



Review

Lithium–oxygen batteries—Limiting factors that affect performance

Richard Padbury, Xiangwu Zhang*

Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, North Carolina State University,
2401 Research Drive, Raleigh, NC 27695-8301, USA

ARTICLE INFO

Article history:

Received 21 November 2010

Received in revised form 6 January 2011

Accepted 7 January 2011

Available online 5 February 2011

Keywords:

Lithium–oxygen battery

Reaction kinetics

Energy density

Electrode structure

Electrolyte

ABSTRACT

Lithium–oxygen batteries have recently received attention due to their extremely high theoretical energy densities, which far exceed that of any other existing energy storage technology. The significantly larger theoretical energy density of the lithium–oxygen 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. Before the lithium–oxygen batteries can be realized as high performance, commercially viable products, there are still many challenges to overcome, from designing their cathode structure, to optimizing their electrolyte compositions and elucidating the complex chemical reactions that occur during charge and discharge. The scientific obstacles that are related to the performance of the lithium–oxygen 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 article is a summary of the most significant limiting factors that affect the performance of the lithium–oxygen batteries from the perspective of the authors. The article indicates the relationships that form between various limiting factors and highlights the complex yet captivating nature of the research within this field.

© 2011 Elsevier B.V. All rights reserved.

Contents

1. Introduction	4436
2. Electrochemical reactions of lithium–oxygen battery	4438
3. Limiting factors on performance	4439
3.1. Overpotentials	4439
3.2. Catalysts	4439
3.3. Diffusion and solubility	4440
3.4. Electrolytes	4440
3.5. Electrolyte filling of the cathode	4441
3.6. Structural importance of porosity and carbon content	4441
3.7. The relationship between surface area and porosity	4442
3.8. Operational conditions	4442
4. Commercial initiatives	4443
5. Conclusion—the ideal lithium–air battery	4444
Acknowledgement	4444
References	4444

1. Introduction

Climate change and energy consumption share a direct relationship. The demand for energy is putting pressure on fossil fuel reserves, which in return is having a negative impact on the climate

as increasing quantities of carbon dioxide and other adverse gasses are expelled into the atmosphere. While the mechanism of climate change is a challenge to decipher, it is evident that our demand for energy is leading to an energy crisis where increasing prices are a direct result of declining fossil fuel reserves. Technology will progressively become a limiting factor in our utilization of fossil fuels as unexcavated reserves become scarcer and the processes required to extract the material become more difficult to implement. World energy demand is expected to double by the year 2050 and triple by

* Corresponding author. Tel.: +1 919 515 6547; fax: +1 919 515 6532.
E-mail address: xiangwu.zhang@ncsu.edu (X. Zhang).

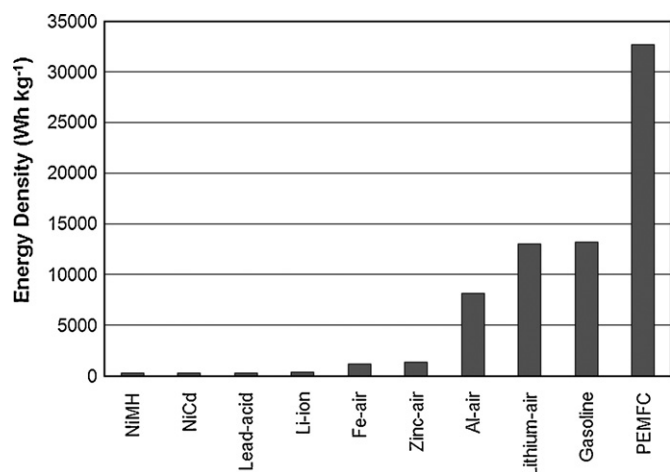


Fig. 1. Current and developing energy storage technologies and the comparisons of their respective theoretical energy densities.

the end of the century. Therefore, along with the growing concerns for the climate, there has been substantial interest in renewable energy sources such as wind and solar. However, these technologies have a random and variable energy output which makes them difficult to manage [1]. It is clear that the advancement of energy storage technologies is required for the effective utilization of renewable energy sources in future smart grids and power delivery systems. This article focuses on the development of the lithium–oxygen battery which was first discovered by Littauer and Tsai at Lockheed [2] in 1976. The project was abandoned in the late 80s due to the undesirable reaction of lithium with water through the use of aqueous electrolytes; however, Abraham et al. were the first to introduce a successful secondary lithium–oxygen battery in the late 90s which incorporated an organic electrolyte [3].

Fig. 1 shows a range of energy storage technologies available or currently under development and compares their respective theoretical energy densities [4]. One of the most well-known energy storage technologies is the lithium-ion battery (LIB), which is the power source of choice in a wide variety of portable applications such as laptops and cell phones [5]. The total sale of lithium-ion batteries in 2007 was approximately 8 billion dollars [6]. The profitability of lithium-ion batteries is due to their many qualities such as higher voltage, higher energy density, and longer cycle life compared with traditional rechargeable batteries such as lead acid and nickel–cadmium (Ni–Cd) batteries [7]. However, the energy density of lithium-ion batteries is limited by both the anode and cathode because their specific capacities are restricted by the weight of the active materials which are typically graphite (170 mAh g^{-1}) for the anode and metal oxide such as LiCoO_2 (130 mAh g^{-1}) for the cathode [8]. As a result, the energy density of lithium-ion batteries is only between 75 and 160 Wh kg^{-1} [9]. In recent years, nano-structured carbon materials such as carbon nanotubes, carbon nanofibers and carbon nanocomposites have been used to construct lithium-ion anodes [10]. The future challenges in the development of lithium-ion batteries are to maintain their good capacity retention, high rate capability and safe operation over many cycles [11].

The most obscure energy storage technologies, due to the numerous challenges faced by researchers, are the metal–air batteries. Several metal–air batteries have been investigated due to their promising energy densities such as iron–air, aluminum–air and zinc–air batteries [12]. While iron–air batteries have a long cycle life, they suffer from low voltage and specific energy compared with other metal–air batteries [13]. Aluminum–air batteries are desirable because aluminum is one of the Earth's most abun-

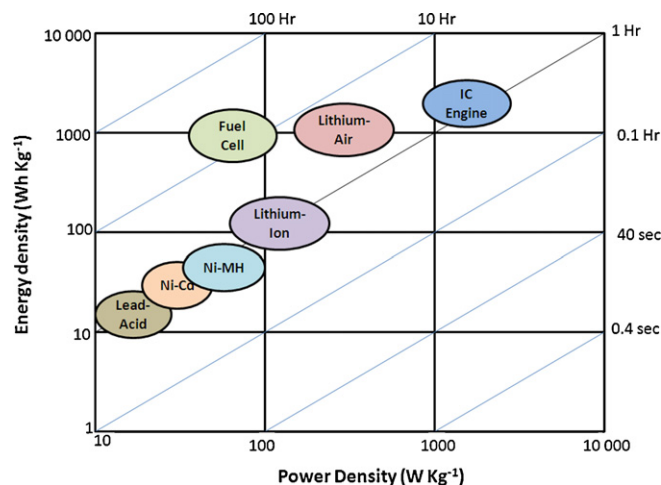


Fig. 2. Ragone plot comparing the practical energy and power densities of current energy storage technologies with the lithium–air battery. The plot is based on data from Refs. [26–28].

