The development and challenges of rechargeable non-aqueous lithium–air batteries

Lei-Lei Zhang, Zhong-Li Wang, Dan Xu, Xin-Bo Zhang and Li-Min Wang

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, People’s Republic of China; Graduate University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China

(Received 27 August 2011; final version received 16 January 2012)

Lithium–air (Li–air) batteries have recently received much attention due to their extremely high theoretical energy densities. The significantly larger theoretical energy density of Li–air batteries is due to the use of a pure lithium metal anode and the fact that the cathode oxidant, oxygen, is stored externally since it can be readily obtained from the surrounding air. However, before Li–air batteries can be realized as high-performance, commercially viable products there are still numerous scientific and technical challenges that must be overcome, from designing the cathode structure, to optimizing the electrolyte compositions and elucidating the complex chemical reactions that occur during charge and discharge. The scientific obstacles that are related to the performance of Li–air batteries open up an exciting opportunity for researchers from many different backgrounds to utilize their unique knowledge and skills to bridge the knowledge gaps that exist in current research projects. This review article is a summary of the most significant developments and challenges of practical Li–air batteries and the current understanding of their chemistry.

Keywords: lithium–air battery; high energy density; electrolyte; separator; catalyst

1. Introduction

With the rapid depletion of finite fossil fuels and global warming linked to carbon dioxide emissions there is an urgent need to achieve efficient use of energy and to seek renewable and green energy sources that can substitute fossil fuels to enable the sustainable development of our economy and society [1,2]. Thanks to its high energy density, simplicity and reliability, electrochemical energy storage has become an issue of strategic importance as it will play a critical role in clean energy generation and use.

Figure 1 shows the battery technologies available or currently under development and compares their energy densities [3,4]. Among all advanced battery systems, lithium-ion batteries (LIBs) are generally considered as a scientific breakthrough in this context because of their high energy and/or power density. Indeed, LIBs can store up to three times more electricity and generate twice the power of nickel (Ni)–metal hydride batteries now widely in use. Although the existing LIBs have taken less than 20 years to successfully capture the portable electronic market, such as mobile phones, laptop computers, digital cameras, music players, etc., when it is proposed that they conquer the upcoming markets

*Corresponding author. Email: xbzhang@ciac.jl.cn

© 2013 Taylor & Francis
Figure 1. A comparison of current and developing batteries.

of electric transportation (e.g. hybrid electric vehicles) and renewable energies (e.g. wind or solar energy), significant improvements in energy density are urgently needed [5,6].

The specific energy density of conventional LIBs is determined by the limited amount of active materials stored inside the battery. Alternately, when replacing the LIB cathode with an O\textsubscript{2} electrode, which can be readily obtained from the surrounding environment, the energy density of the lithium–air (Li–air) battery with respect to the anode can reach 13,000 Wh kg\textsuperscript{−1}, which is quite close to the value for one of the most energy-dense common liquids, i.e. gasoline (13,200 Wh kg\textsuperscript{−1}) [7–9]. The Li–air battery was first proposed by Littauer and Tsai in 1976 [10], but its progress was very slow until Abraham and Jiang presented the Li–air system with non-aqueous electrolyte in 1996 [11]. The introduction of non-aqueous electrolytes resulted in a major suppression of anode corrosion and also opened up a substantial enhancement of Li–air cell voltage (up to a theoretical value), which, in turn, paved the way for a further rise in the cell specific energy. Thenceforth, Li–air batteries have attracted worldwide attention [6,11–17], especially after their attractive rechargeability was demonstrated by Bruce in 2006 [12]. Note also that IBM and its partners have launched the Battery 500 project to evaluate Li–air batteries for automotive application.

Currently, four chemical architectures of Li–air batteries are being pursued worldwide. These include three versions with liquid electrolytes: a fully aprotic liquid electrolyte, an aqueous electrolyte and a mixed system with an aqueous electrolyte immersing the cathode and an aprotic electrolyte immersing the anode. The fourth approach is an all-solid-state battery with a solid electrolyte. Although the fundamental electrochemistry depends upon the electrolyte around the cathode, all these four configurations will ultimately have to solve the difficult problem of developing a high throughput air-breathing system that passes O\textsubscript{2} while keeping out environmental contaminants (e.g. H\textsubscript{2}O, CO\textsubscript{2} and N\textsubscript{2}). Because only the aprotic configuration of a Li–air battery has shown any promise of electrical rechargeability, this configuration has attracted the most effort worldwide to date, and we focus principally on this configuration for the remainder of this article.
As shown in Figure 2, a typical design for an aprotic Li–air battery contains a metal Li anode, an electrolyte comprising a dissolved lithium salt in an aprotic solvent, a conducting porous carbon supported O₂-breathing cathode and a Li-ion conducting membrane separating the anode and cathode. The fundamental battery chemistry during discharge is thought to be the electrochemical oxidation of lithium metal at the anode and reduction of oxygen from air at the cathode, i.e.

\[
\text{Anode: } \text{Li} \rightarrow \text{Li}^+ + e^- \tag{1}
\]

\[
\text{Cathode: } 2\text{Li} + \text{O}_2 + 2e^- \rightarrow \text{Li}_2\text{O}_2 \quad E_{\text{rev}} = 2.96V_{\text{Li}}, \tag{2}
\]

\[
4\text{Li} + \text{O}_2 + 4e^- \rightarrow 2\text{Li}_2\text{O} \quad E_{\text{rev}} = 2.91V_{\text{Li}}. \tag{3}
\]

With aprotic electrolytes, it is believed that the process can be reversed by applying an external potential, i.e., that such a battery can be electrically recharged.

In this review article, Section 2, the bulk of the article, summarizes the current development and main limiting factors of the Li–air battery. Section 3 introduces the current understanding of its chemistry. Finally, Section 4 concludes the information provided in this article and describes the key areas for future research from the perspective of the authors.

2. Development and challenges

If successfully developed, the Li–air battery could provide an energy source for electric vehicles rivaling that of gasoline in terms of usable energy density. However, even after a decade of intensive research, Li–air batteries are still in the opening development stage and there are numerous scientific and technical challenges that must be overcome if this alluring promise is to turn into reality. We will summarize the development and the most significant limiting factors of Li–air batteries, from designing their cathode composition and structure, to optimizing their electrolyte compositions and investigating the separator and others that affect the performance of Li–air batteries.
2.1. Porous carbon-based air cathode

An air or oxygen cathode is the key component related to the performance of a Li–air battery, in which the electrons are confined inside the electrode material while the oxygen is in both the gaseous and solution phases and the lithium ions are contained in the electrolyte solution. Upon discharge, the oxygen molecules accept electrons from the cathode and combine with lithium ions to complete the half-cell reaction. In order to complete the combination, each reactant has to overcome their respective boundaries, which slows the reaction kinetics and affects the overall performance of the battery. The air cathode in non-aqueous Li–air batteries is normally a carbon supported porous structure, which acts as gas transport channels involved in the formation and storage of products during the discharge process. In an aprotic Li–air battery system, the discharge products are not soluble in non-aqueous electrolyte, depositing on the cathode surface and thus often inhibiting oxygen diffusion. This ultimately starves the discharge reaction and leads to a lower specific capacity than the theoretical value. Therefore, developing and optimizing the morphology and structure of carbon materials are very important to enhance the performance of Li–air batteries.

Up to now, various commercially available carbons, including activated carbon (AC), Super P, Vulcan XC-72, Ketjen black (KB), carbon nanotubes (CNTs), etc. [7,18–23] have been employed in Li–air batteries. As shown in Table 1, AC has the largest surface area (2100 m² g⁻¹); however, its specific capacity is the lowest (414 mAh g⁻¹). This is due to its small pore size of only 2 nm in diameter. In contrast, although with relatively low surface area (62 m² g⁻¹), Super P has the highest specific capacity (1736 mAh g⁻¹) [24], which is due to its larger pore diameter (50 nm). Park et al. [25] have compared the performance of other kinds of carbons (Table 2). To date, among all the employed commercial carbon materials, KB EC600JD has both the largest surface area and pore volume and thus the highest specific capacity (2600 mAh g⁻¹). These results suggest that high surface area and, especially, high pore diameter (volume) are essential to the high discharge capacity of Li–air batteries.

