

Understanding Rechargeable Li–O₂ Batteries via First-Principles Computations

Xu Zhang,^[a] An Chen,^[a] Menggai Jiao,^[a] Zhaojun Xie,^[a] and Zhen Zhou^{*[a]}

Driven by the growing demand of energy storage devices, rechargeable Li–O₂ batteries, especially non-aqueous ones, are considered as one of the most promising technologies due to their ultrahigh energy density. However, there are still many challenges, including poor catalytic activity, low conductivity and solvent degradation, to be overcome before their implementation in practical applications. Over decades, first-principles computations have made great progress and become a power-

ful tool to predict key performances of various components in rechargeable Li–O₂ batteries at atomic level. In this review, we introduce first-principles approaches, and summarize the recent advancement in computational investigations on cathode catalysts, products and solvents for rechargeable Li–O₂ batteries. In addition, the challenges and potential research directions are also briefly discussed.

1. Introduction

Energy storage systems are crucial to extensive applications in daily life, from portable electronic devices to smart grids and electric vehicles (EVs).^[1] Batteries that can convert chemical energy to electricity have been used to store energy and supply power for various applications over one hundred years.^[2] Among numerous batteries, lithium-ion batteries (LIBs) have dominated the power market of mobile electronics and EVs.^[3]

With the advantages of low-carbon economy and environmental protection, EVs have been becoming the trend of auto industry. However, the current EVs are powered by LIBs and the low energy density of LIBs greatly limits the driving range, thus capping the marked size of EVs.^[4] Generally, the energy density of gasoline (12000 Wh kg⁻¹) is about fifty times larger than that of LIBs (~200 Wh kg⁻¹).^[4,5] Therefore, the exploration of novel energy storage systems which could far exceed the energy density of LIBs is the central to the development of EVs.

Among various kinds of next-generation batteries, Li–air batteries are mainly based on the electrochemical couple between metallic Li at the anode and air (mainly oxygen) at the cathode. Generally, via the reaction of $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$, the discharge product is Li₂O₂ which could yield a high theoretical specific energy of ~3500 Wh kg⁻¹.^[6] Note that the high theoretical specific energy is based on the total mass of the lithium metal anode and cathode including O₂. Such excellent characteristics can further extend the running distance of EVs and enable their worldwide extensive applications.

The development of practical Li–air batteries faces various formidable challenges, and the understanding of Li–O₂ electrochemistry is extremely critical, particularly from atomic level. Many advanced experimental techniques have been used to investigate Li–O₂ batteries;^[7] however, it is still highly expensive and difficult to characterize the electrochemical process and performance at atomic level. In addition, the development of novel materials for Li–O₂ batteries is traditionally time and cost consuming.

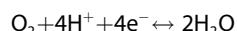
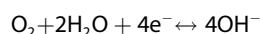
With the rapid progress in supercomputers and high-performance computations, computer simulations have greatly accelerated the investigations in materials science. First-principles computations directly on basis of quantum mechanics could predict fundamental properties and reaction processes at the atomic and electronic scale without requiring any higher order parameters such as experimental data. Currently, density functional theory (DFT) developed by Kohn and co-workers^[8] is one of the most powerful and widely used tools to predict promising functional materials and the corresponding properties before successful synthesis. Furthermore, if the simulation model is well consistent with the experimental conditions, the computations could be more reliable to thoroughly understand the reaction and mechanism.

First-principles computations have been extensively used to explore LIBs and Li–O₂ batteries. Many intrinsic properties of electrode materials, such as voltage, ionic mobility, thermal and electrochemical stability, and electronic properties, could be accurately achieved. There have been many reviews about computational investigations on LIBs.^[9] However, the reviews on simulations of Li–O₂ batteries mainly focus on finite element methods to investigate the transport within a cell or interface,^[10] and first-principles computational investigations on Li–O₂ batteries have not been comprehensively summarized. Therefore, we fill the gap in this review by focusing on first-principles computational insights into oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) on air cathodes and the properties of Li₂O₂ and solvents.

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 An invited contribution to a Special Collection dedicated to Metal-Air Batteries.

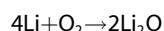
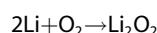
2. Oxygen Evolution Reaction and Oxygen Reduction Reaction

Air cathodes have been widely used in aqueous air batteries, which contain an aqueous electrolyte-air interface, such as Zn-air, Mg-air or Al-air batteries.^[11] In these systems, O₂ molecules react with water and typically there are two kinds of half-cell reactions on air cathodes relying on the pH value of aqueous electrolytes:



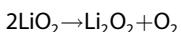
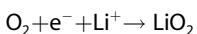
which are essentially different from the electrochemical processes in non-aqueous Li-air batteries.

In 1996, Abraham et al.^[12] for the first time reported a non-aqueous Li-air battery system and proposed the following reaction mechanism:



Then, Ogasawara et al.^[13] reported that in a non-aqueous Li–O₂ battery, the electrochemical reaction of $2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O}_2$ could be reversible. Typically, in a non-

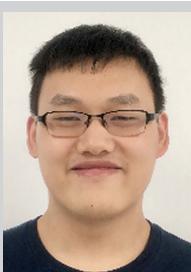
aqueous Li–O₂ battery, O₂ is reduced to Li₂O₂ during discharge and it is reversed during charge. The reaction processes of reduction of O₂ to Li₂O₂ is generally via the intermediate LiO₂:



However, due to the sluggish reaction kinetics of OER and ORR, the electrical efficiency of Li–O₂ batteries is limited in both discharge and charge.^[6b,13] Therefore, the investigation of electrochemical processes is essential for the development of practical Li–air batteries. In this section, we focus on the computational investigations on OER and ORR. Generally, the free energies of the elementary reactions of OER and ORR were computed to evaluate the potential dependence of OER and ORR. Then the overpotential can be calculated by the difference between the calculated equilibrium potential and rate-limiting potential and the cathode catalytic performance can be evaluated on the computed overpotential.

