tunnels can function as "highways" to supply the oxygen to the interior carbon while the small pores on the walls are the "exits", which provide triphase regions for oxygen reduction and Li−O$_2$ product storage. The hierarchically porous graphene air electrode shows a discharge capacity of 15 000 mAh/g carbon, which is the highest capacity reported to date.[92]

From the perspective of materials and chemistry, functionalized carbon might provide advantages, as in the case of oxygen reduction in aqueous systems.[121−123] Kichambare et al.[90] reported the enhanced performance of nitrogen-doped carbon (N−C, pristine carbon is a mixture of Ketjenblack EC 600JD and Calgon activated carbon). They found that,[90] even though the BET surface area, pore volume, pore size, and porosity of carbon black only slightly increase (<12%) after nitrogen doping, the capacity (if limiting discharge voltage at 2.0 V) increases by a factor of 5, and the discharge voltage is also higher for N−C. This indicates the superior intrinsic activity from nitrogen doping.[90] The Sun group[89] also reports that a Li−air battery with nitrogen-doped carbon nanotubes (N-CNT) exhibit a higher discharge capacity (about 50% improvement) and high discharge voltage, even though the BET surface area and pore volume (with the same pore size) of N-CNT are lower than those of pristine CNT. These indicate the benefit of the functional groups in improving the capacity and oxygen reaction kinetics (i.e., the rate capability) in Li−air batteries. The fundamental mechanisms of functionalized carbon enhancing Li−air performance still need more investigation so that this strategy can be more effectively deployed.

3.2. Metal Oxides. Bruce and co-workers[23] studied various transition metal oxides (La$_{0.8}$Sr$_{0.2}$MnO$_3$, Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, NiO, CuO, CoFe$_2$O$_4$) as oxygen electrocatalysts for Li−air batteries. These materials are widely used oxygen catalysts in aqueous systems (e.g., fuel cells, Zn−air batteries). They found that among the catalysts studied, the highest capacity retentions

were observed with Fe$_3$O$_4$, CuO, and CoFe$_2$O$_4$. Co$_3$O$_4$ gave the best compromise between initial capacity and capacity retention, as well as the lowest charging voltage of 4 V. They later studied the widely used electrocatalysts MnO$_2$ with various morphologies and surface areas.[21] The morphology and the performance are shown in Figure 8. They found that the α-
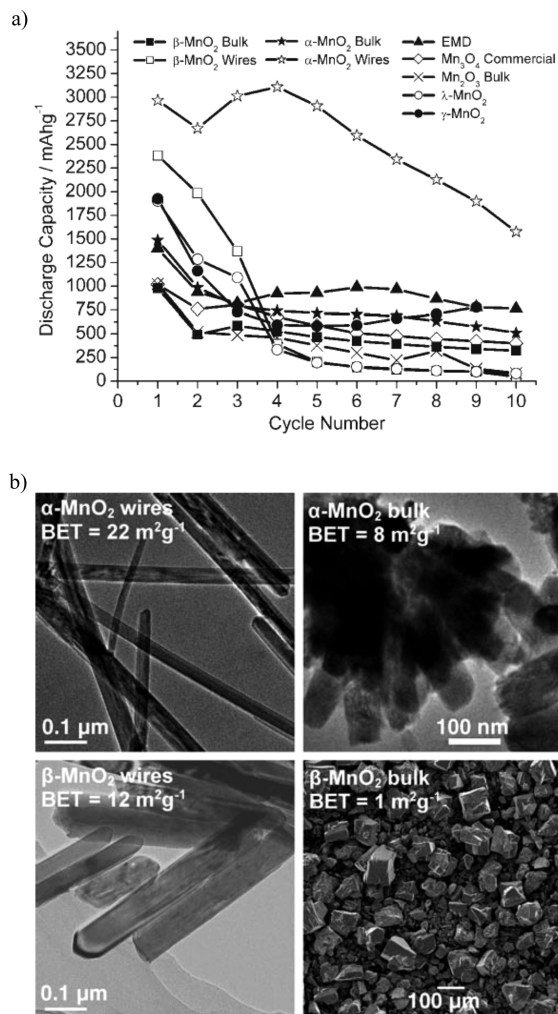

Figure 8. (a) Variation of discharge capacity with cycle number for several porous electrodes containing manganese oxides as catalysts.[21] (b) TEM/SEM images of bulk and nanowire forms of α- and β-MnO$_2$ polymorphs showing their morphologies and surface areas.[21].