The results obtained from commercial carbons have inspired people to further increase the specific capacity by using new carbon materials with finely tuned surface, porosity, pore volume, and so forth. Mirzaeian and Hall synthesized and were the first to use porous carbon aerogels as the air cathode in a Li–air battery. It was confirmed that the discharge capacity increases with an increase of the total pore volume and average pore diameter of the carbon aerogels [26–28]. Yang et al. reported that mesocellular carbon foam (MCF-C), prepared by a nanocasting technology using mesocellular foam silica hard template [24],

| Carbon material | Surface area (m² g⁻¹) | Pore diameter (nm) | Specific capacity (mAh g⁻¹) |
|----------------|----------------------|-------------------|-----------------------------|
| Super P        | 62                   | 50                | 1736                        |
| Vulcan XC-72   | 250                  | 2                 | 762                         |
| AC             | 2100                 | 2                 | 414                         |
| CNT            | 40                   | 10                | 583                         |
| Graphite       | 6                    | —                 | 560                         |
| Ball-milled graphite | 480           | —                 | 1136                        |
| MCF-C          | 824                  | 30                | 2500                        |

*aActivated carbon; bcarbon nanotube; cmesocellular carbon foam.*
Table 2. Specific capacity (0.1 mA cm$^{-2}$, the cutoff voltage is 1.5 V), surface area and pore volume of some commercial carbon materials [25].

| Carbon material   | Specific capacity (mAh g$^{-1}$) | Surface area (m$^2$ g$^{-1}$) | Pore volume (m$^3$ g$^{-1}$) |
|-------------------|----------------------------------|--------------------------------|-----------------------------|
| KB EC600JD        | 2600                             | 1325                           | 2.47                        |
| Super P           | 2150                             | 62                             | 0.32                        |
| KB EC300JD        | 956                              | 890                            | 1.98                        |
| Denka black       | 757                              | 60                             | 0.23                        |
| Ensaco 250G       | 579                              | 62                             | 0.18                        |

can deliver much higher discharge capacity than all the commercial carbons, as shown by Table 1. A novel form of carbon, graphene nanosheets (GNSs), is reported to have a comparable electrocatalytic activity for the oxygen reduction reaction (ORR) as commercial platinum/carbon (Pt/C) catalyst in a hybrid electrolyte Li–air battery [29,30]. Li et al. then used them in a non-aqueous Li–air battery [31], and, surprisingly, they exhibit an excellent electrochemical performance with a high discharge capacity of 8705.9 mAh g$^{-1}$ at a current density of 75 mA g$^{-1}$. This might be attributed to the unique structure of GNSs, which form ideal three-dimensional three-phase (solid–liquid–gas) electrochemical interface areas and thus could be employed as the diffusion channels for the electrolyte and O$_2$

This three-phase interface is very important for aprotic Li–air batteries, because only where the liquid electrolyte with Li$^+$ ions, O$_2$ from the environment and the insoluble solid products, i.e. lithium oxides, coexist can they react simultaneously. The pore structure and distribution have been theoretically and experimentally verified to effectively increase the three-phase interfacial area [8,31–33]. As shown in Figure 3 [34], micropores would be sealed when Li oxide particles are formed near the orifice of the micropores, which would result in the inside pore surface becoming inaccessible. Larger pores can store more Li oxide particles and ensure the flow of the electrolyte and O$_2$ at the same time.

On the other hand, in order to improve the performance of Li–air batteries, besides tuning the carbon materials with a proper pore size, one would also need to control the

![Figure 3. Accommodation of lithium oxides in pores of various sizes [34]. Copyright 2010, with permission from Elsevier.](image_url)
morphology and distribution of discharge products. When the insoluble discharge products (Li oxides) cram the pores of the porous electrode, the supply of electrolyte will be stopped and a dense and compact Li oxides film will form on the surface of the activated surface of carbon, which will prevent further reduction of O\textsubscript{2} and ultimately induce the passivation of the electrode. To overcome this problem, modifying the carbon surface with long-chain hydrophobic molecules could significantly reduce the passivation and increase the discharge capacity [35].

Cathode structure is another critical factor that could influence the performance of a Li–air battery. In this context, Zhang et al. prepared freestanding CNT/nanofiber (CNF) mixed buckypaper by filtering dimethylformamide suspensions of CNT and CNF [36]. When this buckypaper is directly used as air electrode without any binder, a specific capacity as high as 2540 mAh g\textsuperscript{−1} at 0.1 mA cm\textsuperscript{−2} discharge current density is achieved, which is much higher than that of pure CNTs [23]. Mitchell et al. successfully prepared a hollow CNF with diameters on the order of 30 nm grown on a ceramic porous substrate using the chemical vapor deposition method [37]. The CNF as the O\textsubscript{2} electrode without any binder or catalyst greatly improved the energy and power density of Li–O\textsubscript{2} batteries.

Besides the above factors, another important factor that should also be considered is the carbon loading amount. The air cathode should contain an optimal loading of porous carbons to maintain the porosity, electronic conductivity, diffusion of oxygen and transport of electrolyte [20,38]. If the carbon loading is too low to only adhere to the framework of porous current collector, pore volume for depositing the insoluble discharge products will be not sufficient and thus the discharge capacity will reduce. On the contrary, too high carbon loading would close the open structure of the current collector and then impede the flow of oxygen [25,39]. On the other hand, the discharge products are deposited near the air electrode/air interface and only can reach as far as the oxygen diffusion length. When the thickness of the air cathode is greater than the oxygen diffusion length, the carbon outside of the oxygen diffusion length cannot be used effectively, which will result in a lower specific capacity [36]. It should be noted that different carbon materials have different optimal loading amounts since every carbon material has a separate intrinsic nature. How to optimize the effective carbon loading is still a challenge.

2.2. Catalysts

In a typical aprotic Li–air battery, based on thermodynamic data, the standard potential ($U_0$) for the discharge reaction is calculated using the Nernst equation to be $U_0 = 2.96$ V. However, for most of current Li–air batteries, the discharge potential is approximately only 2.5–2.7 V and the charge potential is above 4.0 V [40,41]. The overpotential severely reduces the electrical energy efficiency for a discharge–charge cycle (only 62.5%). It is generally believed that electrocatalysts can reduce the overpotential and thus increase the round trip efficiency and ultimately improve the cyclic performance. Up to now, three types of catalysts have shown good promise: metal oxide catalysts, metal phthalocyanine complexes and noble metal catalysts.

2.2.1. Metal oxide catalysts

Manganese oxides are the most widely used catalysts for Li–air batteries due to their low cost, low toxicity, ease of preparation and high catalytic activity [21,35,42–54]. Bruce and co-workers have systematically compared the performance of various MnO\textsubscript{x} catalysts [7,43], including commercial Mn\textsubscript{2}O\textsubscript{3} and Mn\textsubscript{3}O\textsubscript{4}, bulk MnO\textsubscript{2} ($\alpha$, $\beta$, $\gamma$ and $\lambda$), $\alpha$-MnO\textsubscript{2}
nanowires and \(\beta\)-MnO\(_2\) nanowires. Their results show that \(\alpha\)-MnO\(_2\) nanowires are the most effective catalysts for rechargeable Li–air batteries due to their special polymorph crystal structure and high surface area. A battery assembled with the \(\alpha\)-MnO\(_2\) nanowires delivers a specific capacity of 3000 mAh g\(^{-1}\), which is much higher than that obtained with other catalysts (Figure 4). When restricting the depth of discharge, the capacity retention is also satisfying.