2.1. OER and ORR on Pure Li₂O₂

By means of first-principles computations, the energy of important intermediates can be estimated and based on this,



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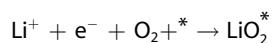
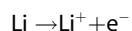


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OER and ORR can be investigated in detail. First, OER and ORR processes on pure Li_2O_2 surface will be discussed. Hummelshøj et al.^[14] for the first time simulated ORR on an $\text{Li}_2\text{O}_2(100)$ surface to investigate the reaction mechanism in an aprotic $\text{Li}-\text{O}_2$ battery via computations. By calculating the free energy of each important intermediate, the possible origin of overpotential in discharge/charge processes could be identified. For the estimation of free energy, the entropy of solid phases was ignored and the entropy of gas-phase O_2 was considered. The following steps were investigated:



The free energy of $\text{Li}^+ + \text{e}^-$ at potential of 0 equals to that of bulk Li.

The calculated reaction steps in Figure 1 are only the adsorption and desorption processes and therefore, some additional energy barriers may be missing. However, the authors proposed that the free energy of the adsorption can represent the potential-dependent part and then the free energy diagram could be applied to understand the potential dependence of the process. The discharge reaction steps, that is, ORR, are downhill until the potential reaches 2.03 V, which indicates that the electrode reaction would be facile. If the potentials are higher, the last step will be uphill, which is the origin of the slow kinetics of the discharge process. The overpotential should be calculated by $2.47 - 2.03 = 0.43$ V, where 2.47 V is the calculated equilibrium potential in this work. The current density depends exponentially on the overpotential of discharge reactions, indicating that the electrode processes are rate determining.

Similarly, the charge process could be investigated in this way. The charge reaction would be all downhill at a potential of 3.07 V; thus the charge overpotential is $3.07 - 2.47 = 0.60$ V,

which is higher than the discharge overpotential. This result is consistent with the experimental observation that the charge overpotential is larger than the discharge one.

In addition, they also investigated the electron transfer of Li_2O_2 . Pure Li_2O_2 possesses a large band gap of 4.91 eV. However, Li_2O_2 with Li vacancies possesses more holes in the valence band and becomes an electronic conductor; therefore, there would be metallic state on the surface of Li_2O_2 during the operation in $\text{Li}-\text{O}_2$ batteries. However, the free energy diagram of the charge reaction was computed based on the inverse process of ORR and the mechanism of OER was not investigated.

Since the OER process plays an important role in the decomposition of Li_2O_2 , Mo et al.^[15] investigated the fundamental mechanism of OER. The decomposition of Li_2O_2 starts typically from its surface; therefore, the reaction path and barriers would be affected by the surface structure. Several slab

modes of (0001), (1120), (1100), (1121) and (1101) surface were constructed and the terminations were obtained by removing the corresponding atoms on the surface. For all the surfaces, the decomposition of Li_2O_2 would start from the removal of Li to form a superoxide like LiO_2 structure which is consistent with the experimental phenomenon that LiO_2 is the intermediate.^[6d,16] Then the oxygen evolution which possesses the highest energy barrier in the decomposition path occurs. The kinetic rate can be evaluated from the computed OER activation energies and the results indicate that on the abundant surfaces the kinetics is slow and on higher energy surfaces is faster.

Then Hummelshøj et al.^[17] further developed a model to investigate the electrochemical growth and dissolution of Li_2O_2 on various facets, terminations and sites, including terrace, steps and kinks of a Li_2O_2 surface. They reported that this model is reasonable to describe the discharge and charge of $\text{Li}-\text{O}_2$ batteries over most discharge/charge cycles. Since the electrochemical crystal growth/dissolution is very complicated with the contribution of many facets, terminations and sites (terrace, steps and kinks), they investigated the $\text{Li}-\text{O}_2$ electrochemistry on variety of them and found low thermodynamic overpotentials (< 0.2 V) for both discharge and charge at different facet sites, consistent with the low kinetic overpotential observed in experiments. However, some other discharge/charge paths possess higher overpotentials; therefore, the phase space of the electrochemistry would open up with overpotentials.

2.2. ORR and OER on Cathode Catalysts

Generally, the air cathodes play a critical role in $\text{Li}-\text{O}_2$ batteries. One of the most important features is that cathodes could exhibit highly catalytic activity towards ORR and OER, giving lower overpotentials.^[6d] However, in the above reports, the effects of cathode catalysts are not considered. Xu et al.^[18] investigated the oxygen reduction by Li (Li-ORR) on Au(111) and Pt(111) surfaces. The results indicate that compared with

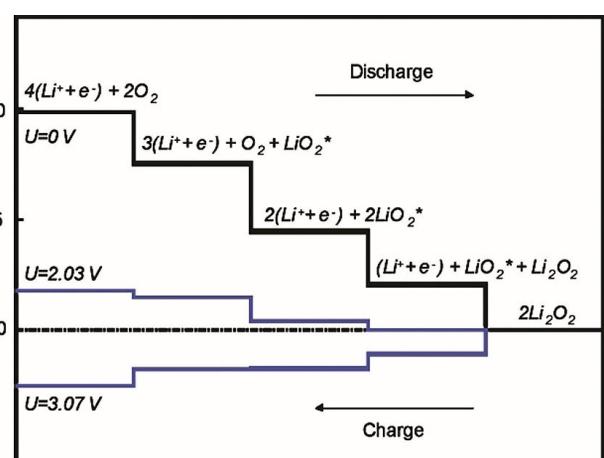


Figure 1. Free energy diagram of the reactions on the cathode in an aprotic $\text{Li}-\text{O}_2$ battery. Reproduced with permission from Ref. [14]. Copyright (2010) AIP.

Au(111), Pt(111) stabilizes O more than Li oxide species, limiting its reversible potential of the reduction of O. Therefore, they proposed that more oxophilic metal surfaces than Pt(111) could not enhance the reversible potential of Li–ORR. Subsequently, the effect of Au(111) and Pt(111) interfaces on the electronic transport was investigated by Chen et al.^[19] based on DFT and non-equilibrium Green's function computations. The electronic conduction is sensitive to the orientation and lattice matching of the interface and the transport relies on the alignment of O_2^- in Li_2O_2 to metal surface. Besides, the lithium vacancies can be present under charging conditions and pin the Fermi level at the top of the anti-bonding of Li_2O_2 , causing reduced transport during charging and thus providing explanation for the higher overpotential during charge than discharge.