MnO$_2$ nanowires have much higher capacity and cyclability than other materials, including β-MnO$_2$ nanowires. They stated that the nature, morphology, and surface area of catalysts are the key factors controlling the performance of the oxygen electrode, especially the capacity.

Trahey et al.[124] proposed a new approach for designing electrocatalysts for a Li−air battery by activating lithium metal oxides with a high Li$_2$O content. The activation was accomplished by removing Li$_2$O either electrochemically within the cell or chemically with acid prior to cell assembly. Both electrochemically activated Li$_5$FeO$_4$ (5Li$_2$O·Fe$_2$O$_3$) and acid-activated Li$_2$MnO$_3$·LiFeO$_2$ ([Li$_2$O·MnO$_2$]·[Li$_2$O·Fe$_2$O$_3$]) materials provide high discharge capacities, with the latter being even better. The electrode processes can be considered as reversible Li$_2$O extraction and reinsertion in host structures, which can accommodate Li$_2$O within its interstitial space and

no severe structure changes on Li_2O removal. Trahey et al.'s approach might provide an alternative strategy in developing Li−air positive electrode materials with enhanced cyclability based on a mechanism (Li_2O extraction/reinsertion) different from conventional Li−air catalysis.[124,125]

Giordani et al.[126] packed various metal oxide electrocatalysts with Li_2O_2 and studied their catalytic effect on Li_2O_2 decomposition during charge. It is known that during charge process, the artificially packed discharged electrode (Li_2O_2) proceeds only through the decomposition of Li_2O_2 ($Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$).[16,68] Therefore, they can avoid the complicated Li−O_2 reactions, especially the side reactions with nonaqueous electrolytes, and focus only on the electrochemical decomposition of Li_2O_2. Figure 9 shows their
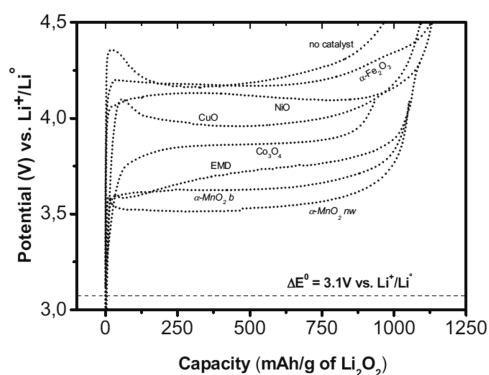
Figure 9. Charge curve of prepacked Li_2O_2 electrode with various metal oxide electrocatalysts.[126]

results.[126] MnO_2 is the best among the studied metal oxides. The ability of MnO_2 to promote the electrochemical decomposition of Li_2O_2 depends on their structures and morphologies, with the nanowires showing the lowest charge voltage (highest activity). Giordani et al.'s results are consistent with Bruce and co-workers' results,[21,23] even though the latter might involve significant side reactions of Li−O_2 with electrolytes, which leads to the main discharge products of Li_2CO_3, LiOH, and lithium alkyl carbonates.[16] This indicates a possible correlation between Li_2O_2 decomposition and the electrochemical decomposition of other lithium compounds (Li_2CO_3, LiOH, lithium alkyl carbonates). It is worth noting that the commercial Li_2O_2 particles might be quite different from the electrochemically formed Li_2O_2 during Li−O_2 discharge in terms of size, surface chemistry/physics and even bulk properties.[127,128] Therefore, further investigations are needed.

3.3. Nonprecious Metals. Dobley et al.[129] investigated the effect of various metal catalysts on the performance of lithium−air batteries. They showed that among the different metal catalysts studied, the manganese-catalyzed air cathodes gave the highest specific energy, which was approaching 4000 mAh/$g_{(carbon)}$.