Jin et al. successfully synthesized titanium-containing \(\gamma\)-MnO\(_2\) hollow spheres using a simple co-precipitation method [44]. Interestingly, when used as the catalyst in a Li–air battery, a very high discharge specific capacity (up to 2300 mAh g\(^{-1}\) of carbon) is achieved, while the effect of titanium incorporation on the electrocatalytic performance remains unclear. Li et al. synthesized MnO\(_2\) nanoflakes uniformly coated on multi-walled CNTs by simply immersing multi-walled CNTs into an aqueous KMnO\(_4\) solution [45]. Using the MnO\(_2\)/multi-walled CNTs composite as air cathode directly can enhance the oxygen reduction and evolution reaction and exhibit a low charge potential of 3.8 V. Zhang et al. prepared a composite paper air electrode mixed with CNTs and CNFs and studied their performance in Li–air batteries with/without \(\alpha\)-MnO\(_2\) nanorods as cathode catalysts [46]. It was found that the catalysts do not increase the discharge capacity but greatly enhance the charge capacity and cyclability. Crisostomo et al. synthesized \(\gamma\)-MnOOH as the catalyst for Li–air batteries and achieved good results [47]. Combined with other reports [48], Zhang et al. [46] concluded that \(\alpha\)-MnO\(_2\) can react with the discharge product Li\(_2\)O to form Li\(_2\)MnO\(_3\) during discharge process and then Li\(_2\)O and \(\alpha\)-MnO\(_2\) could be regenerated in the charge process, which could enhance the charge behavior. Similarly, Trahey et al. reported that lithium–metal oxides with a high formal Li\(_2\)O content, such as Li\(_3\)FeO\(_4\) (5Li\(_2\)O–Fe\(_2\)O\(_3\)) and Li\(_2\)MnO\(_3\)–LiFeO\(_2\) composites (\{Li\(_2\)O–MnO\(_2\}\}–\{Li\(_2\)O–Fe\(_2\)O\(_3\}\}), exhibit superior electrochemical behavior [49]. It should be noted that although manganese oxides are very effective candidates for the catalysts of Li–air batteries, the catalytic mechanism requires fundamental research in the future.

Other types of transition metal oxides have also been employed as catalysts in Li–air batteries [40]. Among them, at a constant current of 70 mA g\(^{-1}\), Fe\(_2\)O\(_3\) shows
the highest initial capacity, Fe$_3$O$_4$, CuO and CoFe$_2$O$_4$ exhibit better capacity retention capability, while Co$_3$O$_4$ reaches a compromise between initial capacity and capacity retention. Although La$_{0.6}$Sr$_{0.4}$MnO$_3$ was tested to be not a good catalyst, Minowa et al. believe that La$_{0.6}$Sr$_{0.4}$Fe$_{0.6}$Mn$_{0.4}$O$_3$ can greatly improve the cycle properties [55]. Suntivich et al. have discussed that perovskite oxides such as LaCrO$_3$ and LaFeO$_3$ are good catalysts for the ORR in metal–air batteries [56]. Under rational design, the perovskite oxides could be effective catalysts for Li–air batteries. In addition, nanocrystalline spinels, synthesized by Cheng et al. using a facile and fast route at room-temperature, have proved to be an effective bifunctional electrocatalyst for both the ORR and oxygen evolution reaction (OER) [57], which implies that they may also be a good catalyst for Li–air batteries.

2.2.2. Metal phthalocyanine complexes

Another kind of oxygen reduction catalyst, metal phthalocyanine complexes, was first employed in non-aqueous electrolyte Li–air batteries by Abraham and Jiang [11]. Heat-treated FeCu-phthalocyanine complex exerts at least 0.2 V higher discharge voltage at 0.2 mA cm$^{-2}$ than those with pure carbon [58]. Interestingly, pyrolyzed FeCu macrocycle compounds supported on KB carbon display a higher discharge voltage of over 200 and 500 mV than these with KB carbon and super P carbon, respectively [18].

2.2.3. Noble metal catalysts

Compared with the metal oxide catalysts, there are few reports on noble metal catalysts for Li–air batteries. Lu et al. reported that gold (Au) can enhance the ORR that occurs during discharging, and Pt can facilitate OER during charging [59]. They further demonstrated that combinational decorating a carbon cathode with Pt–Au particles, measuring just a few nanometers in diameter, can serves as bifunctional catalysts, leading to a record-setting round-trip efficiency of roughly 77% [19]. The discharge voltage shown in Figure 5 is higher than that of pure Vulcan XC-72 carbon by 150–360 mV, and the average charge voltage of PtAu/C is 3.6 V, which is 900 mV lower than that of pure carbon (about 4.5 V). Thapa et al. mixed Pd and $\alpha$-MnO$_2$ as the catalyst cathode (no carbon was used) for Li–air batteries [60,61]. By addition of a small amount of Pd to mesoporous $\alpha$-MnO$_2$, the discharge plateau increases to 2.9–2.7 V, while the charge potential decreases to 3.6 V, leading to a high specific energy efficiency of 82%.

![Figure 5](image.png)
It should be noted that the conventional way to evaluate catalyst activity is to first fabricate a carbon-based porous cathode and then measure the discharge and charge voltage and capacity profiles in a Li–air single cell configuration. Although the above obtained results through this method are promising, the evaluation of the intrinsic electrocatalytic activity of catalysts via such method is often complicated and strongly depends on changing of discharge current, weight of catalysts or carbon, design of electrodes and cells, etc. Thus, it is necessary to build a method to enable a quantitative determination of the intrinsic catalytic activity of various electrode materials intended to be used in Li–air batteries. To this end, Lu et al. have developed a rotating disk electrode (RDE) technique that can explore the fundamental parameters and mechanisms that govern the activity of Li–air cathode catalysts for the ORR and OER [62]. They investigated the ORR activity on the surfaces of glassy carbon (GC) as well as polycrystalline Au and Pt electrodes by the RDE technique, and found that Au is the most active with an activity trend of Au > GC > Pt. Note that air electrodes with Vulcan carbon or Au or Pt nanoparticles supported on Vulcan were also examined in Li–air single cells, where the observed discharge cell voltages follow the catalytic trend established by RDE measurements, highlighting the power of RDE technique in guiding the development of highly active air electrodes that are prerequisites for viable rechargeable Li–air batteries. Interestingly, Giordani et al. reported that the H2O2 decomposition could be a reliable, useful and fast screening tool for materials that promote the charging process of the Li–O2 battery and thus may ultimately give insight into the charging mechanism [63]. However, as a part of the cathode in Li–air battery, the catalytic mechanisms of these catalysts are more complex. In a recent report, Freunberger et al. have revealed that the $\alpha$-MnO2 nanowires mainly progress the decomposition of electrolytes to produce HCO2Li, CH3CO2Li and Li2CO3, not Li2O2 [64]. More evidence and research are needed in the future.