Then, Dather et al.^[20] investigated the catalytic activity of several noble metals for Li–ORR. The results indicate that the electrochemical reduction of O is generally limited to the first electron transfer; therefore, the equilibrium potential (U_{eq}) of this step was further investigated. The Li–ORR activity eval-

uated by U_{eq} of six noble metals, Au, Ag, Pt, Pd, Ir and Ru, forms a volcano-like trend with respect to the adsorption energy of atomic O as shown in Figure 2a. Pd and Pt are located on the top of the volcano, consistent with the experiments as shown in Figure 2b.^[21] The results indicate that too strong interaction between O and metal (Ru and Ir) reduces the capability of O to bond with Li while too weak O-metal interaction (Au and Ag) hinders O_2 activation. Thus, the researchers proposed that the adsorption of O should be close to that of Pt and Pd as an active Li–ORR electrocatalyst. Then, Krishnamurthy et al.^[22] proposed a descriptor to evaluate the nucleation overpotential for the formation of Li_2O_2 in non-aqueous Li–air batteries. The limiting potential of the nucleation of the discharge product on Ag(100), Au(100), Au(111) and Pt(111) forms a volcano-like profile with respect to the adsorption free energy of LiO_2 . The results indicate a low nucleation overpotential of the formation of Li_2O_2 , which is smaller than that of the formation of Li_2O .

Besides pure noble metal catalysts, the researchers proposed that bimetallic alloys consisting of noble metals and third-row late transition metals, such as Pt_3Co , Pt_3Fe and Pt_3Ni , would exhibit excellent catalytic activity towards ORR by hydrogen (H-ORR).^[23] Inspired by this, Kim et al.^[24] designed PtCo bimetallic catalysts with electron-rich Pt skin via first-principles computations to achieve low overpotentials in Li–O₂ batteries. The designed PtCo catalysts exhibit low Li–ORR and OER overpotentials of 0.19 and 0.20 V, respectively, which are lower than those of pure Pt and Pt_3Co . The excellent performance could be attributed to the high Li and low LiO_2 adsorption energies; therefore, the researchers suggested that the adsorption energies of Li and LiO_2 could be the descriptors for the catalytic activity, consistent with the aforementioned reports. Besides, replacing Co in Pt_3Co with Ti could also decrease the overpotential of OER and ORR, indicating that bimetallic catalysts with poor H-ORR catalytic activity might exhibit super performances in Li–O₂ batteries. Similarly, Lee et al.^[25] investigated Pt–Cu bimetallic alloys and reported that PtCu possesses significantly reduced overpotential compared with Pt and Pt_3Cu , which could also be attributed to the moderate attractive force of LiO_2 on PtCu.

Noble metals or alloys exhibit excellent catalytic activity in Li–O₂ batteries. However, noble metals are unacceptable for large-scale commercial applications. Many transition metal oxides (TMOs) have been experimentally found to exhibit catalytic activity in Li–O₂ batteries.^[6a,26] Therefore, TMOs with good catalytic activity were widely investigated for Li–O₂ batteries. Among various TMOs, spinel Co_3O_4 is a promising electrocatalyst since it could greatly reduce the OER overpotential.^[27] To further reveal the catalytic mechanism of Co_3O_4 for OER in Li–O₂ batteries, Zhu et al.^[28] constructed a $Li_2O_2/Co_3O_4/O_2$ interfacial model (Figure 3) and computationally investigated the Li_2O_2 OER mechanism on Co_3O_4 (111) and (110) surfaces. Experimental results reveal that the oxidation of Li_2O_2 preferentially occurs at the cathode/ Li_2O_2 interfaces within individual particles;^[29] therefore, the model with Li_2O_2 nanoparticles deposited on Co_3O_4 surface to form a solid-solid interface was constructed, as shown in Figure 3. Two possible desorption steps, $Li^+ \rightarrow Li^+ \rightarrow O_2$ and $Li^+ \rightarrow O_2 \rightarrow Li^+$ were consid-

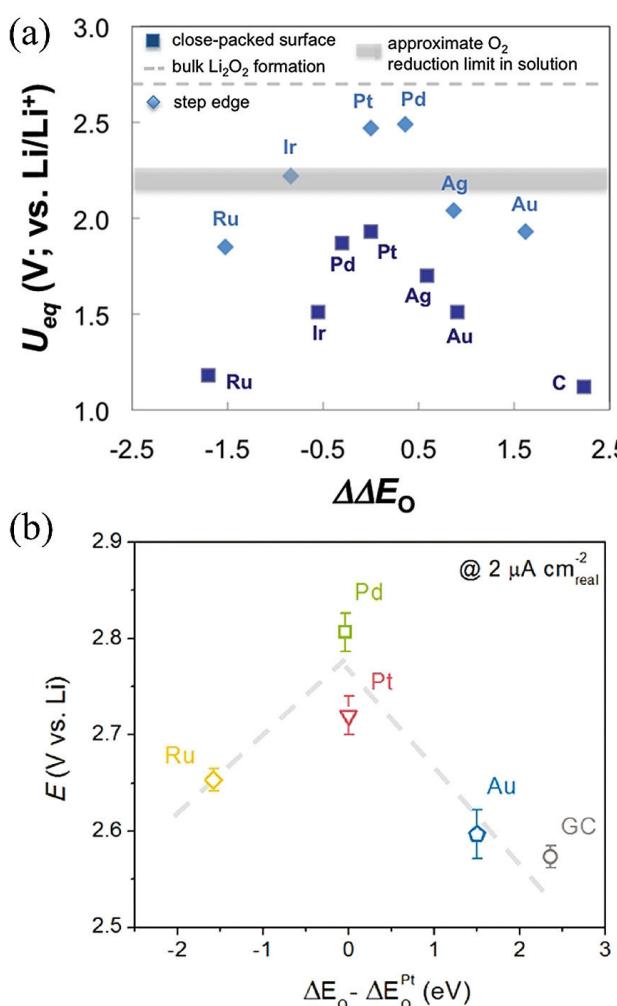


Figure 2. a) Equilibrium potential of the first electron transfer step in Li–ORR and b) Li–ORR potentials at $2 \mu A \text{ cm}^{-2}$ against the adsorption energy of atomic O relative to that on Pt. Reproduced with permission from Refs. [20], copyright (2012) ACS and [21], copyright (2011) ACS.

ered in this work. The computations indicate that the O-rich $\text{Co}_3\text{O}_4(111)$ surface exhibits high activity in reducing the overpotential and O_2 desorption barrier since the electron significantly transfers from Li_2O_2 to the underlying surface. Besides, the p-type doping on $\text{Co}_3\text{O}_4(111)$ surface could reduce O_2 desorption barrier and the charging overpotential. They proposed that the ionization potential of the doping transition metal atoms plays extremely important role in the regulation of the catalytic activity of metal oxides. With similar method, Zhang et al.^[30] investigated the OER activity for the decomposition of Li_2O_2 on the spinel NiFe_2O_4 by means of first-principles computations, and revealed that NiFe_2O_4 has high catalytic effects on the OER of Li_2O_2 and the prediction was confirmed in experiments.