Recently, Ren et al.[20] studied nonprecious metal electrocatalysts (CuFe/C, CuFe supported on Ketjenblack carbon) which were originally developed for aqueous alkaline fuel cells.[130,131] They found that the catalysts can significantly improve the discharge voltage and rate capability (Figure 10). A Li−air cell with a CuFe/C cathode exhibited a higher (over +200 mV) discharge voltage than that of a cell with a Ketjenblack carbon cathode without catalysts. The enhancement is even more significant at high discharge rates. Their Li−
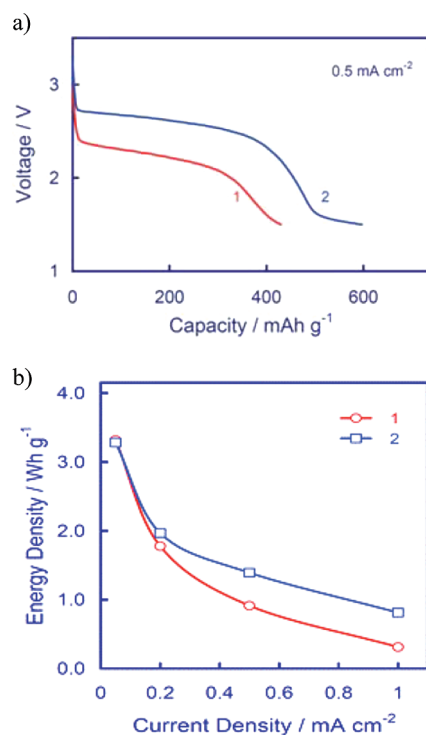
Figure 10. (a) Li/air cell discharge voltage curves at 0.5 mA/cm^2. (b) Plot of specific energy as a function of discharge current density. (1) Carbon and (2) CuFe−carbon.[20]

air cell with a CuFe/C cathode demonstrated a specific energy of over 800 Wh/kg (1 mA/cm^2), which is more than twice that of the cell with a Ketjenblack carbon cathode without catalysts at the same rate. This indicates that the electrocatalyst (CuFe/C) improves the ORR kinetics. They attributed the higher ORR activity to the higher level of free catalytically active site density in CuFe/C, which decreases the ORR polarization.[20] They stated that the termination of the cell discharge process is due to the rapid build-up of Li−O_2 products covering the active sites, instead of the clogging of pores at the cathode.[7,9,19,57,95] The deactivated catalytic sites can be regenerated only by removing the Li−O_2 products into electrolyte or other nonactive sites in an 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. This mechanism is partially supported by other research. For example, adding a certain solvent in a Li−air cell that can dissolve Li−O_2 products,[132] or modifying air electrode surface with macromolecules that can prevent electrodes from passivation[117] can improve the performance of a Li−air battery. The recent modeling results also support this, which indicates that electrical passivation of an electrode surface (deactivation of active sites) is the dominant capacity-limiting mechanism instead of mass transfer limitation.[71] The mechanism proposed by Ren et al. needs further investigation with carefully designed experiments. In-situ microscopic study of the discharge process may give more conclusive evidence on this mechanism.

3.4. Precious Metals. Shao-Horn and co-workers[28,36] reported precious metals (alloy)-based electrocatalysts for a Li−air battery (Figure 11). They first found that Au/C promotes the discharge process (ORR) and Pt/C promotes
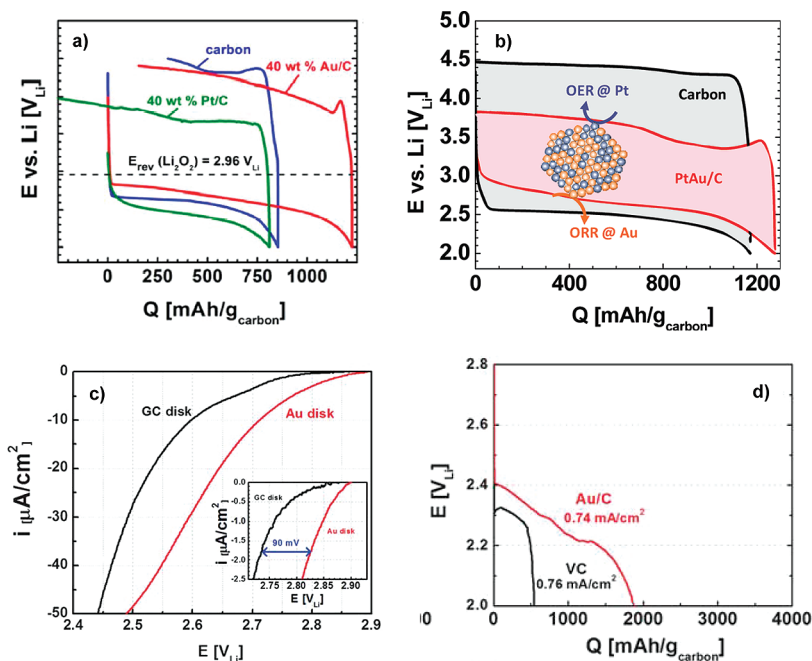
Figure 11. (a) Li−O$_2$ cell discharge/charge (second cycle) at 0.1 mA/cm^2 electrode.[22] (b) Li−O$_2$ cell discharge/charge profiles of carbon (black, 85 mA/g carbon) and PtAu/C (red, 100 mA/g carbon) in the third cycle at 0.04 mA/cm^2 electrode.[24] (c) Capacitive and IR-corrected ORR polarization curves of GC and Au in pure O$_2$ 0.1 M LiClO$_4$/DME (20 mV/s, 100 rpm).[104] (d) Discharge profiles of Li−O$_2$ cells of VC and Au/C at 2000 mA/g carbon (VC = Vulcan carbon).