dant resources and these batteries have high specific energy; however, they are limited by a low Coulombic efficiency [14]. Primary zinc–air batteries are commercially available, and have been used for applications where high specific energy is important and low discharge rates are acceptable, for example, in hearing aids [15]. Zinc–air batteries offer higher energy densities compared with conventional primary batteries as well as exhibiting a flat discharge voltage, long shelf life, high safety, and low energy cost [16]. However, the energy densities of zinc–air batteries still cannot meet the requirements of many high-energy applications. Recently, there has been an increase in awareness of the lithium–oxygen technology due to its extremely high energy density and this has resulted in an increase of intensive research programs [17–19].

Lithium–oxygen batteries promise to far exceed the energy densities of intercalation electrode-based energy storage technologies with some researchers predicting a 5–10-fold increase over lithium-ion batteries [20]. The large theoretical energy density of the lithium–oxygen battery is due to the fact that the cathode oxidant, oxygen, is not stored in the electrode and can be readily obtained from the surrounding environment. The stored energy content of a battery can also be maximized by having a large chemical potential difference between the electrodes and making the mass of the reactant per exchange of electron as small as possible [21]. Hence, the theoretical energy density of the lithium–oxygen battery is also attributed to the low atomic mass of lithium metal at the anode and its low electronegativity which means that electrons are donated more readily producing positive ions [22]. Considering the atomic mass of lithium metal alone, the gravimetric energy density of the lithium–oxygen battery with respect to the anode is approximately $13,000 \text{ Wh kg}^{-1}$ [4], which is comparable to the energy density of gasoline ($13,200 \text{ Wh kg}^{-1}$) [23]. Another technology, proton exchange membrane fuel cell (PEMFC), has even higher theoretical energy density due to the much lower atomic mass of hydrogen [4]. The PEMFC is an attractive power source for transportation, distributed power, and portable power applications due to its high-energy efficiency and environmental compatibility [24]. However, the implementation of the PEMFC technology is currently limited by problems ranging from difficulties in hydrogen generation, storage, and transportation, to unsatisfactory performance and high cost of current PEMFCs as a result of expensive catalysts [25].

Fig. 2 is a Ragone plot which compares the practical power and energy densities of current and developing energy-storage tech-

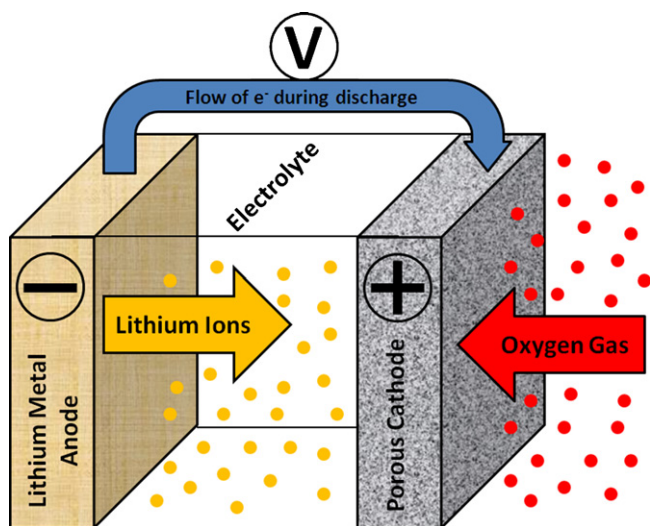


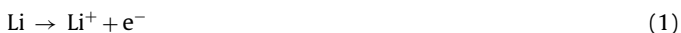
Fig. 3. Schematic diagram of a lithium–oxygen battery showing reduction of oxygen at the porous cathode and oxidation of lithium metal at the anode.

nologies and is based on the data stated in Refs. [26–28]. The diagonal lines indicate the discharge times with low discharge rates displayed at the top left corner of the Ragone plot. One can see that at high discharge rates, lower energy densities are obtained due to the increase in internal resistance that is typical of high discharge rates. Fig. 2 shows the highly attractive energy density of the lithium–air battery; however, the lithium–air battery still suffers from a relatively low power density as compared to the internal combustion engine that uses gasoline. This is an important area of research if the lithium–air battery is to be used in applications such as the electric vehicle and consumer products.

In this article, Section 2 introduces the half cell reactions that take place within a lithium–oxygen battery and describes the discharging mechanism at the cathode in more detail. The bulk of the article, Section 3, introduces the main limiting factors that affect the performance of the lithium–oxygen batteries. The authors would like to express the significance of the relationships that form between various limiting factors and the importance of considering a broad range of aspects when developing new technologies. Section 4 introduces some of the most important commercial initiatives that have been proposed by some of the leading companies involved in the research and development of lithium–oxygen batteries. Finally, Section 5 concludes the information provided in this article and describes the ideal lithium–oxygen battery along with potential research directions.

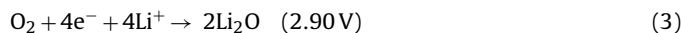
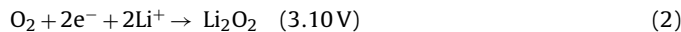
2. Electrochemical reactions of lithium–oxygen battery

The lithium–oxygen battery consists of a porous carbon cathode designed to promote oxygen diffusion and reduction and a pure lithium metal anode as shown in Fig. 3. The two electrodes are separated by a lithium-ion conducting electrolyte. During discharge, lithium metal at the anode is oxidized to lithium ions and liberates electrons as described by the following half cell reaction:



The electrons are transported via an external circuit to the cathode. As the electrons flow through the external circuit, the dissociated lithium ions flow through the electrolyte to the cathode via the mechanism of an electrochemical potential gradient. At the cathode, oxygen is reduced in either a two or four electron process

as described by the following half cell reactions [29–31]:



The potentials stated after each half cell reactions are the standard potentials associated with each reaction and these values can be verified using the Nernst equation:

$$\Delta E = \Delta E^0 - \frac{RT}{nF} \ln Q \quad (4)$$

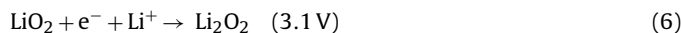
where ΔE is the cell potential, ΔE^0 the standard cell potential, R the universal gas constant, T the absolute temperature, n the number of moles of electrons transferred in the cell reaction or half-reaction, F the Faraday constant, and Q the reaction quotient.