Besides, MnO_2 is a widely used electrocatalyst in $\text{Li}-\text{O}_2$ batteries.^[29b] Trahey et al.^[31] reported that α - MnO_2 /ramsdellite- MnO_2 electrocatalysts could improve the electrochemical behavior of $\text{Li}-\text{O}_2$ batteries and they performed DFT computations to investigate $\text{Li}-\text{O}_2$ reactions with α - MnO_2 and ramsdellite- MnO_2 . The computations indicate that Li oxides can form in the 2×2 tunnels of α - MnO_2 . The Li intercalation into the tunnels is conducive to the formation of O-rich surfaces in Li_2O_2 particles, reducing the OER overpotential. Then, the adsorption of Li-O species in the tunnels of α - MnO_2 was systematically investigated via DFT computations.^[32] The computations reveal that the insertion of Li oxides into α - MnO_2 is the key step of the decomposition of Li_2O_2 . Besides, the spatially confined interaction between Li and O_2 is very important for O_2 dissociation in the tunnels and with increasing the intercalated excess Li in Li_xO_2 , the length of O-O bond is gradually elongated. Importantly, Li oxide inserted α - MnO_2 is half metallic, facilitating the electron transport, ensuring the reversible formation and decomposition of Li oxides.

Mellan et al.^[33] investigated the adsorption and coadsorption of Li and oxygen on the surface of β - MnO_2 computationally and the results indicate that the adsorption of O_2 can be stabilized by Li at the surface and the dissociative structure where the O atoms bind the surface Mn and Li atoms is the most stable. Therefore, β - MnO_2 can be used to lower the energy of the initial reduction of O_2 . δ - MnO_2 was also applied as a catalyst in $\text{Li}-\text{O}_2$ batteries.^[34] Liu et al.^[35] investigated the interaction between Li oxides and δ - MnO_2 monolayers. Based on the adsorption energies of Li, O_2 and Li_xO_y , the authors proposed that δ - MnO_2 exhibits strong affinity for LiO_2 and Li_2O_2 , therefore facilitating the formation of Li_2O_2 films on the surface. Moreover, the further reduction of Li_2O_2 to Li_2O is inhibited due to the high overpotential of 1.21 V while the overpotential of the formation of Li_2O_2 on δ - MnO_2 surface is only 0.49 V. The results demonstrate that Li_2O_2 is the predominant discharge product and the low overpotential indicates that δ - MnO_2 possesses excellent ORR catalytic activity. Similarly, on basis of the adsorption energies of Li, O_2 and Li-O species and Gibbs free energies, the Li-ORR/OER catalytic activity for various metal oxides, including RuO_2 ,^[36] CeO_2 ,^[37] and LiScO_2 ^[38] was also investigated by means of DFT computations. Generally, the catalysts exhibit strong affinity to LiO_2 and Li_2O_2 species, which

is beneficial to reduce the charge overpotential and increase the contact area between the products and cathode catalysts.

In order to unravel a descriptor of the catalytic activity in $\text{Li}-\text{O}_2$ batteries based on the physical properties of catalysts, Zhu et al.^[39] investigated the OER mechanism of Li_2O_2 on the surfaces of transition metal compounds by DFT computations and reported that the surface acidity can be applied as the descriptor of catalytic activity for OER in $\text{Li}-\text{O}_2$ batteries. The surface acidity (V_{sa}) was defined as: $V_{\text{sa}} = \frac{S_0}{S} \frac{E_{Q_0+qS/S_0} - E_{Q_0}}{e}$, in which E_{Q_0} and E_{Q_0+qS/S_0} are the total energy of a specific catalyst surface and the surface with certain added electrons, respectively; S represents the surface model area and S_0 is the specific surface area. The results suggest that the O_2 desorption barrier exhibits linear correlation with the surface acidity (black line in Figure 4a) while the Li^+ desorption energies show a second order curve (red line in Figure 4a). Besides, the charging voltage also shows a second order correlation with the surface acidity (blue line in Figure 4a). Based on the O_2 desorption energy and charging voltage, the researchers predicted that the compounds with a surface acidity of 2.4–3.1 V would have the highest catalytic activity. The correlation curves of the O_2 desorption energy (black line in Figure 4b,) and charging voltage (red line in Figure 4b) with the surface acidity are calculated and several transition metal compounds, such as CoO , Co_3O_4 , and Mn_2O_3 , are predicted to have high activity towards OER in $\text{Li}-\text{O}_2$ batteries. Importantly, the compounds with high activity have also been confirmed in experiments.^[29b,40]

In addition, ceramic-based materials, such as TiC, exhibit excellent catalytic activity in $\text{Li}-\text{O}_2$ batteries.^[40b] The excellent performance could be attributed to the formation of oxide layers and good electrical conductivity of TiC. Wang et al.^[41] performed DFT computations to further investigate the catalytic mechanism of TiC. The researchers proposed that planar Li_2O_2 clusters decompose when interacting with the Ti-terminated TiC(111) surface, and Li and O atoms would rearrange to form a saturated two layered structure. Besides, the oxidized Ti-terminated TiC(111) surface was also used to construct interface models and the results suggest that it is feasible for the continuous electrochemical growth of Li_2O_2 on oxidized Ti-terminated TiC(111) surface through a surface conduction mechanism, consistent with the experimental results.^[40b] Subsequently, they gave a full account of the adsorption and deposition of Li_2O_2 clusters on low-index surfaces of TiC and the

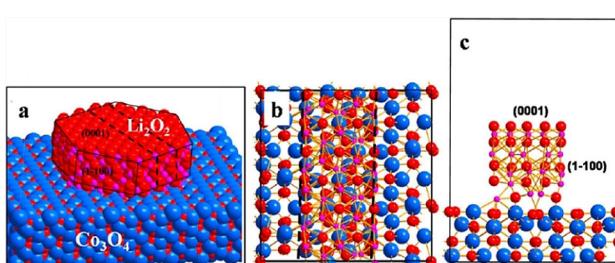


Figure 3. a) Diagram of Li_2O_2 deposited on the surface of Co_3O_4 . b) Top and c) side view of the $\text{Li}_2\text{O}_2/\text{Co}_3\text{O}_4/\text{O}_2$ interfacial model. Reproduced with permission from Ref [28]. Copyright (2015) ACS.