the charge process (OER) in a Li−air battery.[22,37] They later found that the intrinsic activity of Au for the ORR is much higher than carbon, and the ORR overpotential is significantly decreased, especially at high discharge rates.[104] They designed a bifunctional electrocatalyst—Pt−Au alloy—for rechargeable Li−air batteries.[24] The new bifunctional Pt−Au electrocatalyst significantly decreases the overvoltage, especially for the charge process, thus increasing the round-trip efficiency of the Li−air battery from 57% to 73%. The charging voltage on their Pt−Au/C is considerably lower than various manganese oxides,[21,58,70] and cobalt (oxides)-based electrocatalysts.[1,23]

Even though the use of precious metals might make a Li−air battery economically impractical, the idea of developing bifunctional electrocatalysts is a good strategy for future development of Li−air battery electrocatalysts. This, in fact, tells that the electrocatalysts for the ORR and OER could be (or must be) different for a Li−air battery, which is consistent with the different mechanisms for ORR and OER.[42,50,51] This is similar to oxygen electrocatalysis in aqueous systems. For example, Pt is an excellent electrocatalyst for oxygen reduction, but not good for oxygen evolution; in contrast, iridium and iridium oxide exhibit poor electrocatalytic activity for oxygen reduction but outstanding activity for oxygen evolution.[133−135]

In this section, we have discussed the electrocatalysts that have been studied for Li−air batteries. These catalysts show potential promise for improving the Li−O$_2$ reaction kinetics and, thus, the rate capability and cycling efficiency of Li−air batteries; however, significant challenges still exist. For the discharge process (i.e., ORR), the performance of current electrocatalysts is still too low. This can be seen from the unacceptably low discharge current density (i.e., low rate capability). Of course, the rate capability of a Li−air battery depends on many factors, and the catalysts should be one of the key contributors. For the charge process (i.e., OER), there are significant ambiguities in most of the previous studies on

electrocatalysts for nonaqueous Li−air batteries because the exact chemical composition of Li−O$_2$ products was not positively identified (this should not influence the discharge process much, since all these lithium compounds are nonconductive and form a solid film covering the surface of the air electrode). In these previous studies, it was assumed that the discharge product is Li$_2$O$_2$; however, several recent reports indicate that Li−O$_2$ products are much more complicated than expected (see Section 4.1).[14,16,47,49,67,68] Even though there is a possible correlation between Li$_2$O$_2$ decomposition and the electrochemical decomposition of other lithium compounds (Li$_2$CO$_3$, LiOH, lithium alkyl carbonates),[126] the true electrocatalytic efforts of these catalysts still need further investigation, especially for the electrochemical formation and decomposition of Li$_2$O$_2$.

4. PERSPECTIVE ON LI−AIR BATTERY ELECTROCATALYSTS

Li−air battery technology, especially rechargeable Li−air batteries, is still in its very early development stage. Significant efforts are needed for the fundamental understanding of Li−O$_2$ reactions and the materials design/development. In this section, we provide a perspective on electrocatalyst development for nonaqueous Li−air batteries.

4.1. Challenges beyond Electrocatalysts. Recently, it has been found by several independent research groups that the widely used organic carbonate-based solvents, such as propylene carbonate (PC), are not stable in oxygen-rich conditions in a Li−air battery.[15,16,47,49,64,68,136] The intermediates during oxygen reduction, for example, O$_2^-$, O$_2^{2-}$, and LiO$_2$/LiO$_2^-$,[59] can react with nonaqueous solvents in many different ways: for example, as a strong nucleophile, a Brønsted base, a one-electron reductant, and an oxidant.[46,53,60−63] They can easily decompose carbonate-based solvents. This leads to Li−air battery discharge products of Li$_2$CO$_3$, LiOH, and lithium