Since the standard potentials of reactions (2) and (3) are close to each other, it is highly probable for either lithium peroxide or lithium oxide to be the most abundant reduction product after discharge. This can be deduced by the fact that the operating potential of the lithium–oxygen battery (approximately 2.0–2.8 V) is also close to the standard potentials of formation for the reduction products stated in reactions (2) and (3). This could be more evident if a particular type of catalyst is used which has the capability to favor one reaction over the other [32]. However, based on the studies of Abraham [3] and Bruce [33] using Raman spectrometry, lithium peroxide in reaction (2) was identified as the most abundant reduction product formed after discharge. Despite these findings, the authors recommend incorporating the analysis of the cathode before and after discharge to verify the most abundant reduction product. This can be achieved by in situ X-ray diffraction analysis of the cathode during discharge using the Swagelok configuration [34].

Alternative mechanisms have also been suggested in order to further elucidate the chemical reactions that occur at the cathode during discharge. For example, Laoire et al. [35] proposes a mechanism in which oxygen is reduced at the cathode to form lithium superoxide as described by the following reaction:



The mechanism states that, towards the end of the battery discharge when the reduction products have progressively filled the pores available for oxygen diffusion, the lithium superoxide further reacts via another one electron reaction as indicated by the following step:



Another mechanism has been stated by Hummelshøj et al. [36] using density function theory (DFT) to describe the electrochemical reactions at the cathode. The mechanism describes the growth of lithium peroxide via the following reactions:



where $*$ is a surface site on lithium peroxide where the growth proceeds.

Mizuno et al. [37] have recently studied the electrochemical stability of carbonate-based liquid electrolytes on electrodes. The research describes the complicated cathode reactions that involve an O_2 radical. Lithium alkylcarbonate ($\text{RO}-(\text{C}=\text{O})-\text{OLi}$) and lithium carbonate (Li_2CO_3) were formed after discharge which suggests that the carbonate solvents highly influence the final discharge product and creates speculation over the actual cathode reaction mechanism.

These suggested mechanisms for oxygen reductions at the cathode demonstrate the complexity and uncertainty of the elec-

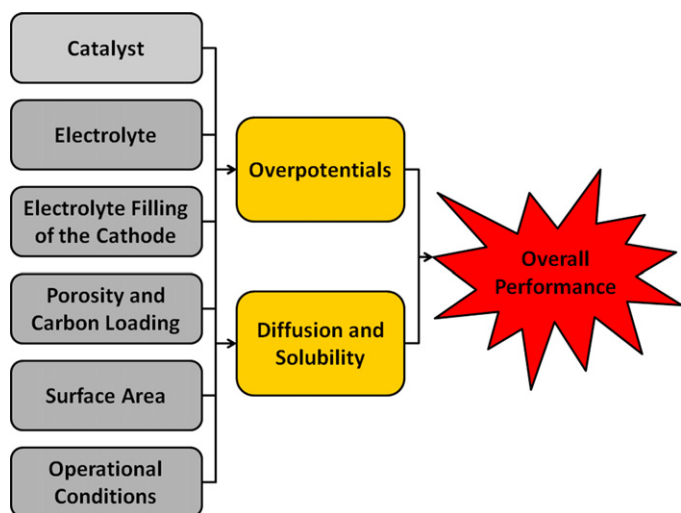


Fig. 4. Limiting factors that affect the overall performance of lithium–oxygen batteries.

trochemical reactions; hence further investigations are required to clarify the reactions that take place during discharge.

3. Limiting factors on performance

Lithium–oxygen batteries have extremely high energy density. However, the theoretical energy density of lithium–oxygen batteries cannot be fully achieved in practice. As with any energy storage medium including gasoline, which stores energy between carbon and hydrogen bonds, thermodynamics dictates that some energy will be lost to the surroundings. Therefore, all energy devices are never 100% efficient. With respect to the lithium–oxygen batteries, the efficiency is limited by the components that make up their overall structure. Each component has its own internal resistance, which is associated with the reduction in the electrochemical reaction kinetics and restricts the charge-transfer mechanism. Typically, a low internal resistance and efficient charge-transfer mechanism correspond to good kinetics which could lead to high performance of the energy storage cell. In a typical lithium–oxygen battery, 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 discharging, the oxygen molecules accept electrons from the cathode and combines with lithium ions to complete the half cell reaction. In order to complete the combination, each reactant has to overcome their respective boundaries which slow the reaction kinetics and affect the overall performance of the battery.

Fig. 4 shows a flow chart which indicates the most important limiting factors that affect the performance of the lithium–oxygen batteries. Primary factors are situated at the center of the flow chart and they indicate the important mechanisms that are associated with the overall performance of the lithium–oxygen batteries. Secondary factors are situated at the left-hand-side of the flow chart. These factors represent the physical components of typical lithium–oxygen batteries that need to be optimized in order to increase the reaction kinetics. The following discusses how the limiting factors affect the performance of lithium–oxygen batteries.

3.1. Overpotentials

The standard potential of the lithium–oxygen battery is determined by the active materials contained at the cathode and the anode. It can be calculated from the free-energy data of each half cell reaction or acquired experimentally. Alternatively, the stan-

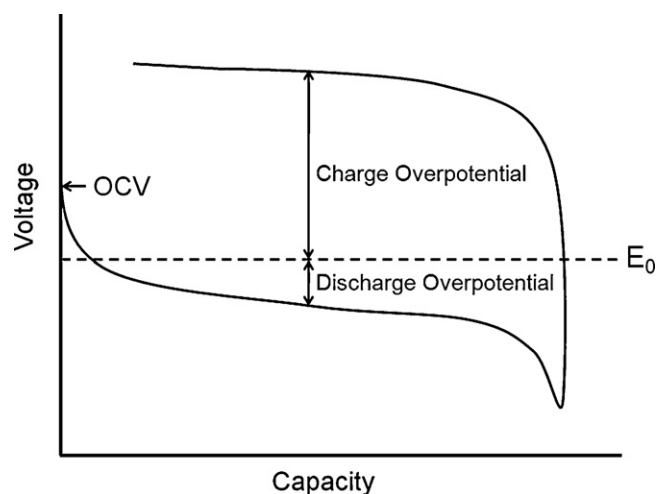


Fig. 5. Diagrammatic representation of a typical charge/discharge curve of the lithium–oxygen battery. The open circuit voltage (OCV), standard potential (E_0) and overpotentials are indicated in the chart.

standard potential of the lithium–oxygen battery can also be calculated using the Nernst equation stated in Eq. (4). Since the electrode reactions are suppressed by the limiting factors that affect the reaction kinetics, the charging and discharging potentials deviate from the standard potential and this can be explained in terms of overpotentials. The overpotentials are the extra energy required, over the energy stated by thermodynamics, to drive the reactions at a specific current density. The overpotentials are dependent on the reaction kinetics because a slow reaction with a small exchange current density leads to a large overpotential while a fast reaction with a large exchange current density corresponds to a smaller overpotential. Fig. 5 shows a typical charge/discharge curve and the overpotentials are positive on charging and negative on discharging. When a non-aqueous electrolyte is used, the sign conventions of the overpotentials are related to the insoluble reduction products. Firstly, the overpotential is positive on charging due to the extra energy required to reverse the reaction that occurs on discharging. Secondly, on discharging the lithium peroxide increases the internal resistance of the cell and reduces the reaction kinetics, which is indicated by the negative overpotential. Finally, when the reduction products have clogged the porous network of the cathode, the reduction reaction will terminate and the rate at which the reaction terminates determines whether a high or low capacity is achieved. The asymmetry between the charging potential and the discharging potential is due to the large potential difference that is required to dissociate the lithium peroxide on charging.