2.3. Electrolytes

The organic electrolyte in an aprotic Li–air system is used to stabilize the anode, conduct Li+ ions, dissolve O2 and provide a reaction interface. Properties of the electrolyte such as ionic conductivity, O2 solubility, viscosity and contact angle strongly influence the cell discharge performance [38,65–67]. Generally, it is believed that higher O2 solubility in electrolyte could ensure larger concentration of O2 for the reduction reaction. Similarly, low viscosity and high ionic conductivity would also benefit the specific capacity because the Li+ ions could transport to the cathode more easily. Furthermore, Xu et al. have reported that the electrolyte polarity is another even more important parameter in determining the specific capacity – an electrolyte with high polarity could generate more three-phase regions, thus leading to a higher capacity [68]. The organic solvents used to date include organic carbonates (ethylene carbonate, propylene carbonate, dimethyl carbonate), ethers (tetrahydrofuran, dioxolane) and esters ($\gamma$-butyrolactone), and the commonly used solvate lithium salts are LiPF6, LiClO4, C2F6LiNO3S2 and LiSO3CF3 [69,70]. Ogasawara et al. have demonstrated the rechargeability of a Li–air battery with a carbonate-based organic electrolyte for 50 cycles [7]. Toyota has increased this to 100 cycles and achieved high capacity retention of over 60%. However, the main product formed in the discharge process, as investigated by transmission electron microscope observations and Fourier transform infrared spectroscopy is not Li2O2 but Li2CO3. Freunberger et al. also
confirmed the decomposition of carbonate-based organic electrolyte by the technology of in-situ surface enhanced raman spectroscopy [71]. Ether-based electrolytes perform well in organic Li–air batteries, with good stability, excellent rate capacity and high solubility of O2 [72]. Especially, the viscosity of ether-based electrolytes is lower than that of carbonate-based electrolytes of similar oxygen solubility. Read has confirmed that once a certain level of oxygen solubility is reached, viscosity becomes the determining factor [73]. Further work on ether-based electrolytes is in progress with the aim of reducing the electrolyte viscosity to improve cell performance. Crown ethers as an additive could enable the capability to coordinate with lithium ions and thus increase the ionic conductivity of the electrolyte [74–76]. Xu et al. have studied several crown ethers added to a carbonate-based electrolyte separately and found that the crown ether largely increases the capacity of Li–air battery only at an optimum content [77]. The clear effect and selectivity of crown ethers need further works. However, recently, Freunberger et al. have reported that ether-based electrolytes also exhibit decomposition [64]. Unlike the organic carbonate-based electrolyte, the first discharge products of ether-based electrolyte are accompanied by Li2O2. For all that, the ether-based electrolytes are still not suitable for Li–O2 cells because the Li2O2 disappears in future cycling. Identifying suitable electrolytes remains a major challenge.

Furthermore, the discharge products, lithium oxide and lithium peroxide, are normally insoluble in an organic solvent, which is considered as the major reason to the unwanted ending of discharge. Some additives or co-solvents to the electrolyte can partially dissolve the discharge products and improve the cell performance. Although the addition of tris(pentafluorophenyl)borane (TPFPB) increases the viscosity, decreases the conductivity and contact angle [68], it still retains a much higher capacity than those using an electrolyte without TPFPB. This is because TPFPB can help partially dissolve Li2O and Li2O2 [60,78–81].

Another factor constraining the capacity and cycle performance of a Li–air battery is the vaporization of electrolyte and hydrolysis of the anode. Hydrophobic ionic liquid electrolyte may be a promising candidate to solve this problem owing to its hydrophobicity and negligible vapor pressure. Kuboki et al. first used an ionic liquid consisting of 1-alkyl-3-methylimidazolium tetrafluoroborate as the electrolyte to study the discharge behavior in air [33]. The cell showed a high discharge capacity of 5360 mAh g−1 even after 56 days. Zhang et al. have synthesized a hydrophobic ionic liquid–silica–PVDF–HFP polymer composite electrolyte which can effectively stabilize the interface and diminish lithium corrosion by water [50]. Hydrophobic ionic liquid provides an opportunity for practical application of rechargeable Li–air batteries.

The electrolyte amount is another important factor in determining the capacity of a Li–air battery [22,25,39,57,68,82]. As shown in Figure 6 [69], when neglecting the effect of solvent evaporation, a maximum cell discharge capacity can be achieved at an optimal electrolyte amount. Below the optimum, an increase in electrolyte amount increases the cell capacity. Above the maximum, the cell performance deteriorates significantly. The capacity of Li–air batteries directly depends on the status of electrolyte filling, which might be related to the wetness of cathode. It is generally believed that the increase of the electrolyte amount could facilitate the dissolution of O2 and transportation of Li+ ions, and thus improve the battery performance. However, when the electrolyte amount exceeds the maximum, the pores inside the carbon cathode become flooded, which would decrease the three-phase regions and thus deteriorate the cell performance.
2.4. Separators

As an indispensable and important part of a Li–air battery, an ideal separator should be a determined block for gases, excellent penetrator for lithium ions, good reservoir for electrolyte, etc. Currently, there are three kinds of separators: inorganic ceramic membranes [52, 83–87], polymer–ceramic (PC) compound separators [88–90] and polymer separators [11, 91].

The inorganic ceramic separator is usually a fast ionic conducting ceramic such as LISICON and LIPON, which exhibits excellent gas blocking performance and favorable ionic conductivity. However, its fragile nature and high cost restrict its extensive application. On the contrary, PC separators could improve the mechanic strength and reduce the cost simultaneously. Cui et al. have prepared a PC separator with a sandwich structure which enhances mechanical strength [89]. Yu et al. have developed a multi-layer LIPON/PC composite separator to achieve good hydrophobicity and obstruction of gases [90]. The cell with a glass ceramic/PC separator laminate fabricated by Kumar et al. has exhibited excellent reversibility [88]. Although the PC composite separator can improve the performance, it is still encumbered with the high cost due to the complex fabricating process. Alternately, conventional LIB separators, such as Celgard porous polyolefin separators and glass fibers [40, 92], have been applied to Li–air batteries due to their high ionic conductivity, low resistance and low cost. Abraham and Jiang developed the first Li–air battery with a non-aqueous thin solid polymer electrolyte membrane as the separator [11]. However, these separators cannot effectively hinder gases and this would result in the oxidation of anode. In addition, the polyolefin separators with large pores are not beneficial to maintain enough electrolyte. Modifying the conventional separator is still urgently needed to improve its performance [91].

2.5. Other factors

Lithium dendrite formation is a common problem in Li–metal anode batteries, which can eventually lead to shorts between the anode and cathode and thus reduce the cycle life...
and safety of batteries. Solving the problem is a topic of a large body of research. The major approach is developing homogeneous, highly Li ion-conductive artificial protective layers coating the metallic lithium to form a stable solid electrolyte interface (SEI) [93–95]. The SEI films are composed of Li ion-conducting polymer segment, glasses or ceramics. Another solution is to use solid electrolyte instead of liquid electrolyte, namely the all-solid-state Li–air battery [85,88]. All these approaches need further research.

Most researchers working on Li–air batteries simplify their experimental setups by supplying the cells with dry oxygen, which avoids real-world problems caused by moisture, CO2 and other air components. It is found that the discharge capacity of Li–air battery increases with increasing oxygen pressure from 1 to 10 atm, especially at a high discharge rate [96]. This is due to that high oxygen pressure can facilitate the oxygen dissolving in the electrolyte and thus increase the reaction rate. However, it should be noted that high oxygen pressure is unfavorable when enabling Li–air batteries to be put into actual use [33,88].

In order to operate Li–air batteries in ambient air, an oxygen-selective permeation membrane is thus urgently needed [21,84,97,98]. Recently, Zhang et al. [22] reported such success by using a heat-sealable polymer as an oxygen-diffusion membrane and a moisture barrier. The Li–air battery can last longer than one month and an energy density of 362 Wh/kg reached on the basis of the total weight of the battery including packaging.

The current collector might be another important factor that is crucial to the performance of a Li–air battery. Up to now, although porous Ni foam, Ni mesh, aluminum grid and stainless steel grid, etc., have been reported for use as current collectors, the majority of Li–air studies have used a Ni current collector. However, Veith and Dudney reported that the Ni clearly promotes the electrochemical degradation of electrolyte [99], which will directly impact the capacity, rechargeability and the lifetime of a rechargeable Li–air battery, indicating that Ni should be used with caution in rechargeable Li–air batteries at potentials greater than 3.5 V. Graphitic carbon electrode appears to be a more suitable cathode current collector in their report as it does not decompose the electrolyte at potentials below 4.4 V.

The environment temperature also has a significant impact on the cell system. However, there have been few systematic studies and a lack of understanding on the performance of the Li–air battery as influenced by temperature. To this end, Behl et al. described the temperature performance of a Li–O2 battery using non-aqueous electrolyte and correlated this to changes in electrolyte viscosity with temperature [100]. The results indicate that both the capacity and output potential decrease with decreasing temperature from +40 to −30°C. Interestingly, Kumar et al. reported that the solid-state battery with a separator fabricated from glass ceramic and PC can work for 40 discharge/charge cycles even in the temperature range 30–105°C [88].