alkyl carbonates,[14,16,48,49,64−66] instead of the desired product—Li_2O_2—which solely can make Li−air battery truly rechargeable.[16,67] The decomposition of solvents and the resultant formation of lithium carbonates and other lithium compounds are among the main reasons for the poor cyclability and low energy efficiency of a Li−air battery (a Li−O_2 cell with Li_2O_2 as a main discharge product has shown lower charge voltages[66,82]). Unfortunately, almost all of the above electrocatalysts studies were carried out in carbonate-based electrolytes, even though in some reports, Li_2O_2 is claimed to be a discharge product.[21,91,108] Although an ether-based electrolyte may lead to the formation of Li_2O_2,[16,49,88,104,137] other side reaction products were still observed in the discharge products, and the sustainable discharge/charge of Li_2O_2 is still not achieved.[14] This raises an important question:[82] can these electrocatalysts work in other (stable) electrolyte systems for the sustainable formation/decomposition of Li_2O_2?

Therefore, a stable electrolyte system that can lead to the exclusive formation/decomposition of Li_2O_2 is critical (which is out of the scope of this article) for future investigation of electrocatalysts used in Li−air batteries.

4.2. Criteria for Practical Electrocatalysts. What kinds of materials can be used as electrocatalysts for future practical Li−air batteries? It is intuitive and interesting to compare Li−air batteries with PEM fuel cells, both of which have an oxygen electrocatalytic electrode. In current PEM fuel cells, a power density of 1.0 W/cm^2 (corresponding to ~1.5 A/cm^2 at a 0.7 V cell voltage) can be easily achieved with a catalyst loading of 0.2−0.4 mg Pt/cm^2.[138] Currently, the rate performance of a Li−air battery is limited to 0.1−1.0 mA/cm^2, with an average discharge voltage of ~2.5 V[5,37,55,138] (in fact, most of these data were achieved in pure or even high-pressure pure oxygen with a catalyst loading of around 10 mg/cm^2;[57,84] only a few groups report the data with ambient operation[115,139−141]). The long-term performance target for a Li−air battery could be 10 mA/cm^2 with a catalyst loading of 1.0 mg/cm^2, corresponding to a power density of ~25 mW/cm^2.[5,37,138] From the above data, one can estimate that, in comparison with PEM fuel cell, the amount of catalysts per watt (g/W) used in a Li−air battery is 3−5 *orders of magnitude higher* if based on current technology and over *2 orders of magnitude higher* even if based on the long-term targeted technology. The main reason for such a high catalyst usage is the extremely low rate capability (mA/cm^2) of Li−air batteries. This will eliminate the possibility of using any precious metals in practical Li−air batteries. Therefore, electrocatalysts with no precious metals are required for practical Li−air batteries.

In summary, the key criteria for future electrocatalyst study for a practical rechargeable Li−air battery are (1) To exclusively promote the formation/decomposition of Li_2O_2, but not other compounds. (Li_2O is not rechargeable, either.[67] Recently, it was pointed out by Zhang et al. that some catalysts might promote the formation of Li_2O through catalyzing the chemical disproportionation of Li_2O_2, so further study is needed to confirm or disapprove this.[142]) (2) To eliminate precious metals and use only nonprecious metals and other very low-cost materials. (3) Electrocatalyst study must be carried out in stable electrolytes.

4.3. Future Research Directions. Here, we recommend a few topics worthy of attention in the future investigation of oxygen electrocatalysts for Li−air batteries.