The use of a catalyst in the electrochemical reactions has the prospect of reducing the overpotentials closer to the standard potential value and reducing the asymmetry that is observed in the charge/discharge curve.

3.2. Catalysts

A reduction in asymmetry between the charge/discharge overpotentials improves the round trip efficiency of the lithium–oxygen battery as shown by Shao-Horn et al. [32] by incorporating a platinum–gold/carbon (PtAu/C) bifunctional catalyst into the carbon cathode. The employment of a catalyst can enhance the charge reaction by reducing the voltage required to dissociate the reduction products into lithium metal and oxygen. Fig. 6 as given by Bruce et al. [38] compares typical charge/discharge curves of lithium–oxygen batteries with and without manganese dioxide catalysts. In this particular case, the introduction of the catalyst improves the capacity from 850 to approximately 1000 mAh g⁻¹

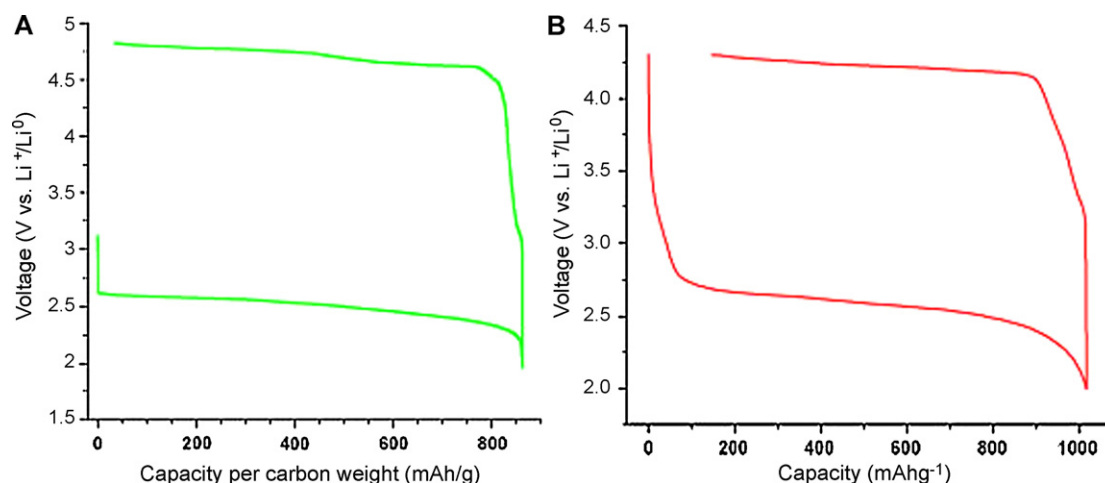


Fig. 6. Charge/discharge curves (A) without and (B) with electrolytic manganese dioxide catalyst (EMD). Both (A) and (B) are composed of the same carbon material Super S, and are charged/discharged at the same current density [36].

as well as lowering the charging potential by approximately 0.5 V. One could conclude from these results that the catalyst has facilitated the charge reaction by reducing the charge potential. It is also possible that in aiding the electrochemical reactions, the catalyst has assisted the discharge reaction kinetics resulting in an increase in the specific capacity of the battery. Since the electron moves towards the region of the highest potential, the large voltages required to charge the lithium–oxygen battery may also lead to oxidation of the electrolyte. This process degrades the electrolyte solution which decreases the charge/discharge performance and also decreases the life of the lithium–oxygen battery.

3.3. Diffusion and solubility

Diffusion is an important mechanism that is related to the reaction kinetics of the battery. Firstly, at the cathode, oxygen enters the porous electrode at the cathode–oxygen interface and diffuses through the network of pores to combine with lithium ions dissolved in the electrolyte and electrons from the carbon electrode. At the same time, it is also important for the lithium ions to diffuse from the anodic side of the battery to the cathode, which occurs in the form of an electrochemical potential gradient. The diffusion of oxygen is related to the porosity of the carbon cathode because a clear oxygen path is required to facilitate the transport of oxygen through the cathode.

The solubility of oxygen also affects the kinetics of the battery since it has to dissolve into the electrolyte at the cathode–oxygen interface before it can diffuse through the porous network of the cathode to combine with lithium ions and electrons. Oxygen in solution is less mobile than oxygen in the gaseous phase, which further decreases the reaction kinetics and affects the overall performance of the battery. However, it has been shown that increasing the partial pressure of the oxygen enhances the diffusivity and concentration of oxygen in the cathode, which corresponds to higher specific capacities [39,40].

Both diffusion and solubility are related to the porosity of the cathode as well as the type and structure of the electrolyte–cathode system that is utilized in the lithium–oxygen battery as discussed below.

3.4. Electrolytes

There are four types of electrolyte systems that could be used in lithium–oxygen batteries:

- aqueous electrolyte,
- non-aqueous electrolyte,
- mixed electrolyte system that incorporates an aqueous electrolyte at the cathode and a non-aqueous electrolyte at the anode, and
- solid state electrolyte that takes advantage of the properties of a lithium-ion conducting polymer or ceramic.

Due to the reactivity between lithium and water, it is not practical for the lithium–oxygen battery to use directly an aqueous electrolyte unless the anode can be protected from parasitic degradation [41]. One solution to this issue is to form an entirely solid state battery [42] or incorporate a mixed electrolyte system [43] to avoid the undesirable reactions between the lithium anode and an aqueous electrolyte. While there are studies with solid state lithium–oxygen batteries and mixed electrolyte systems, the largest proportion of the studies referenced in this article incorporate a non-aqueous electrolyte [3,20,29,33,44–49]. Fig. 7 shows the comparisons between the cathode reactions in aqueous and non-aqueous electrolytes [46].

Fig. 7A describes the gas–liquid–solid three-phase relationship that occurs at the cathode when an aqueous electrolyte is used. Oxygen, in the gaseous phase, combines with electrons from the catalyst/carbon structure. In comparison to reactions (2) and (3), the chemical reaction that describes the cathode reaction with an aqueous system is shown below for alkaline solutions [50].



The product, OH^- , is dissolved in the aqueous solution.