effects of surface oxidation.^[42] The detailed investigations further prove that the oxidization could increase the stability of TiC and facilitate the deposition of Li₂O₂ on TiC surface. Recently, Yang et al.^[43] have compared the stability and OER catalytic activity of the oxidized and pure TiC(100) surface in Li–O₂ batteries. On basis of DFT thermodynamics computations, the researchers reported that the oxidized TiC(100) surface would be stable and have lower Li–OER barrier and charge voltage. They suggested that a strong electron-withdrawing behavior is very important to enhance the electron transfer of O₂^{x-} ($x=2, 1$ and 0), therefore improving the Li–OER activity.

Graphene-based materials also attracted great attention for the catalytic activity of the reactions in Li–O₂ batteries due to their low cost, large surface area and excellent electronic conductivity.^[6d,44] Therefore, basic understanding of the detailed mechanism of OER/ORR on graphene-based materials is essential. Jing and Zhou^[45] systematically investigated the initial ORR processes on the surface of various kinds of N-doped (graphitic N, pyridinic N, and pyrrolic-like N) graphene (Figure 5) in comparison with those on the pristine graphene based on DFT computations. With the growth of Li₂O₂, the charge transfer from Li₂O₂ clusters to the carbon substrate will increase and the overpotential of the controlling step would decrease. The in-

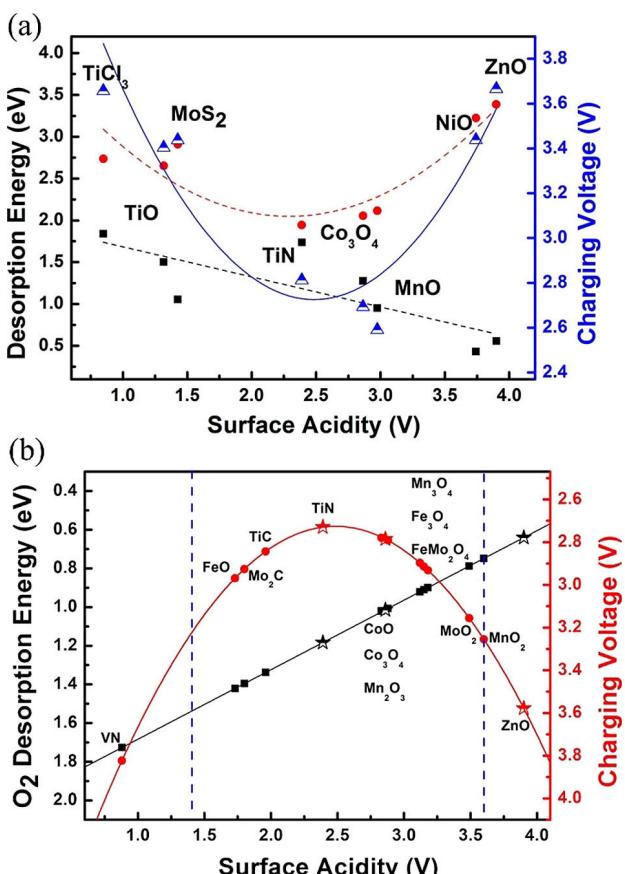


Figure 4. a) Desorption energies of Li⁺ and O₂ and charging voltage as a function of surface acidity. b) Predicted catalytic activities of some transition metal compounds based on the correlation of O₂ desorption and charging voltage with the surface acidity. Reproduced with permission from Ref [39]. Copyright (2015) ACS.

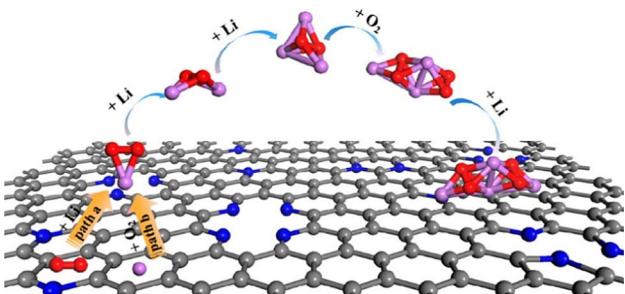


Figure 5. Schematic of various kinds of N-doping configurations in graphene and the nucleation process of Li₄O₄. Reproduced with permission from Ref [45]. Copyright (2015) ACS.

plane pyridinic N could reduce the overpotential more effectively than the graphitic N, facilitating the nucleation of Li₂O₂, which can be attributed to the electron-withdrawing configurations. Due to the promising ORR catalytic activity of graphene-based materials, the adsorption of lithium oxides and mechanisms were widely investigated via computations.^[46]

Besides ORR, Ren et al.^[47] performed first-principles thermodynamic computations to investigate the OER catalytic performance of X-doped graphene (X=B, N, Al, Si and P) in Li–O₂ batteries. The electron-withdrawing center of B-doped graphene can enhance the charge transfer from Li₂O₂ to the substrate, further reducing the O₂ evolution barrier. P-doped graphene shows the highest activity in lowering the charge voltage. Therefore, combining the two catalytic effects, B,P-codoped graphene can not only reduce the voltage but also lower the O₂ evolution barrier. Jiang et al.^[48] also reported that B-doped graphene is a good catalyst for Li–O₂ batteries.

Kang et al.^[49] designed graphene-based active catalysts for ORR and OER in Li–O₂ batteries through DFT computations. The adsorption energies of LiO₂ and Li₂O₂ could describe OER and ORR catalytic performance similar to that on metal surface. The catalytic activity can be optimized by N doping and employing overlaid Cu(111) surface. These results indicate that graphene/Cu is an excellent catalyst towards both ORR and OER in Li–O₂ batteries. Then, Tu et al.^[50] reported that the catalyst of N-doped graphene shell encapsulating Co is promising for Li–O₂ batteries and the prediction was confirmed in experiments. Lee et al.^[51] reported that h-BN/Ni(111) can be a good cathode catalyst for Li–O₂ batteries. These results demonstrate that metal substrates can effectively improve the catalytic performance. Belonging to the same group of carbon, Si and Ge can form stable two-dimensional (2D) materials with C. Li and coworkers predicted OER and ORR catalytic performance of monolayer siligraphenes and germanium carbides in Li–O₂ batteries computationally and the results reveal that these materials have excellent catalytic activity.^[52] Other 2D materials, such as doped h-BN,^[53] MXene^[54] and monochalcogenides^[55] were also investigated as cathode catalysts in non-aqueous Li–O₂ batteries with good catalytic performance.