4.3.1. Limiting Factors in Li−O_2 Electrochemistry and Electrocatalyst Roles. Electrocatalysts are designed to decrease

ORR/OER overpotentials; therefore, identifying the determining factors of the overpotentials is critical for electrocatalyst development.[5,50,71] The Li−O_2 reaction products' being solid and an insulator makes the electrocatalysis in Li−air batteries much more complicated and presents more challenges to identifying the determining contributors to the overpotential. Generally speaking, the contributors should come from two kinds of processes: electrochemical and nonelectrochemical ones. Albertus et al.[71] recently reported their experimental and modeling results on limiting factors of Li−air battery capacity, and the passivation of an air electrode by nonconducting Li−O_2 products is shown to be a critical one (Figure 12).
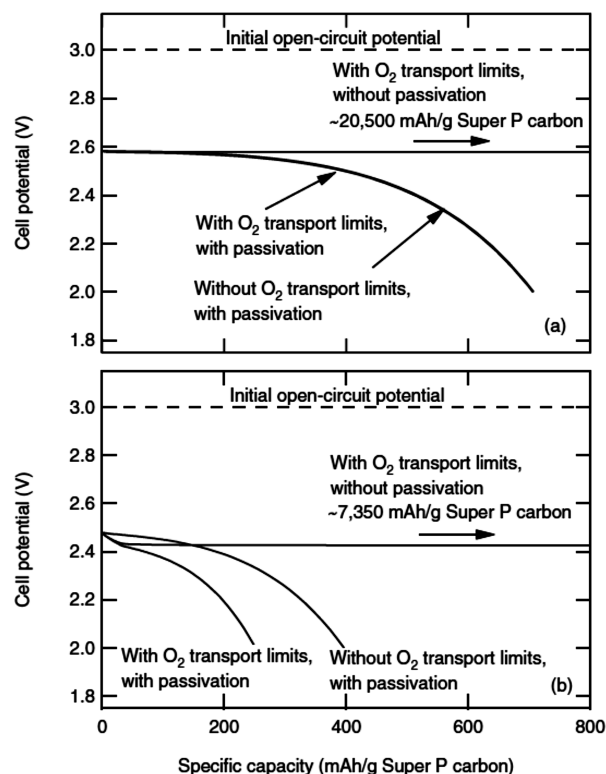

Figure 12. Simulation results demonstrating the relative impacts of eliminating oxygen transport limitations and eliminating the electronic resistance of the discharge products: (a) 0.08 and (b) 0.47 mA/cm^2.[71]

We believe that the nonelectrochemical factors that mainly result from the passivation of an air electrode by Li−O_2 products should play an important role, if not a dominating role, for both ORR and OER. In addition to the transfer of oxygen and Li$^+$ on which electrocatalysts may have no influence, other possible factors that influence the overpotential might include the particle size and morphology of Li_2O_2, the surface/bulk chemistry/physics (defect/vacancies) of Li_2O_2, the interfacial properties between Li_2O_2 and electrocatalysts, etc. Some recent results also provide insight into this aspect.

(1) OER potential for an artificially packed Li_2O_2 electrode (4.65 V) is quite different from that for electrochemically deposited Li_2O_2 (Li_2O_2 formed in the battery discharge process) (3.2−4.6 V).[49] We think this is mainly due to the different contact between Li_2O_2 and the active carbon surface. For the electrochemically deposited Li_2O_2, the in situ-formed fine particles (tens of nanometers) have intimate contact with the carbon surface. This will largely reduce the OER potential during the charge process. In contrast, the large size (tens of

micrometers) of artificially packed Li_2O_2 has a much poorer contact with the surface.[49] The particle size and morphology of Li_2O_2 might be influenced by the discharge profile and electrocatalyst properties.[5,71,88] This needs further investigation, especially using in situ microscopy.

(2) The computed band gaps suggest that the electronic resistivity of Li_2O_2 is orders of magnitude smaller than that of Li_2O or Li_2CO_3.[71] Furthermore, the presence of vacancies, dopants, and amorphous structures may result in an even lower electronic resistivity of Li_2O_2,[50,143] which is advantageous for the discharge/charge of a Li−air battery.

Recent theoretical calculations[127] reveal that the most stable Li_2O_2 surfaces are oxygen-rich. This leads to the formation of a thin metallic and ferromagnetic region (i.e., half-metallic behavior) localized at the surface, with an estimated electrical conductivity of $\sim10^5$ Ω^{-1}/m. In contrast, Li_2O surfaces are predicted to be insulating and nonmagnetic. This may explain why Li_2O_2 is rechargeable but Li_2O is not.[48] On the basis of this calculation, it is reasonable to assume that the oxygen-rich surface of Li_2O_2 has a structure similar to LiO_2. The decomposition overpotential of LiO_2 is lower than that of Li_2O_2, as can be seen from the CV results.[52] This might explain the fact that O_2 evolution potential can be as low as 2.9 V[82] and more than one charge potential plateaus for a Li−O_2 cell with Li_2O_2 as the main discharge product (such as DME as electrolyte solvent).[49] The first charge plateau might be due to the decomposition of surface Li_2O_2 (e.g., oxygen-rich, LiO_2 similar structure), which is more conductive and less stable, and the remaining are due to the decomposition of bulk Li_2O_2. If this is true, one of the key questions is how to increase the percentage of oxygen-rich Li_2O_2 so that the average charge voltage can be decreased. The particle size of Li_2O_2 should be one of the key factors: the smaller particles have a higher specific surface area so that the surface oxygen-rich Li_2O_2 content is higher.