Fig. 7B shows the liquid–solid two-phase relationship that forms when a non-aqueous electrolyte is used. The oxygen is in the electrolyte solution and combines with electrons from the catalyst/carbon structure and lithium ions from the electrolyte to complete the reaction. The cathode reactions can be described using reactions (2) and (3). The major difference between aqueous and non-aqueous electrolytes is that the reduction products in the later system are not soluble in the electrolyte and they form a thin deposit on the surface of the carbon cathode, as shown in Fig. 7B. Therefore, the specific capacity of the lithium–oxygen battery is often normalized to the carbon cathode. The weight of carbon is used in the calculations for specific capacity since the reduction products on discharging fill the available pores for deposition.

The non-aqueous system is advantageous because it has been proved that the lithium peroxide reduction product can be dissociated into the original reagents of the oxygen reduction reaction.

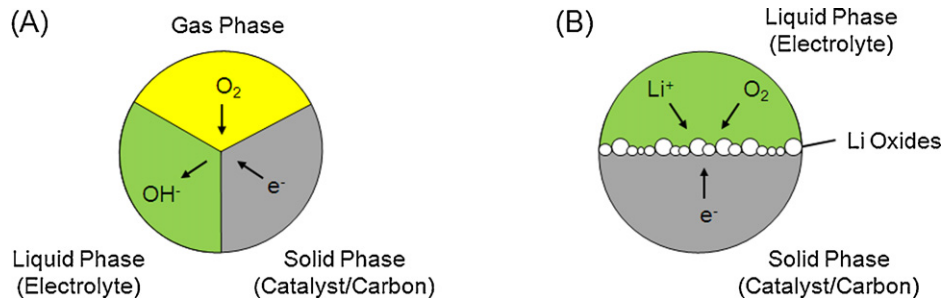


Fig. 7. Diagrams to show the three and two phase systems in (A) aqueous electrolyte and (B) non-aqueous electrolyte, respectively.

This is aptly named the oxygen evolution reaction (OER) and signifies the recharge ability of the lithium–oxygen battery using a non-aqueous electrolyte [51]. This has been verified by Bruce et al. using in situ differential electrochemical mass spectrometry (DEMS) to detect the evolution of oxygen during the charge process and powder X-ray diffraction to verify the composition of the cathode before and after charging [20].

Table 1 shows the variation in specific capacity with respect to a series of common non-aqueous electrolytes [44]. The data in Table 1 refer to the relationship between oxygen solubility, electrolyte composition and the specific capacity of the battery. The Bunsen solubility coefficient of oxygen for each electrolyte is given by α along with conductivity σ and electrolyte viscosity η . The table indicates that as the solubility (indicated by α) of oxygen in the electrolyte increases, the specific capacity of the battery also increases due to a larger concentration of oxygen available for the reduction reaction. The other parameters such as conductivity and viscosity have their own effect on the specific capacity of the battery; for example, low viscosity and high conductivity of the electrolyte ensure the access of lithium ion to the cathode. This indicates the importance of selecting the best overall electrolyte for the lithium–oxygen batteries.

3.5. Electrolyte filling of the cathode

It is also important to consider how the electrolyte filling of the cathode affects the overall performance of the lithium–oxygen battery [46]. Based on the electrolyte filling, the lithium–oxygen battery cathodes can be classified as flooded, dry, and wetted cathodes (Fig. 8). Firstly, in a flooded cathode, the oxygen has to dissolve into the electrolyte at the cathode–oxygen interface and as stated previously, oxygen in solution is less mobile than oxygen in the gaseous phase. Therefore, the kinetics of this system is slow due to the rate determining step of oxygen dissolving into the electrolyte. Since the reaction tends to take place where the oxygen concentration is the greatest, one would expect that as the battery discharges more reduction products will form at the oxygen side of the cathode. Contrary to this, if the cathode is insufficiently

filled with electrolyte (*i.e.*, dry cathode), oxygen can penetrate easier and deeper into the cathode. However, the lithium ions that are in solution will only be present at the cathode–electrolyte interface. Therefore, one would expect more reduction products to form at the cathode–electrolyte interface. Finally, a wetted cathode is an intermediate state of filling between the flooded cathode and dry cathode. A wetted cathode maintains the oxygen diffusion length through the cathode which increases the oxygen kinetics and creates a more uniform concentration of oxygen and lithium ions in the cathode. This means that the optimal area of the cathode is being used during the discharge reaction.

Fig. 9 as given by Kowaluk et al. [30] shows the steady-state variation of oxygen concentration with electrode depth in a cathode flooded with $1 \text{ mol dm}^{-3} \text{ LiPF}_6$ in PC:DME (1:1). The curve is formed from the diffusion equation:

$$C = \alpha \exp\left(\frac{-xR}{8640\alpha D}\right) \quad (10)$$

where D is the oxygen diffusion coefficient, α the Bunsen solubility coefficient, and C the concentration of oxygen at any distance x from the outer side of the cathode. Fig. 9 clearly shows a larger concentration of oxygen at the cathode–oxygen interface, *i.e.*, the outer side of the cathode. As mentioned previously, this is where the majority of the reduction products will deposit which limits the specific capacity of the lithium–oxygen battery. Fig. 9 also shows that the variation of oxygen concentration with electrode depth is a strong function of current density.

3.6. Structural importance of porosity and carbon content

The deposition of reduction products during discharge has a direct relationship with the porosity of the electrode. As stated previously, the reduction products are not soluble in a non-aqueous electrolyte, hence deposits are formed on the cathode surface and they often block the pores available for oxygen diffusion. This ultimately starves the discharge reaction, which in turn leads to a lower specific capacity. It must also be stated that lithium peroxide is a poor electric conductor therefore, as the discharge reaction progresses, the internal resistance increases as the transfer of the

Table 1

Composition of various non-aqueous electrolytes utilized in lithium–oxygen batteries. Respective values for Bunsen solubility coefficient α , conductivity σ and viscosity η are compared with specific capacity at different current densities [44].