3. Reaction mechanism

It is crucial to understand the O2 reaction mechanisms in non-aqueous Li+ electrolytes. Important progress has been made using electrochemical measurements, including those recently by Laoire et al. [101]. As shown previously in Equations (2) and (3), the formation of LiO2 and Li2O2 is thermodynamically possible at nearly identical potentials. Thus, the actual products are controlled by ORR and OEV kinetics. Cyclic voltammetry and RDE techniques have been employed to study the underlying reaction mechanism [62,101,102]. A possible reaction mechanism is as follows [62].
The superoxide radicals, as a weakly adsorbed species, are first formed.

\[ O_2 + e^- \rightarrow O_2^-. \] (4a)

Subsequently, it might be solvated by various species such as salt cations or solvents and then diffuse into the bulk of the electrolyte. Alternatively, the weakly adsorbed superoxide radicals could react with Li\(^+\) to form surface-adsorbed LiO\(_2\):

\[ O_2^- + Li^+ \rightarrow LiO_2. \] (4b)

The surface-adsorbed LiO\(_2\) can be reduced to solid Li\(_2\)O\(_2\), which is considered strongly dependent on the oxygen adsorption nature of the catalyst surface:

\[ LiO_2 + e^- + Li^+ \rightarrow Li_2O_2. \] (4c)

Further reaction of Li\(_2\)O\(_2\) to LiO\(_2\) (\(E_{rev} = 2.86 \text{ V}_\text{Li}\)) is thermodynamically possible. However, the nature of the ORR products is likely to depend on the catalyst, with a preference for Li\(_2\)O\(_2\) formation for catalysts that have low oxygen adsorption strength (e.g. C) and a preference for Li\(_2\)O for catalysts with high oxygen catalyst bond strength (e.g. Pt). Unfortunately, no literature data are available on the discharge product distribution as a function of catalyst and this will be examined in our future work.

Another mechanism of electrochemical growth of Li\(_2\)O\(_2\) has been stated by Hummelshøj et al. using density functional theory \([103]\). The cathode reactions can be described as follows:

\[ O_2 + e^- + Li^+ + \ast \rightarrow LiO_2\ast, \] (5a)

\[ Li^+ + e^- + LiO_2 \rightarrow Li_2O_2, \] (5b)

where \(\ast\) denotes a surface site on Li\(_2\)O\(_2\) where the growth proceeds.

To identify directly the species involved in the reaction, Peng et al. \([92]\) presented in situ spectroscopic data (Figure 7) that provide direct evidence that LiO\(_2\) is indeed an intermediate on O\(_2\) reduction, which then disproportionates to the final product Li\(_2\)O\(_2\). Spectroscopic studies of Li\(_2\)O\(_2\) oxidation demonstrated that LiO\(_2\) is not an intermediate on oxidation, i.e. oxidation does not follow the reverse pathway to reduction.

However, it should be pointed out that the main discharge product is electrolyte dependent, especially for Li–air batteries with a carbonate-based electrolyte \([51,71,104–106]\). For example, Freunberger et al. have also studied the reactions in rechargeable Li–O\(_2\) batteries with alkyl carbonate electrolytes \([71]\). Surprisingly, there is no evidence for the formation of Li\(_2\)O\(_2\). The discharge products are C\(_3\)H\(_6\)(OCO\(_2\)Li)\(_2\), LiCO\(_3\), HCO\(_2\)Li, CH\(_3\)CO\(_2\)Li, CO\(_2\) and H\(_2\)O, which might be due to electrolyte decomposition. Among them, the C\(_3\)H\(_6\)(OCO\(_2\)Li)\(_2\), LiCO\(_3\), HCO\(_2\)Li and CH\(_3\)CO\(_2\)Li can be oxidized during the charge process accompanied by CO\(_2\) and H\(_2\)O evolution. However, it should be noted that the discharge and charge cycle is not a strictly reversible process as the latter does not reverse that of the former.

Up to now, no less than five different mechanisms for O\(_2\) reduction in Li\(^+\) electrolytes have been proposed over the last 40 years based on electrochemical measurements.
The mechanism for cathode reactions are complex and uncertain because they are electrolyte-, catalyst- and sometimes even battery operation environment-dependent. It is still a great challenge and intensive research is urgently needed to clarify the cathode reactions.

4. Conclusions and perspective

Li–air batteries have received much attention as possible batteries for electric vehicle propulsion applications. If successfully developed, this battery could provide an energy source for electric vehicles rivaling that of gasoline in terms of usable energy density. Although significant developments have been achieved, including the porous carbon-based cathode, catalyst, electrolyte, separator and reaction mechanism, which could help researchers understand the Li–air battery clearly, the Li–air battery is still at an embryo stage and there are numerous scientific and technical challenges that must be overcome if the alluring promise of the Li–air battery is to turn into reality. From the perspective of the authors, the key areas for future research are as follows:
(1) Design and synthesis of a novel porous carbon material with high conductivity, which would ensure sufficient pores to store discharge products, channels to diffuse oxygen and good electrolyte wettability. In a word, it would provide an adequate and suitable three-phase interface for the charge/discharge process.

(2) Screening bifunctional cathode catalysts with improved activity for both the ORR during discharge and the OER during charge, achieving a high round-trip efficiency.

(3) Development of stable electrolytes with high O₂ solubility, excellent lithium ionic conductivity, low viscosity and vapor pressure.

(4) Developing a high lithium ionic conducting separator and a high throughout oxygen-breathing membranes used at the cathode to block H₂O, CO₂ and other air components except O₂.

(5) Understanding of the complex chemical reaction mechanisms that occur during charge and discharge.

The scientific and technical impediments facing development of practical Li–air batteries open up an exciting opportunity for researchers with different backgrounds to utilize their unique knowledge and skills to bridge the knowledge gaps that exist in the field of the Li–air battery.

Acknowledgements
This work is financially supported by 100 Talents Programme of The Chinese Academy of Sciences, National Natural Science Foundation of China (Grant No. 21101147), and the Jilin Province Science and Technology Development Program (Grant No. 20100102).

References
[1] B. Richter, D. Goldston, G. Crabtree, L. Glicksman, D. Goldstein, D. Kammen, M. Levine, M. Lubell, M. Savitz, and D. Sperling, Energy Future: Think Efficiency, American Physical Society, College Park, MD, 2008.
[2] D.J. Mackay, Sustainable Energy – Without the Hot Air, UIT Cambridge, Cambridge, UK, 2009.
[3] D. Linden, Handbook of Batteries and Fuel Cells, McGraw-Hill, New York, 1984.
[4] S.J. Visco and E. Nimon, Lithium metal aqueous batteries, 12th International Meeting on Lithium Batteries, Nara, Japan, 2004.
[5] A.S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, Nat. Mater. 4 (2005), pp. 366–377.
[6] M. Armand and J.M. Tarascon, Building better batteries, Nature 451 (2008), pp. 652–657.
[7] T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, and P.G. Bruce, Rechargeable Lι₂O₂ electrode for lithium batteries, J. Am. Chem. Soc. 128 (2006), pp. 1390–1393.
[8] S.S. Sandhu, J.P. Fellner, and G.W. Brutchen, Diffusion-limited model for a lithium/oxygen battery with an organic electrolyte, J. Power Sourc. 164 (2007), pp. 365–371.
[9] K. Abraham, A brief history of non-aqueous metal–air batteries, J. Electrochem. Soc. 3 (2008), pp. 42–67.
[10] E.L. Littauer and K.C. Tsai, Anodic behavior of lithium in aqueous-electrolytes, J. Electrochem. Soc. 123 (1976), pp. 771–776.
[11] K.M. Abraham and Z. Jiang, A polymer electrolyte-based rechargeable lithium/oxygen battery, J. Electrochem. Soc. 143 (1996), pp. 1–5.
[12] P.G. Bruce, Energy storage beyond the horizon: Rechargeable lithium batteries, Solid State Ionics. 179 (2008), pp. 752–760.
[13] B. Ellis, K. Lee, and L. Nazar, Positive electrode materials for Li-ion and Li batteries, Chem. Mater. 22 (2010), pp. 691–714.