(3) In fact, the chemistry and physics (e.g., defects, vacancies) of the surface (even the bulk) of Li−O_2 product Li_2O_2 might be influenced by electrocatalysts. Shao-Horn and co-workers[104] show an enhanced ORR activity on Au/C; Au/C might catalyze the formation of $Li_{2-x}O_2$ with defects/nonstoichiometry, and $Li_{2-x}O_2$ promotes the diffusion of Li ions in the solid state. This is supported by their O K and Li K X-ray absorption near edge structure results, X-ray diffraction data,[104] and previously reported density functional theory (DFT) findings from the Norskov group.[50] This indicates that electrocatalysts can work in such a way that a desired surface chemistry/physics/morphology of the discharge product Li_2O_2 can be obtained on some special electrocatalysts, which in turn is advantageous for charge process. This is a new concept of electrocatalysis that is completely different from the conventional one such as oxygen reduction/evolution electrocatalysis in aqueous systems. Significant effort is needed to develop and deploy this new electrocatalysis concept.

4.3.2. Electrocatalyst Materials. There have been many investigations and great advances in the field of nonprecious metal electrocatalysts, such as metal oxides,[35,144] heteroatom-doped carbon nanostructures,[121−123] transition metals−nitrogen−carbon nanostructures.[145,146] Even though most of these electrocatalysts were originally developed for aqueous systems such as PEM fuel cells and zinc air batteries, they could provide guidance for the electrocatalysts' design and development for Li−air battery if a relationship between aqueous oxygen

electrocatalysis and nonaqueous electrocatalysis can be constructed.

In fact, because of the similarity between H_2O_2 and Li_2O_2, a relationship has been tentatively constructed among the catalytic activities of a series of materials toward H_2O_2 decomposition reaction and that toward the charge voltage of a Li−air battery (the electrochemical decomposition of Li−O_2 products, ideally Li_2O_2).[126] H_2O_2 decomposition is then put forward as a fast selection tool for electrocatalysts in a Li−air battery.[126,147] In fact, in an aqueous oxygen electrocatalysis system, the enhanced activity of certain electrocatalysts such astransition metal oxides is mainly due to their catalytic activity toward H_2O_2 decomposition.[35] This indicates that knowledge of aqueous oxygen electrocatalysis will provide valuable guidance for development of Li−air electrocatalysts.

Recently, Suntivich et al.[144] reported design principles for oxygen-reduction electrocatalysts based on perovskite oxides (ABO_3, or $AA'BB'O_3$) in aqueous electrolyte. They claimed that the ORR activity for perovskite catalysts primarily correlates to σ^*-orbital (e_g) occupation and the extent of B-site transition-metal−oxygen covalency, which are considered to be the primary and secondary activity descriptors. They compared the ORR activity of the perovskites and the d-electron number per B cation and found an M-shaped relationship, with the maximum activity attained near d^4 and d^7.[144] This is similar to the trend for the oxidation activity of gas-phase CO and hydrocarbon on perovskites.[148,149] They further found that the intrinsic ORR activity of the oxides exhibits a volcano shape as a function of the e_g-filling of B ions, with the maximum at $e_g \approx$ 1. They later demonstrated that this is true for OER:[150] a transition metal oxide having a surface cation e_g occupancy close to unity and high B-site oxygen covalency has the highest OER catalytic activity. This is reasonable because of the synergism effect between OER and ORR.[151] This indicates high-performance bifunctional oxide electrocatalysts can be designed and developed on the basis of the concept.

We believe that this work[144] is also related to nonaqueous oxygen reactions. Fundamentally, oxygen electrocatalysis in nonaqueous systems is based on the interaction between oxygen (and intermediates) and electrocatalysts: the adsorption energy, which is the same as that in aqueous systems. This can be seen from a recent report that shows a volcano dependence of electrocatalytic activity on oxygen adsorption energy.[152] Identifying this relationship between aqueous and nonaqueous systems will be a key driver for development of Li−air electrocatalysts.