Electrolyte	α ($\text{cm}^3 \text{ O}_2 \text{ cm}^{-3}$)	σ (mS cm^{-1})	η (cps)	Specific capacity (mA g^{-1}) at different current densities (mA cm^{-2})			
				0.05	0.1	0.2	0.3
1 M LiPF ₆ PC:EC (1:1)	0.0482	6.5	7.73	519	512	224	160
1 M LiPF ₆ PC	0.0516	5.5	8.06	648	380	203	129
1 M LiPF ₆ PC:DME (1:1)	0.0722	13.2	2.59	1409	999	628	452
1 M LiPF ₆ PC:DMC (1:1)	0.0729	9.4	3.50	817	652	524	363
1 M LiPF ₆ PC:DEC (1:1)	0.0787	6.7	4.78	1881	1308	591	338
1 M LiPF ₆ PC:DME (1:2)	0.0998	15.9	1.98	1599	1095	678	518
0.5 M LiPF ₆ PC:DME (1:2)	0.1218	12.2	1.19	1650	1257	809	676

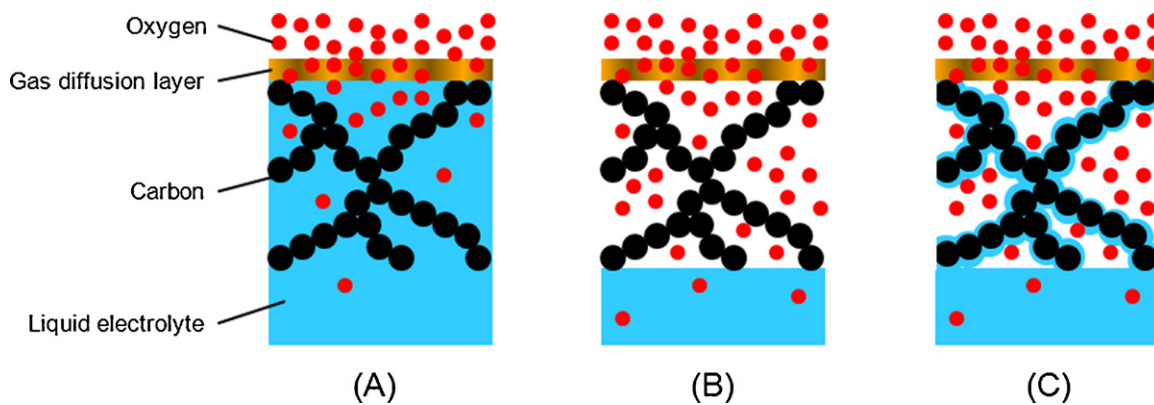


Fig. 8. Electrolyte filling in (A) flooded cathode, (B) dry cathode, and (C) wetted cathode.

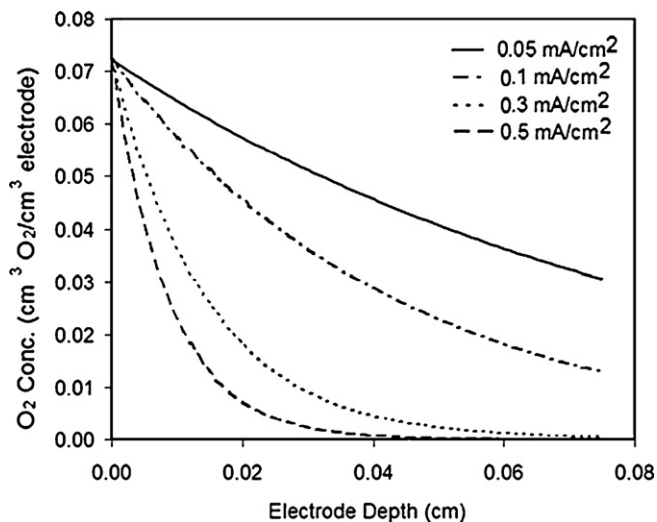


Fig. 9. Variation of oxygen concentration as a function of cathode depth. The effect of increasing current density is also shown [30].

electron from the carbon surface is prohibited by the lithium peroxide deposits.

Fig. 10 as given by Zheng et al. [18] is from a theoretical study that modeled the effect of increasing porosity on the specific capacity of a typical lithium–oxygen battery. It is seen that as the porosity increases, the specific capacity of the battery increases. However, Fig. 10 does not indicate the ideal pore size necessary to improve the kinetics and capacity of the battery. Another work by Yang et al.

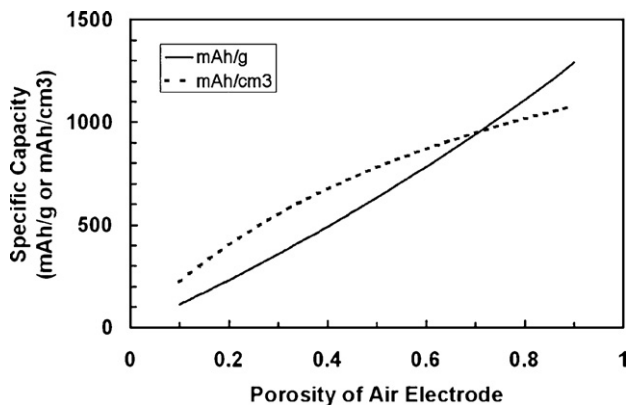


Fig. 10. Effect of increasing porosity on the specific capacity of the lithium–oxygen cell using a non-aqueous electrolyte [18].

[40] suggests that pores with diameters less than 10 nm are insufficient to sustain oxygen diffusion and accommodate the reduction products during discharge.

A further important factor to consider is the relationship that forms between the porosity and the carbon content of the cathode. As the carbon content increases, the porosity of the cathode decreases and leads to a decrease in oxygen diffusion length, which in return reduces the reaction kinetics and results in a lower specific capacity [52]. However, it is important to optimize the carbon content of the cathode to retain good electronic conductivity while maintaining the oxygen diffusion length and volume available for the deposition of the reduction products.

3.7. The relationship between surface area and porosity

The surface area of the carbon cathode is important for the performance of lithium–oxygen batteries during the electrochemical reaction. Typically, a larger surface area provides more surface to uniformly disperse catalyst particles and more active sites to aid the electrochemical reactions.

However, it has been shown in a previous study that larger surface area carbons do not always correspond to larger specific capacities [53]. This observable fact is summarized in Table 2 as given by Yang et al. [40], which shows a variety of carbon materials that can be used as the cathode material. The table shows that the carbon material with the largest surface area, activated carbon (AC), actually has one of the smallest overall capacities. This reinforces the importance of porosity and in particular, the size of the pore diameter. Super P, for example, has one of the smallest surface areas but it exhibits the largest pore diameter. A large pore diameter corresponds to a larger volume available for good oxygen diffusion and the necessary space to accommodate the deposition of reduction products during discharge. The table shows that the micro-pores possessed by the remaining carbon materials have an adverse effect on the battery performance because they are not sufficient to accommodate oxygen diffusion or the reduction products as indicated by the lower specific capacities. While the ideal lithium–oxygen battery should have a good meso-pore network, a large surface area is still necessary to disperse more catalyst particles and to increase the current density on discharge. Since the cathode reactions take place on the surface of the carbon cathode, a larger surface area corresponds to more area for reactions to take place leading to higher electrochemical performance.

3.8. Operational conditions

It is important to control the operational conditions of the lithium–oxygen batteries during discharge. The performance is

Table 2

Examples of carbon materials that have been used in cathodes. Respective surface areas and pore diameters are stated along with the different capacities achieved with each carbon material at a current density of 0.1 mA cm^{-2} [40].