[14] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, and W. Wilcke, Lithium–air battery: Promise and challenges, J. Phys. Chem. Lett. 1 (2010), pp. 2193–2203.

[15] A. Kraysberg and Y. Ein-Eli, Review on Li–air batteries – opportunities, limitations and performance, J. Power Sourc. 196 (2011), pp. 886–893.

[16] R. Padbury and X. Zhang, Lithium–oxygen batteries – limiting factors that affect performance, J. Power Sourc. 196 (2011), pp. 4436–4444.

[17] M.-K. Song, S. Park, F.M. Alamgir, J. Cho, and M. Liu, Nanostructured electrodes for lithium-ion and lithium–air batteries: The latest developments, challenges, and perspectives, Mater. Sci. Eng. R 72 (2011), pp. 203–252.

[18] X. Ren, S.S. Zhang, D.T. Tran, and J. Read, Oxygen reduction reaction catalyst on lithium/air battery discharge performance, J. Mater. Chem. 21 (2011), pp. 10118–10125.

[19] Y.-C. Lu, Z. Xu, H.A. Gasteiger, S. Chen, K. Hamad-Schifferli, and Y. Shao-Horn, Platinum–gold nanoparticles: A highly active bifunctional electrocatalyst for rechargeable lithium–air batteries, J. Am. Chem. Soc. 132 (2010), pp. 12170–12171.

[20] S.D. Beattie, D.M. Manolescu, and S.L. Blair, High-capacity lithium–air cathodes, J. Electrochem. Soc. 156 (2009), pp. A44–A47.

[21] O. Crowther, B. Meyer, M. Morgan, and M. Salomon, Primary Li–air cell development, J. Power Sourc. 196 (2011), pp. 1498–1502.

[22] J.-G. Zhang, D. Wang, W. Xu, J. Xiao, and R.E. Williford, Ambient operation of Li/air batteries, J. Power Sourc. 195 (2010), pp. 4332–4337.

[23] Y. Li, J. Wang, X. Li, J. Liu, D. Geng, J. Yang, R. Li, and X. Sun, Nitrogen-doped carbon nanotubes as novel cathode for lithium–air batteries, Electrochem. Comm. 13 (2011), pp. 668–672.

[24] X.H. Yang, P. He, and Y.Y. Xia, Preparation of mesocellular carbon foam and its application for lithium/oxygen battery, Electrochem. Comm. 11 (2009), pp. 1127–1130.

[25] C.K. Park, S.B. Park, S.Y. Lee, H. Lee, H. Jang, and W.I. Cho, Electrochemical performances of lithium–air cell with carbon materials, Bull. Kor. Chem. Soc. 31 (2010), pp. 3221–3224.

[26] M. Mirzaeian, High capacity carbon-based electrodes for lithium/oxygen batteries, Power Syst. Techn. 31 (2007), pp. 90–96.

[27] M. Mirzaeian and P.J. Hall, Preparation of controlled porosity carbon aerogels for energy storage in rechargeable lithium–air batteries, Electrochim. Acta 54 (2009), pp. 7444–7451.

[28] M. Mirzaeian and P.J. Hall, Characterizing capacity loss of lithium oxygen batteries by impedance spectroscopy, J. Power Sourc. 195 (2010), pp. 6817–6824.

[29] E. Yoo and H. Zhou, Li–air rechargeable battery based on metal-free graphene nanosheet catalysts, ACS Nano 5 (2011), pp. 3020–3026.

[30] Y. Wang and H. Zhou, To draw an air electrode of a Li–air battery by pencil, Energ. Environ. Sci. 4 (2011), pp. 1704–1707.

[31] Y. Li, J. Wang, X. Li, D. Geng, R. Li, and X. Sun, Superior energy capacity of graphene nanosheets for a nonaqueous lithium–oxygen battery, Chem. Comm. (2011), pp. 9438–9440.

[32] Y. Wang, L. Cheng, F. Li, H. Xiong, and Y. Xia, High electrocatalytic performance of Mn3O4/mesoporous carbon composite for oxygen reduction in alkaline solutions, Chem. Mater. 19 (2007), pp. 2095–2101.

[33] T. Kuboki, T. Okuyama, T. Ohsaki, and N. Takami, Lithium–air batteries using hydrophobic room temperature ionic liquid electrolyte, J. Power Sourc. 146 (2005), pp. 766–769.

[34] C. Tran, X.Q. Yang, and D.Y. Qu, Investigation of the gas-diffusion-electrode used as lithium/air cathode in non-aqueous electrolyte and the importance of carbon material porosity, J. Power Sourc. 195 (2010), pp. 2057–2063.

[35] C. Tran, J. Kafle, X.Q. Yang, and D. Qu, Increased discharge capacity of a Li–air activated carbon cathode produced by preventing carbon surface passivation, Carbon 49 (2011), pp. 1266–1271.

[36] G.Q. Zhang, J.P. Zheng, R. Liang, C. Zhang, B. Wang, M. Hendrickson, and E.J. Plichta, Lithium–air batteries using SWNT/CNF buckypapers as air electrodes, J. Electrochem. Soc. 157 (2010), pp. A953–A956.

[37] R.R. Mitchell, B.M. Gallant, C.V. Thompson, and Y. Shao-Horn, All-carbon-nanofiber electrodes for high-energy rechargeable Li–O2 batteries, Energ. Environ. Sci. 4 (2011), pp. 2952–2958.
[38] J. Read, *Characterization of the lithium/oxygen organic electrolyte battery*, J. Electrochem. Soc. 149 (2002), pp. A1190–A1195.

[39] J. Xiao, D.H. Wang, W. Xu, D.Y. Wang, R.E. Williford, J. Liu, and J.G. Zhang, *Optimization of air electrode for Li/air batteries*, J. Electrochem. Soc. 157 (2010), pp. A487–A492.

[40] A. Débart, J. Bao, G. Armstrong, and P.G. Bruce, *An O₂ cathode for rechargeable lithium batteries: The effect of a catalyst*, J. Power Sourc. 174 (2007), pp. 1177–1182.

[41] D. Zhang, Z. Fu, Z. Wei, T. Huang, and A. Yu, *Polarization of oxygen electrode in rechargeable lithium oxygen batteries*, J. Electrochem. Soc. 157 (2010), pp. A362–A365.

[42] B. Scrosati and J. Garche, *Lithium batteries: Status, prospects and future*, J. Power Sourc. 195 (2010), pp. 2419–2430.

[43] A. Débart, A. Paterson, J. Bao, and P.G. Bruce, *α-MnO₂ nanowires: A catalyst for the O₂ electrode in rechargeable lithium batteries*, Angew. Chem. Int. Ed. 47 (2008), pp. 4521–4524.

[44] L. Jin, L. Xu, C. Morein, C.H. Chen, M. Lai, S. Dharmaratha, A. Dobley, and S.L. Suib, *Titanium-containing γ-MnO₂ (TM) hollow spheres: One-step synthesis and catalytic activities in Li/air batteries and oxidative chemical reactions*, Adv. Funct. Mater. 20 (2010), pp. 3373–3382.

[45] J. Li, N. Wang, Y. Zhao, Y. Ding, and L. Guan, *MnO₂ nanoflakes coated on multi-walled carbon nanotubes for rechargeable lithium–air batteries*, Electrochem. Commun. 13 (2011), pp. 698–700.

[46] G. Zhang, J. Zheng, R. Liang, C. Zhang, B. Wang, M. Au, M. Hendrickson, and E. Plichta, *α-MnO₂/carbon nanotube/carbon nanofiber composite catalytic air electrodes for rechargeable lithium–air batteries*, J. Electrochem. Soc. 158 (2011), pp. A822–A827.