The interaction between O_2 and electrode surface (electrocatalyst) determines not only ORR activity, but also ORR product distribution (H_2O vs H_2O_2 in aqueous solution).[37,153] This should also be applicable for Li−air electrocatalysis. It is speculated that the Li−O_2 products are influenced by catalysts; the formation of Li_2O_2 is preferred on catalysts that have low oxygen adsorption strength, and Li_2O is preferred on catalysts with high oxygen catalyst bond strength.[37]

Other lessons from aqueous systems should be pursued and combined in new electrocatalyst design. It is well-known that, in aqueous systems, carbon materials with defects/functional groups are more electrocatalytically active.[29,121−123,154−158] Recently, Xiao et al.[92] demonstrated that an air electrode based on functionalized graphene with more defects/functional groups exhibits better performance in a Li−air battery. Their SEM/TEM observations and DFT calculations indicate that Li−O_2 products prefers to nucleate at the defects/functional

group sites and that the Li−O$_2$ discharge product particles are smaller and more uniformly dispersed on graphene with more defects/functional groups. Xu et al. also revealed from DFT calculations that oxygen functional groups and defects on carbon materials can accelerate oxygen reduction under Li$^+$-containing conditions by decreasing the overpotential.[159] This is significant for electrocatalyst design, especially for a rechargeable Li−air battery: since Li−O$_2$ products are solid and nonconductive, the efficient contact between catalyst and Li−O$_2$ products is critical for the electrocatalytical decomposition of Li$_2$O$_2$, and smaller sized Li$_2$O$_2$ is much easier to decompose, as has been experimentally confirmed.[49]

On the basis of Xiao et al.'s work and recent discovery of a triple junction structure in which a metal catalyst is stabilized at metal−metal oxide-defect graphene,[160] an efficient bifunctional electrocatalytic structure might be constructed: electrocatalysts can be formed at the defect sites of porous carbon materials such as graphene; during discharge, Li$_2$O$_2$ will be deposited at the position of defect/electrocatalysts, which leads to highly effective contacts between catalysts and small-size Li$_2$O$_2$. This is beneficial, especially for the OER process.

Recently, Chen and co-workers[161] reported a core−corona structured bifunctional catalyst consisting of lanthanum nickelate centers supporting nitrogen-doped carbon nanotubes for rechargeable metal−air batteries. The nanostructured design of the catalyst allows the core and corona to catalyze the oxygen evolution reaction and oxygen reduction reaction, respectively. Even though this catalyst is designed for oxygen reaction in aqueous systems, the concept design of a bifunctional catalyst should be beneficial for Li−air batteries.

4.3.3. Alternative Electrocatalysts. Since the existing nonaqueous solvents may not be able to suppress all of the side reactions and promote only the formation of Li$_2$O$_2$, in addition to thinking of the catalyst as promoting Li−O$_2$ reactions, a "negative" catalyst which can suppress the side reactions except the formation of Li$_2$O$_2$ might enable truly rechargeable Li−air (or Li−O$_2$) batteries. No investigation has been carried out from this perspective but it is worthy of study. The combination of these two kinds of electrocatalysts, the one to promote of Li−O$_2$ reactions to form Li$_2$O$_2$ and the one to suppress the side reactions, should be a direction for Li−air electrocatalyst development.

5. SUMMARY

The Li−air battery is a very promising energy storage technology. Experimental studies and theoretical calculations have shown that the Li−air battery has a potential to provide four times higher specific energy than state-of-the art Li ion batteries.[5,7] Its cost is also expected to be much lower than Li ion batteries. However, current the Li−air battery is limited by its poor power density, poor cyclability, and low round-trip energy efficiency. Electrocatalysts have been shown to significantly improve both power density and round-trip energy efficiency, even though the sustainable discharge/charge of the Li−air battery with these electrocatalysts has not been fully verified, mainly because of the instability of the electrolytes. In this article, we have reviewed and given a perspective on the status, the challenges, and future directions of the investigation of oxygen electrocatalysts for nonaqueous Li−air batteries. The key points include the following:

1 A proper and stable electrolyte system should be established for electrocatalyst study and for a practical Li−air battery operation.

2 New concepts of electrocatalysis for the formation and decomposition of Li$_2$O$_2$ should be developed. This may include (1) electrocatalyst-enabled modification of Li$_2$O$_2$ with desired chemical/physical properties and structures and (2) alternative electrocatalysts that can suppress the side reactions, etc.

3 Nonprecious bifunctional electrocatalysts (i.e., for both ORR and OER) are required for Li−air batteries. Electrocatalysts should promote the formation/decomposition of Li$_2$O$_2$ exclusively and suppress the formation of other lithium compounds because only Li$_2$O$_2$ can be sustainably recharged.

4 Lessons could be learned from aqueous oxygen electrochemistry, especially fuel cells and alkaline metal−air batteries.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: (J.L.) jun.liu@pnnl.gov; (Y.W.) yong.wang@pnnl.gov; (J.G.Z.) Jiguang.zhang@pnnl.gov.

Notes
The authors declare no competing financial interest.

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