Samples	Super P	XC-72	AC	CNT	Graphite
Specific capacity (mAh g^{-1})	1736	762	414	583	560
Surface area ($\text{m}^2 \text{g}^{-1}$)	62	250	2100	40	6
Pore diameter (nm)	50	2	2	10	–

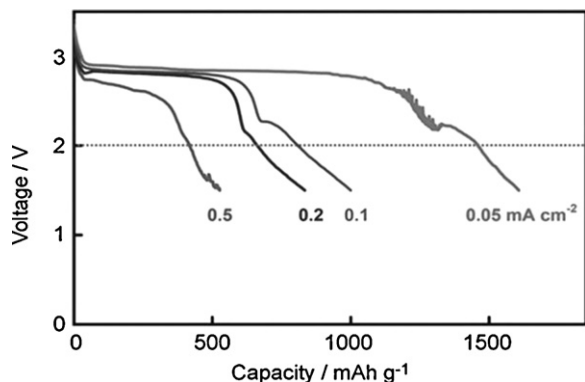


Fig. 11. Variation of specific capacity with increase in current density [46].

sensitive to the magnitude of the current density and the depth of discharge, which have significant effects on the overall specific capacity and capacity retention. It has been shown by experiments that maintaining a low current density (typically $0.05\text{--}0.1 \text{ mA cm}^{-2}$) improve the overall specific capacity of the lithium–oxygen battery as shown in Fig. 11 [46]. However, in a practical battery, high operational current density is desired to achieve high power. Therefore, one key aim in the development of high-performance lithium–oxygen batteries is to maximize the electrode reaction kinetics so that higher current densities can be withdrawn from the lithium–oxygen battery while maintaining a large and stable specific capacity.

Fig. 12 shows the variation of cut-off voltage and specific capacity with cycle number for three different charge/discharge scenarios [54]. The first scenario as indicated by the curve (a) is a deep discharge state where the lithium–oxygen battery is allowed to completely discharge after charging for each successive cycle. There is a dramatic decrease in specific capacity after the 3rd cycle which is sustained throughout successive cycles. The second sce-

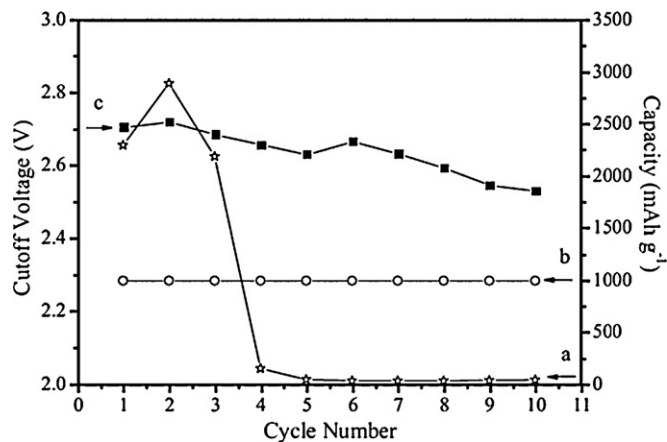


Fig. 12. Cycle performance of the lithium–oxygen battery with (a) deep discharge, (b) restricting capacity to 1000 mAh g^{-1} with a current density of 0.1 mA cm^{-2} , and (c) limited discharge depth with higher voltage cut-offs [54].

nario, as indicated by curve (b), restricts the discharge capacity to 1000 mAh g^{-1} at a current density of 0.1 mA cm^{-2} . It can be inferred from the curve that the discharge capacity and cut-off voltage are sustained up to the 10th cycle. The last scenario is intermediate between the first two and represents a limited discharge depth which corresponds to a gradual decrease in cut-off voltage and discharge capacity. As stated previously, during discharge the reduction products deposit on the surface of the carbon cathode which increases the internal resistance of the cathode and impedes the cell kinetics. It is possible that after a large depth-of-discharge the cathode does not fully recover during charging, *i.e.*, the charge voltage is not sufficient to decompose the lithium peroxide leading to a dramatic decrease in specific capacity for successive cycles. On the other hand, by controlling the depth-of-discharge it is possible to recover the porosity during charging which maintains the oxygen diffusion length and the specific capacity over successive cycles. Fig. 12 demonstrates that depth-of-discharge is an important factor that affects the specific capacity of lithium–oxygen batteries and is a parameter that needs to be controlled in order to achieve high overall performance.

4. Commercial initiatives

The number of applications that require high performance energy storage technologies is constantly growing as the demand for better performing consumer products and the need for greener energy increase. Evolving applications include the consumer products industry, electric vehicles (EVs), hybrid electric vehicles (HEVs), and the future storage of renewable energy. However, each application has its own specific requirements. Batteries designed for the consumer products industry need to be low cost, easily available, light weight, and exhibit high gravimetric energy and power densities. Battery requirements for EVs and HEVs include high gravimetric and volumetric energy density for excellent driving range, high power density for good acceleration, large cycle life, and low cost [55]. Due to its extremely high energy density, with significant research and development, the lithium–oxygen battery is a highly probable candidate as the future energy technology for the above applications.

As mentioned previously, one of the significant drawbacks of the lithium–oxygen batteries is that lithium reacts violently with trace amounts of water limiting their potential application in normal atmospheric conditions. Polyplus, a California based company, has developed and is testing a lithium–oxygen battery designed to overcome this issue. The battery incorporates a protective ceramic electrolyte at the anode made of LISICON [56]. Moreover, the anode is sealed at the edges with an aluminum–polymer laminate. Other related initiatives include IBM's Battery 500 project with the objective of powering a car to 500 miles in one single charge. Recently, IBM announced plans to develop a commercially viable lithium–air battery [57]. Excellatron Solid State LLC, is another US based company developing lithium–air batteries for applications such as mobile phones, aircrafts, and the space industry. The National Institute of Advanced Industrial Science and Technology (AIST) of Japan is also a significant developer of lithium–oxygen batteries and are aiming the technology at consumer products and the military.

5. Conclusion—the ideal lithium–air battery

In present studies it is important to control the current density and it has been shown by the experiments that maintaining a low current density improve the overall specific capacity of the lithium–oxygen battery as well as the capacity retention over a large number of cycles. However, this is neither practical nor beneficial for commercial applications. For the lithium–oxygen battery to be a commercially viable product, with applications in portable devices or electric vehicles, it must be able to cope with varying current densities and depths of discharge. This is something that must be addressed and the ultimate goal is to improve the performance of lithium–oxygen batteries by reducing the limiting factors stated in Section 4 so that greater current densities can be withdrawn during discharge.

Most of the discussions in this article have been based on lithium–oxygen batteries. These batteries were prepared in an inert atmosphere and then electrochemical experiments were conducted in a pure oxygen atmosphere after the batteries have been sealed in an impermeable container. However, in practical applications, the end product will have to be able to cope with ambient atmospheric conditions. Lithium–air battery research opens up more challenges; for example, the development of hydrophobic electrolytes and separators to protect the lithium metal anode from reacting with water. The limiting factors discussed in Section 4 indicate the important areas for future research and development in order to produce a commercially viable lithium–air battery. Possible areas for future research include the development of:

- anodes that are stable or protected from moisture;
- cathode structures that have improved and optimized meso-porosity for facilitating high oxygen diffusivity while maintaining high electrical conductivity;
- electrolytes that have high oxygen solubility and diffusivity along with good lithium-ion conductivity. The development of hydrophobic electrolytes is also important for the development of the lithium–air battery; and
- catalysts that facilitate the oxygen evolution reaction and reduce the over potentials on charging and discharging.