[47] V.M.B. Crisostomo, J.K. Ngala, S. Alia, A. Dobley, C. Morein, C.H. Chen, X. Shen, and S.L. Suib, *New synthetic route, characterization, and electrocatalytic activity of nanosized manganese*, Chem. Mater. 19 (2007), pp. 1832–1839.

[48] C.S. Johnson, S.H. Kang, J.T. Vaughey, S.V. Pol, M. Balasubramanian, and M.M. Thackeray, *Li₂O removal from Li₅FeO₄: A cathode precursor for lithium-ion batteries*, Chem. Mater. 22 (2010), pp. 1263–1270.

[49] L. Trahey, C. Johnson, J. Vaughey, S.H. Kang, L. Hardwick, S. Freunberger, P. Bruce, and M. Thackeray, *Activated lithium–metal oxides as catalytic electrodes for Li–O₂ cells*, Electrochem. Solid-State Lett. 14 (2011), pp. A64–A66.

[50] D. Zhang, R.S. Li, T. Huang, and A.S. Yu, *Novel composite polymer electrolyte for lithium air batteries*, J. Power Sourc. 195 (2010), pp. 1202–1206.

[51] A. Thapa, S. Kazuki, H. Matsumoto, and T. Ishihara, *Lithium–air rechargeable batteries using MnO₂-carbon based air electrode*, 216th Meeting of the Electrochemical Society, Vienna, Austria, 2009.

[52] Y.G. Wang and H.S. Zhou, *A lithium–air battery with a potential to continuously reduce O₂ from air for delivering energy*, J. Power Sourc. 195 (2010), pp. 358–361.

[53] H. Cheng and K. Scott, *Carbon-supported manganese oxide nanocatalysts for rechargeable lithium-air batteries*, J. Power Sourc. 195 (2010), pp. 1370–1374.

[54] K.B. Chung, J.K. Shin, T.Y. Jang, D.K. Noh, Y. Tak, and S.H. Baeck, *Preparation and analyses of MnO₂/carbon composites for rechargeable lithium–air battery*, Rev. Adv. Mater. Sci. 28 (2011), pp. 54–58.

[55] H. Minowa, M. Hayashi, M. Takahashi, and T. Shodai, *Electrochemical properties of carbon materials and La₀.₆Sr₀.₄Fe₀.₆Mn₀.₄O₃ electrocatalysts for air electrodes of lithium–air secondary batteries*, Electrochemistry 78 (2010), pp. 353–356.

[56] J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J.B. Goodenough, and Y. Shao-Horn, *Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries*, Nat. Chem. 3 (2011), pp. 546–550.

[57] F. Cheng, J. Shen, B. Peng, Y. Pan, Z. Tao, and J. Chen, *Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts*, Nat. Chem. 3 (2010), pp. 79–84.

[58] S.S. Zhang, X. Ren, and J. Read, *Heat-treated metal phthalocyanine complex as an oxygen reduction catalyst for non-aqueous electrolyte Li/air batteries*, Electrochem. Acta 56 (2011), pp. 4544–4548.

[59] Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, and Y. Shao-Horn, *The influence of catalysts on discharge and charge voltages of rechargeable Li–oxygen batteries*, Electrochem. Solid-State Lett. 13 (2010), pp. A69–A72.
[60] A.K. Thapa, K. Saimen, and T. Ishihara, \textit{Pd}/MnO$_2$ air electrode catalyst for rechargeable lithium/air battery, Electrochem. Solid-State Lett. 13 (2010), pp. A165–A167.

[61] A.K. Thapa and T. Ishihara, \textit{Mesoporous $\alpha$-MnO$_2$/Pd} catalyst air electrode for rechargeable lithium–air battery, J. Power Sourc. 196 (2011), pp. 7016–7020.

[62] Y. Lu, H. Gasteiger, E. Crumlin, R. McGuire Jr, and Y. Shao-Horn, Electrocatalytic activity studies of select metal surfaces and implications in Li–air batteries, J. Electrochem. Soc. 157 (2010), pp. A1016–A1025.

[63] V. Giordani, S.A. Freunberger, P.G. Bruce, J.M. Tarascon, and D. Larcher, \textit{$\text{H}_2\text{O}_2$} decomposition reaction as selecting tool for catalysts in Li–O$_2$ cells, Electrochem. Solid-State Lett. 13 (2010), pp. A180–A183.

[64] S.A. Freunberger, Y.H. Chen, N.E. Drewett, L.J. Hardwick, F. Bardé, and P.G. Bruce, \textit{The lithium–oxygen battery with ether-based electrolytes}, Angew. Chem. Int. Ed. 50 (2011), pp. 1–6.

[65] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstein, A. Driedger, and D. Foster, \textit{Oxygen transport properties of organic electrolytes and performance of lithium/oxygen battery}, J. Electrochem. Soc. 150 (2003), pp. A1351–A1356.

[66] W. Xu, J. Xiao, J. Zhang, D.Y. Wang, and J.G. Zhang, \textit{Optimization of nonaqueous electrolytes for primary lithium/air batteries operated in ambient environment}, J. Electrochem. Soc. 156 (2009), pp. A773–A779.

[67] I. Kowalczyk, J. Read, and M. Salomon, \textit{Li–air batteries: A classic example of limitations owing to solubilities}, Pure Appl. Chem. 79 (2007), pp. 851–860.

[68] W. Xu, J. Xiao, D.Y. Wang, J. Zhang, and J.G. Zhang, \textit{Effects of nonaqueous electrolytes on the performance of lithium/air batteries}, J. Electrochem. Soc. 157 (2010), pp. A219–A224.

[69] K. Xu, \textit{Nonaqueous liquid electrolytes for lithium-based rechargeable batteries}, Chem. Rev. 104 (2004), pp. 4303–4418.

[70] D. Shanmukaraj, S. Grugeon, G. Gachot, S. Laruelle, D. Mathiron, J.M. Tarascon, and M. Armand, \textit{Boron esters as tunable anion carriers for non-aqueous batteries electrochemistry}, J. Am. Chem. Soc. 132 (2010), pp. 3055–3062.

[71] S.A. Freunberger, Y. Chen, Z. Peng, J.M. Griffin, L.J. Hardwick, F. Barde, P. Novak, and P.G. Bruce, \textit{Reactions in the rechargeable lithium–O$_2$ battery with alkyl carbonate electrolytes}, J. Am. Chem. Soc. 133 (2011), pp. 8040–8047.

[72] Y.C. Lu, D.G. Kwabi, K.P.C. Yao, J.R. Harding, J. Zhou, L. Zuin, and Y. Shao-Horn, \textit{The discharge rate capability of rechargeable Li–O$_2$ batteries}, Energ. Environ. Sci. 4 (2011), pp. 2999–3007.

[73] J. Read, \textit{Ether-based electrolytes for the lithium/oxygen organic electrolyte battery}, J. Electrochem. Soc. 153 (2006), pp. A96–A100.

[74] D. Shanmukaraj, S. Grugeon, G. Gachot, S. Laruelle, D. Mathiron, J.M. Tarascon, and M. Armand, \textit{Boron esters as tunable anion carriers for non-aqueous batteries electrochemistry}, J. Am. Chem. Soc. 132 (2010), pp. 3055–3062.

[75] G. Nagasubramanian and S. Distefano, \textit{12-Crown-4 ether-assisted enhancement of ionic-conductivity and interfacial kinetics in polyethylene oxide electrolytes}, J. Electrochem. Soc. 137 (1990), pp. 3830–3835.

[76] G. Nagasubramanian, A.I. Attia, and G. Halpert, \textit{Effects of 12-crown-4 ether on the electrochemical performance of CoO and TiS cathodes in li polymer electrolyte cells}, J. Electrochem. Soc. 139 (1992), pp. 3043–3046.