Besides the main product Li₂O₂, Li₂CO₃ and LiOH are the dominant side products. Therefore, the understanding of the electrochemical decomposition of Li₂CO₃ and LiOH is important. Ling et al.^[56] investigated the mechanism of the intrinsic barrier

of their electrochemical decomposition and the computations reveal that the electrochemical extraction of Li is the rate-limiting step. The voltage for the decomposition of Li_2CO_3 should be in the range of 4.38–4.61 V while it is in the range of 4.67–5.02 V for LiOH. Therefore, the efficiency for the decomposition of Li_2CO_3 and LiOH in Li–O₂ batteries is estimated to be 66% and 61%, respectively. They suggest that using redox active species as redox mediators is a promising strategy to compensate the electron loss for Li extraction. Besides, Mekonnen et al.^[57] investigated the effect of Li_2CO_3 -like species on the cathode of non-aqueous Li–air batteries. The results demonstrate that the nucleation site of Li_2O_2 would be blocked due to the Li_2CO_3 formation even at a low concentration of CO₂.

Generally, for a good cathode catalyst, the adsorption of O should be close to that of Pt. Besides, the strong affinity for LiO₂ and Li₂O₂ is conducive to the formation of Li₂O₂ and an electron-withdrawing configuration could not only facilitate the nucleation of Li₂O₂ but enhance the charge transfer from Li₂O₂ to substrate and reduce O₂ evolution barrier. Compared with the electrochemical reactions in aqueous electrolytes, the principal products in non-aqueous Li–O₂ batteries are insoluble in electrolytes and deposited on the catalyst surface. Therefore, the properties and charge transfer of the discharge products are important and will be discussed below.

3. Electronic and Magnetic Properties of Li₂O₂

Since lithium peroxide and oxide species constitute the potential discharge products in non-aqueous Li–O₂ batteries, their surface properties are very important for the electrochemical performance in these systems. Radin et al.^[58] systematically investigated the stability and electronic structure of 40 distinct surfaces of Li₂O₂ and Li₂O. They reported that several O-rich (0001) and (1̄ 1 00) facets are more stable for Li₂O₂ while the single stoichiometric (111) surface is the most stable for Li₂O. The variation of stoichiometry of the surface will cause huge difference in surface electronic structure. Although both the bulk Li₂O₂ and Li₂O are insulators, the reduced coordination of O atoms at the surface of Li₂O₂ can lead to the formation of a metallic and ferromagnetic region localized at the surface, while the surfaces of Li₂O are still insulating and nonmagnetic. The results indicate that facile pathways for the electron transport exist at Li₂O₂ surfaces and not at Li₂O surfaces, which can explain the observation that the electrochemical process is reversible in the systems where the discharge product is Li₂O₂ and is irreversible if discharge to Li₂O. Then they studied the electronic structure of bulk and Li₂O₂(0001) surface in detail via first-principles computations.^[59] The results further support their notion. Based on first-principles computations combined with continuum-scale transport theory, they proposed that the incorporation of trace Co into Li₂O₂ effectively improves the charge transport by shifting the balance of Li–ion vacancies and hole polarons which can explain the catalytic ability of Co₃O₄ to promote the oxidation of Li₂O₂ in Li–O₂ batteries.^[60] They also screened 22 additional dopants and speculated that

Ni could also significantly shift the Fermi level and enhance the charge transport in Li₂O₂.

Lau et al.^[61] investigated many possible structures of (Li₂O₂)_n clusters and their corresponding electronic structures. They proposed that the triplet state is stabilized relative to the singlet one for the clusters larger than the dimer. They also found that for a large cluster, (Li₂O₂)₁₆, the high spin state also exists, which can be characterized by the O–O pairs protruding from the surface but chemically bonded to Li atoms of the cluster. The high-spin stoichiometric Li₂O₂ clusters possess superoxide-like surface structures since they have shorter O–O distances and a localized unpaired spin on the surface. The results could explain the ferromagnetism of Li₂O₂, which is very important for understanding the formation and decomposition of Li₂O₂ in Li–O₂ batteries.

4. Charge Transfer

Charge transfer between the cathode and the discharge product is also important. Fast charge transfer from the substrate to the surface via Li₂O₂ layers is important to achieve high power density for non-aqueous Li–air batteries. Therefore, the understanding of charge conduction mechanism of lithium oxide species is essential to improve the electrochemical performance of Li–air batteries. Kang et al.^[62] computationally revealed that the self-trapping of the electron in small polaron states would cause low electron mobility in Li₂O₂ and then low electron mobility would lead to low power and energy density. They suggest that the design of alternative carrier conduction paths for the cathode reaction and the *p*-type doping of Li₂O₂ can effectively improve the electrochemical performance. Then Timoshevskii et al.^[63] reported that Si-doping can cause the formation of conducting impurity states in the band gap of Li₂O₂ and the electronic mobility is significantly improved compared with stoichiometric Li₂O₂. Ong et al.^[64] proposed the computational evidence of the polaronic hole trapping and migration in Li₂O₂, and proposed that a hole forms in the π^* antibonding orbitals of O₂²⁻ which would induce local lattice distortion and cause the polaron. Interestingly, when Li vacancies exist, the hole polaron will be strongly bound to them. These results indicate that the electronic conduction of Li₂O₂ is controlled by the vacancy diffusion.

Radin et al.^[65] studied the concentration and mobility of charge carriers and intrinsic defects in Li₂O₂. The results suggest that Li vacancies and hole polarons are the main charge carriers, consistent with the abovementioned reports. Then, they proposed a continuum transport model, in which the charge transport is mediated by polaron hopping, to investigate the transport mechanism through Li₂O₂.^[66] The model can predict the temperature and current-density dependence of the discharge curves in good agreement with the experiments, therefore supporting their hypothesis that the polaron hopping contributes predominantly to the charge transport. Moreover, the dynamics of the polaron formation in Li₂O₂ was also investigated by density functional perturbation theory.^[67] An intuitive picture of polaron formation in Li₂O₂, called the

repulsive stretching of O_2^{2-} and attractive contraction of Li^+ , was proposed. Varley et al.^[68] systematically investigated the formation energies and charge transport in pure and deficient Li_2O_2 through DFT and non-equilibrium Greens function calculations. Their results indicate that the positive charge V_{Li}^+ , V_O^+ and $V_{O_2}^{2+}$ (V represents the vacancy) are stable for native vacancies of Fermi levels in proximity of the equilibrium potential of the electrochemical reaction in $Li-O_2$ batteries. Since these vacancies are positive, they can give repulsive Coulombic scattering to holes tunneling through bulk Li_2O_2 , which might be primarily responsible for the charge transport through bulk Li_2O_2 . Besides, Geng et al.^[69] proposed that the

$\sum 3(1\bar{1}00)[11\bar{2}0]$ tilt grain boundaries in Li_2O_2 could produce spin-polarized gap states, which could change the electronic properties of Li_2O_2 by opening up a conduction channel without any point defects. As the discharge product in $Li-O_2$ batteries, Li_2O_2 is always polycrystalline; therefore, the presence of grain boundaries can improve the conductivity.

In addition to Li_2O_2 , there will be residual Li_2CO_3 in the discharge product in Li -air batteries. The polaronic conduction of Li_2CO_3 was also investigated computationally.^[70] The results indicate that compared with Li_2O_2 , Li_2CO_3 exhibits poor charge transport, which can be explained by the polaronic model for the conduction.

As mentioned above, LiO_2 is generally an intermediate in $Li-O_2$ batteries since it is thermodynamically unstable against disproportionation to form Li_2O_2 . Bryantsev et al.^[71] investigated several low-lying LiO_2 dimers and proposed that in gas phase LiO_2 , it aggregates only at low temperature. Lau et al.^[72] also reported that LiO_2 is not very stable. However, computations suggest that the energy barrier of the disproportionation of large LiO_2 clusters is significantly higher than that of the LiO_2 dimer, indicating that the disproportionation rate of large clusters is much slower than that of the dimer.^[73] Therefore, the LiO_2 cluster could survive long enough to be incorporated into the discharge product. Then, in 2016, Lu et al.^[74] provided evidence that it is possible to have a one-electron discharge process with forming only LiO_2 in a $Li-O_2$ battery. The superoxide discharge product, LiO_2 , would have better OER efficiency than Li_2O_2 and the ionic conductivity of LiO_2 is 4 orders higher than that of Li_2O_2 .^[75] Besides, the solution mediated mechanism of charging was also investigated and the dissolution energy of LiO_2 is lower than that of Li_2O_2 .^[75] Then, more detailed understanding of charge transport in LiO_2 was provided by Li et al.^[76] The excess electrons and holes in LiO_2 would be localized on the oxygen dimer; therefore, small polarons can form and diffuse by hopping between the lattice sites. The results also suggest that the electronic conductivity of LiO_2 is dominated by hole polarons and is about 8 orders higher than that of Li_2O_2 . These computations indicate that the formation of superoxides instead of peroxides during discharge could help to improve the energy efficiency of $Li-O_2$ batteries.

In addition, Kazemiabnabi et al.^[77] investigated electron transfer at the cathode-electrolyte interface in $Li-O_2$ batteries. They computed the electron transfer rate constants from the graphite cathode to O_2 and the superoxide ion in ionic liquid

electrolytes. The results suggest that the logarithm of the electron transfer reaction rate will decrease with increasing the static dielectric constant of the electrolyte and increase with increasing the operation temperature. Besides, they also investigated the electron transfer at the Li metal anode in $Li-O_2$ batteries,^[78] and proposed that the rate constant for overall electron transfer will increase with increasing the static dielectric constant of the electrolyte. Therefore, the choice of appropriate ionic liquid electrolytes is important to improve the current density in $Li-O_2$ batteries.

5. Solvent Stability

The electrolyte plays a key role in non-aqueous $Li-O_2$ batteries. Therefore, it is extremely important to select a stable solvent which can be resistant to the decomposition in the electrochemical environment of Li_2O_2 . Based on first-principles computations, Laino et al.^[79] studied the reactivity of Li_2O_2 versus propylene carbonate (PC) and reported that Li_2O_2 can irreversibly decompose the carbonate solvent, then leading to alky carbonates. Khetan et al.^[80] proposed that the highest occupied molecular orbital (HOMO) level of the aprotic solvents in $Li-O_2$ batteries can be used as a descriptor to evaluate the solvent stability as shown in Figure 6. The solvents with lower HOMO level exhibit better performance in terms of electrons generated in OER. Then, based on this descriptor, the researchers screened a large number of solvents and proposed several solvents including esters, nitrile-based solvents, acids and alcohols, which can potentially improve the rechargeability of non-aqueous $Li-O_2$ batteries. Subsequently, they further gave a more complete picture of the solvent stability during discharge and charge.^[81] They revealed that the propensity of the solvent to resist H-abstraction is dominated by the acid dissociation constant pK_a and suggested that a stable solvent

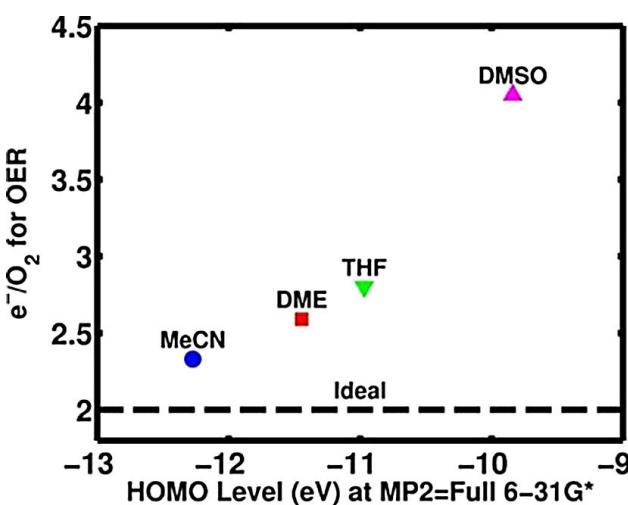


Figure 6. The correlation between solvent HOMO levels and electron released during OER. Since the reaction $Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$ is a $2e^-$ process, the e^-/O_2 value is 2 in an ideal solvent. Reproduced with permission from Ref. [80]. Copyright (2014) ACS.

should have a low HOMO level and high pK_a . However, when the solvents are physisorbed, the electronic energy levels can be shifted, causing the shrinking of electrochemical stability window. Therefore, they further investigated how the electronic energy levels of four widely used solvents including dimethylsulfoxide (DMSO), dimethoxyethane (DME), tetrahydrofuran (THF) and acetonitrile (ACN) shift when physisorbing on the surface of Li_2O_2 .^[82] The computations reveal that when physisorbing on the pristine surface of Li_2O_2 , ACN is the most oxidatively stable followed by DME, THF and DMSO. Besides, compared with pristine surfaces, the solvent molecules would be easier to be oxidized on the defected surface.