[77] W. Xu, J. Xiao, D.Y. Wang, J.A. Zhang, and J.G. Zhang, \textit{Crown ethers in nonaqueous electrolytes for lithium/air batteries}, Electrochem. Solid-State Lett. 13 (2010), pp. A48–A51.

[78] H.S. Lee, X. Sun, X.Q. Yang, and J. McBreen, \textit{Synthesis and study of new cyclic boronate additives for lithium battery electrolytes}, J. Electrochem. Soc. 149 (2002), pp. A1460–A1465.

[79] H.S. Lee, Z.F. Ma, X.Q. Yang, X. Sun, and J. McBreen, \textit{Synthesis of a series of fluorinated boronate compounds and their use as additives in lithium battery electrolytes}, J. Electrochem. Soc. 151 (2004), pp. A1429–A1435.

[80] S.A. Freunberger, Y.H. Chen, N.E. Drewett, L.J. Hardwick, F. Bardé, and P.G. Bruce, \textit{The lithium–oxygen battery with ether-based electrolytes}, Angew. Chem. Int. Ed. 50 (2011), pp. 1–6.

[81] L.F. Li, H.S. Lee, H. Li, X.Q. Yang, K.W. Yang, W.S. Yoon, J. McBreen, and X.J. Huang, \textit{New electrolytes for lithium ion batteries using LiF salt and boron based anion receptors}, J. Power Sourc. 184 (2008), pp. 517–521.

[82] B. Xie, H.S. Lee, H. Li, X.Q. Yang, J. McBreen, and L.Q. Chen, \textit{New electrolytes using Li$_2$O or Li$_2$O$_2$ oxides and tris(pentafluorophenyl) borane as boron based anion receptor for lithium batteries}, Electrochem. Comm. 10 (2008), pp. 1195–1197.
[82] S.S. Zhang, D. Foster, and J. Read, Discharge characteristic of a non-aqueous electrolyte Li/O2 battery, J. Power Sourc. 195 (2010), pp. 1235–1240.

[83] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, and O. Yamamoto, Study on lithium/air secondary batteries – stability of NASICON-type lithium ion conducting glass-ceramics with water, J. Power Sourc. 189 (2009), pp. 371–377.

[84] P. He, Y. Wang, and H. Zhou, A Li–air fuel cell with recycle aqueous electrolyte for improved stability, Electrochem. Comm. 12 (2010), pp. 1686–1689.

[85] B. Kumar and J. Kumar, Cathodes for solid-state lithium–oxygen cells: Roles of NASICON glass-ceramics, J. Electrochem. Soc. 157 (2010), pp. A611–A616.

[86] Y. Shimonishi, T. Zhang, P. Johnson, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, and N. Sammes, A study on lithium/air secondary batteries – stability of NASICON-type glass ceramics in acid solutions, J. Power Sourc. 195 (2010), pp. 6187–6191.

[87] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, and N. Sammes, A novel high energy density rechargeable lithium/air battery, Chem. Comm. (2010), pp. 1661–1663.

[88] B. Kumar, J. Kumar, R. Leese, J.P. Fellner, S.J. Rodrigues, and K.M. Abraham, A solid-state, rechargeable, long cycle life lithium-air battery, J. Electrochem. Soc. 157 (2010), pp. A50–A54.

[89] G.L. Cui, Z.H. Liu, H.B. Wang, X. Chen, and P.X. Han, A separator preparation of Li–air battery (in Chinese), China Patent #101707241, 2010.

[90] A.S. Yu, W.J. Wang, X.R. Zhang, and D. Zhang, High capacity rechargeable all-solid Li–air battery (in Chinese), China Patent #101267057, 2008.

[91] D. Wang, J. Xiao, W. Xu, and J. Zhang, High capacity pouch-type Li–air batteries, J. Electrochem. Soc. 157 (2010), pp. A760–A764.

[92] Z. Peng, S.A. Freunberger, L.J. Hardwick, Y. Chen, V. Giordani, F. Bardé, P. Novák, D. Graham, J.-M. Tarascon, and P.G. Bruce, Oxygen reactions in a non-aqueous Li+ electrolyte, Angew. Chem. Int. Ed. 50 (2011), pp. 6351–6355.

[93] S.J. Visco, B.D. Katz, Y.S. Nimon, and L.C. Dejonghe, Protected active metal electrode and battery cell structures with non-aqueous interlayer architecture, US Patent #7282295, 2007.

[94] M. Singh, I. Gur, H.B. Eitouni, and N.P. Balsara, Solid electrolyte material manufacturable by polymer processing methods, US Patent Application #12271829, 2009.

[95] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, and C.D. Evans, Thin-film lithium and lithium-ion batteries, Solid State Ionics 135 (2000), pp. 33–45.

[96] X. Yang and Y. Xia, The effect of oxygen pressures on the electrochemical profile of lithium/air battery, J. Solid-State Electrochem. 14 (2010), pp. 109–114.

[97] J. Zhang, W. Xu, and W. Liu, Oxygen-selective immobilized liquid membranes for operation of lithium–air batteries in ambient air, J. Power Source. 195 (2010), pp. 7438–7444.

[98] J.A. Zhang, W. Xu, X.H. Li, and W. Liu, Air dehydration membranes for nonaqueous lithium–air batteries, J. Electrochem. Soc. 157 (2010), pp. A940–A946.

[99] G.M. Veith and N.J. Dudney, Current collectors for rechargeable Li–air batteries, J. Electrochem. Soc. 158 (2011), pp. A658–A663.

[100] W.K. Behl, J. Read, A. Pitt, J. Wolfenstine, and D. Foster, Temperature performance of the lithium/O2 battery, J. Indian Chem. Soc. 82 (2005), pp. 1055–1057.

[101] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, and M.A. Hendrickson, Elucidating the mechanism of oxygen reduction for lithium–air battery applications, J. Phys. Chem. C 113 (2009), pp. 20127–20134.

[102] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, and M.A. Hendrickson, Influence of nonaqueous solvents on the electrochemistry of oxygen in the rechargeable lithium–air battery, J. Phys. Chem. C. 114 (2010), pp. 9178–9186.

[103] J.S. Hummelshøj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K.S. Thygesen, A.C. Luntz, K.W. Jacobsen, and J.K. Norskov, Communications: Elementary oxygen electrode reactions in the aprotic Li–air battery, J. Chem. Phys. 132 (2010), pp. 071101-1–071101-4.

[104] W. Xu, V.V. Viswanathan, D.Y. Wang, S.A. Towne, J. Xiao, Z.M. Nie, D.H. Hu, and J.G. Zhang, Investigation on the charging process of Li2O2-based air electrodes in Li–O2 batteries with organic carbonate electrolytes, J. Power Source. 196 (2011), pp. 3894–3899.

[105] W. Xu, K. Xu, V.V. Viswanathan, S.A. Towne, J.S. Hardy, J. Xiao, Z. Nie, D. Hu, D. Wang, and J.G. Zhang, Reaction mechanisms for the limited reversibility of Li–O2 chemistry in organic carbonate electrolytes, J. Power Source. 196 (2011), pp. 9631–9639.
[106] F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoishi, and H. Iba, *Rechargeable Li–air batteries with carbonate-based liquid electrolytes*, Electrochemistry 78 (2010), pp. 403–405.

[107] T. Fujinaga and S. Sakara, *Polarographic investigation of dissolved-oxygen in non-aqueous solvent*, Bull. Chem. Soc. Jpn. 47 (1974), pp. 2781–2786.

[108] D.T. Sawyer, G. Chiericato, C.T. Angelis, E.J. Nanni and T. Tsuchiya, *Effects of media and electrode materials on the electrochemical reduction of dioxygen*, Anal. Chem. 54 (1982), pp. 1720–1724.

[109] D. Aurbach, M. Daroux, P. Faguy, and E. Yeager, *The electrochemistry of noble-metal electrodes in aprotic organic solvents containing lithium salts*, J. Electroanal. Chem. 297 (1991), pp. 225–244.