Besides surface growth mechanism in $\text{Li}-\text{O}_2$ batteries, researchers demonstrated that the solution-mediated growth mechanism can be an alternative mechanism, in which the growth of Li_2O_2 would proceed through the formation of solution-soluble species, including Li^+ and O_2^- , from the dissolution of LiO_2 .^[83] However, O_2^- is a strong nucleophile and will attack the solvents by proton abstraction or substitution. Therefore, the choice of a stable solvent which can promote the solution-mediated growth mechanism would lead to a higher discharge capacity. Khetan et al.^[84] reported a thermodynamic model which can reveal an anticorrelation between the stability of solvents and their ability to enhance the capacity by the solution-mediated growth mechanism. As shown in Figure 7, the solvents with better solvation capability would be relatively unstable to chemical degradation at the same time. Therefore, it is important to search for solvent additives which can improve the discharge capacity without compromising the stability.

Moreover, many other properties related to $\text{Li}-\text{O}_2$ batteries can be investigated on basis of theoretical computations. For examples, Yang et al.^[85] predicted a new kind of discharge products of $\text{Li}-\text{O}_2$ batteries by means of first-principles computations and particle swarm optimization algorithm.

Lastra et al.^[86] investigated the effects of excitonic and vibronic effects on the optical properties of Li_2O_2 . Bryantsev et al.^[87] studied the solvation free energies of Li^+ , O^- and neutral Li–O compounds in acetonitrile. Theoretical computations significantly help researchers further understand the $\text{Li}-\text{O}_2$ battery systems and accelerate their development.

6. Challenges and Perspectives

$\text{Li}-\text{air}$ batteries are regarded as one of the most promising energy storage and conversion systems due to the high energy density. However, there are still many challenges to be overcome for their practical applications. In this review, we have summarized the progress of computational investigations on rechargeable $\text{Li}-\text{O}_2$ batteries. By means of first-principles computations, many important properties of $\text{Li}-\text{O}_2$ batteries can be addressed. Particularly, the catalytic mechanism can be investigated and then the catalytic performance could be predicted from computed properties such as the interaction between Li–O species and catalysts, which would shorten the development cycle of novel catalysts.

The exploration of cathode catalysts with high activity is important. To accomplish this, the catalytic mechanism should be further investigated. However, at the current stage, the surface growth mechanism directly on the catalyst surface was mainly investigated and the solution-mediated growth mechanism has rarely been reported from the computational viewpoint. Therefore, it is extremely important to further explore this mechanism and propose an appropriate solvent to balance the stability and solubility. Besides, most reports involved the reaction pathway from the thermodynamics aspect based on reaction Gibbs free energies but ignored the kinetics. Therefore, it is necessary to build a theoretical model to study the catalytic mechanism from both thermodynamics and kinetics. In addition, the interface between cathode catalysts and discharge products plays a key role in catalytic reaction pathways and charge transfer. As a result, a suitable interface model supported by experimental observation is urgently needed.

Moreover, the redox mediators in $\text{Li}-\text{air}$ batteries have been widely investigated in experiments.^[16a,88] However, there are few computational reports on the catalytic mechanisms. Theoretical design of redox mediators with excellent activity in $\text{Li}-\text{O}_2$ batteries is in the infancy stage and could further speed up the development of redox mediators.

However, first-principles computations generally need atomic structures as input for simulations; therefore, it might be meaningless if invalid assumption was made about atomic structures. Nowadays insufficient understanding of complicated reaction processes, hierarchical catalyst structures and real active sites limit further computational efforts. To fully understand $\text{Li}-\text{O}_2$ batteries, an integrated theoretical model, including cathode catalysts, solvents and discharge products should be built. However, most first-principles investigations on $\text{Li}-\text{O}_2$ batteries focus on a small isolated system, which could not provide enough information. For more complicated practical

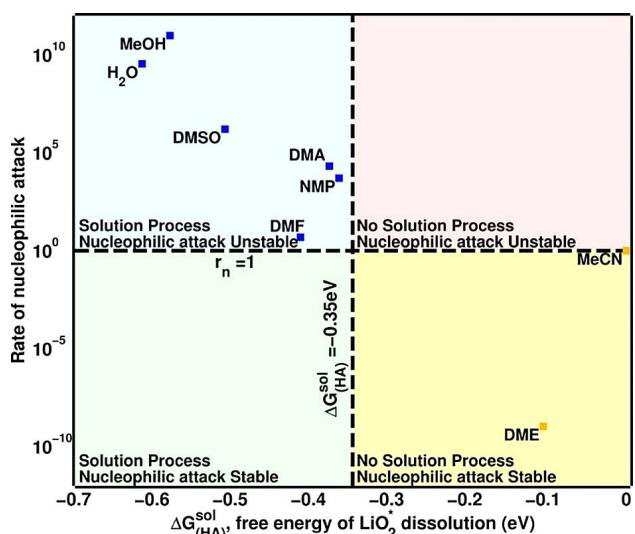


Figure 7. The solvent stability against proton abstraction by nucleophilic attack and the ability to enhance the solution-mediated growth mechanism. Reproduced with permission from Ref. [84]. Copyright (2015) ACS.

Li–air batteries, empirical or semi-empirical methods might be used on basis of close combination with experiments.

In the past decade there has been breakthrough regarding the theoretical investigations on Li–air batteries. However, there is still a long way to go. Further investigations are still urgently needed to achieve practical applications of Li–air batteries.

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Conflict of interest

The authors declare no conflict of interest.

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