Although there are still many problems to overcome with the research and development of lithium–oxygen batteries it is an exciting and challenging field that encompasses the knowledge and expertise of researchers from many different disciplines. The multidisciplinary nature of research in this field has the potential to bridge the knowledge gaps in current research projects which will enhance the development of this technology into a commercially available product.

Acknowledgement

The authors thank Professor Behnam Pourdeyhimi in the College of Textiles at North Carolina State University for the financial support.

References

- [1] M. Mirzaei, P.J. Hall, *J. Power Sources* 195 (2010) 6817–6824.
- [2] E.L. Littauer, K.C. Tsai, *J. Electrochem. Soc.* 123 (1976) 771–776.
- [3] K.M. Abraham, Z. Jiang, *J. Electrochem. Soc.* 143 (1996) 1–5.
- [4] D. Linden, T.B. Reddy, *Handbook of Batteries*, 3rd edition, McGraw-Hill, 2002.
- [5] J. Hassoun, A. Farnicola, M.A. Navarra, S. Panero, B. Scrosati, *J. Power Sources* 195 (2010) 574–579.
- [6] M.G. Kim, J. Cho, *Adv. Funct. Mater.* 19 (2009) 1497–1514.
- [7] Y.G. Guo, J.S. Hu, L.J. Wan, *Adv. Mater.* 20 (2008) 4384–4388.
- [8] H. Cheng, K. Scott, *J. Power Sources* 195 (2010) 1370–1374.
- [9] M. Wakihara, *Mater. Sci. Eng. R: Rep.* 33 (2001) 109–134.
- [10] L. Ji, X. Zhang, *Electrochem. Commun.* 11 (2009) 684–687.
- [11] L. Ji, X. Zhang, *Electrochem. Commun.* 11 (2009) 795–798.
- [12] J.J. Martin, V. Neburchilov, H. Wang, W. Qu, *Electrical Power & Energy Conference (EPEC)*, 2009 IEEE, 2009, pp. 1–6.
- [13] B.T. Hang, S. Yoon, S. Okada, J. Yamaki, *J. Power Sources* 168 (2007) 522–532.
- [14] S. Yang, H. Knickle, *J. Power Sources* 112 (2002) 162–173.
- [15] F.R. McLarnon, E.J. Cairns, *J. Electrochem. Soc.* 138 (1991) 645–664.
- [16] P. Arora, Z.M. Zhang, *Chem. Rev.* 104 (2004) 4419–4462.
- [17] A.K. Thapa, K. Saimen, T. Ishihara, *Electrochem. Solid State Lett.* 13 (2010) A165–A167.
- [18] J.P. Zheng, P. Andrei, M. Hendrickson, E.J. Plichta, *J. Electrochem. Soc.* 158 (2011) A43–A46.
- [19] X.H. Yang, Y.Y. Xia, *J. Solid State Electrochem.* 14 (2010) 109–114.
- [20] Ogasawara, A. Debart, M. Holzappel, P. Novak, P.G. Bruce, *J. Am. Chem. Soc.* 128 (2006) 1390–1393.
- [21] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652–657.
- [22] M. Mirzaei, P.J. Hall, *Electrochim. Acta* 54 (2009) 7444–7451.
- [23] M. Clairol, *Physics of High Energy Densities*, Academic Press, Amsterdam, 1961.
- [24] X. Zhang, *J. Electrochem. Soc.* 154 (2007) B322–B326.
- [25] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, *Appl. Catal. B: Environ.* 56 (2005) 9–35.
- [26] E.J. Cairns, P. Albertus, *Annu. Rev. Chem. Biomol. Eng.* 1 (1) (2010) 299–320.
- [27] H.D. Abruna, J.B. Goodenough, M. Buchanan, *Abstr. Pap. Am. Chem. Soc.* 234 (2007), 28-ANL.
- [28] F. Mizuno, *Fundamental Study on Rechargeable Reaction of Lithium–Oxygen Battery*, Symposium on Energy Storage Beyond Lithium Ion: Materials Perspectives, Oak Ridge National Laboratory, Oak Ridge, TN, 2010, October.
- [29] W. Xu, J. Xiao, J. Zhang, D.Y. Wang, J.G. Zhang, *J. Electrochem. Soc.* 156 (2009) A773–A779.
- [30] I. Kowaluk, J. Read, M. Salomon, *Pure Appl. Chem.* 79 (2007) 851–860.
- [31] J. Kumar, B. Kumar, *J. Power Sources* 194 (2009) 1113–1119.
- [32] Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, Y. Shao-Horn, *Electrochem. Solid State Lett.* 13 (2010) A69–A72.
- [33] A. Debart, A.J. Paterson, J. Bao, P.G. Bruce, *Angew. Chem.—Int. Ed.* 47 (2008) 4521–4524.
- [34] M. Morcrette, Y. Chabre, G. Vaughan, G. Amatucci, J. Leriche, S. Patoux, C. Masquelier, J. Tarascon, *Electrochim. Acta* 47 (2002) 3137–3149.
- [35] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, M.A. Hendrickson, *J. Phys. Chem. C* 113 (2009) 20127–20134.
- [36] J.S. Hummelshøj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K.S. Thygesen, A.C. Luntz, K.W. Jacobsen, J.K. Nørskov, *J. Chem. Phys.* 132 (2010) 071101.
- [37] F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoiishi, H. Iba, *Electrochemistry* 78 (2010) 403–405.
- [38] A. Debart, J. Bao, G. Armstrong, P.G. Bruce, *J. Power Sources* 174 (2007) 1177–1182.
- [39] S.S. Sandhu, J.P. Fellner, G.W. Brutchen, *J. Power Sources* 164 (2007) 365–371.
- [40] X.H. Yang, P. He, Y.Y. Xia, *Electrochem. Commun.* 11 (2009) 1127–1130.
- [41] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, *J. Electrochem. Soc.* 157 (2010) A214–A218.
- [42] B. Kumar, J. Kumar, R. Leese, J.P. Fellner, S.J. Rodrigues, K.M. Abraham, *J. Electrochem. Soc.* 157 (2010) A50–A54.
- [43] Y. Wang, H. Zhou, *J. Power Sources* 195 (2010) 358–361.
- [44] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, *J. Electrochem. Soc.* 150 (2003) A1351–A1356.
- [45] W. Xu, J. Xiao, D.Y. Wang, J. Zhang, J.G. Zhang, *J. Electrochem. Soc.* 157 (2010) A219–A224.
- [46] S.S. Zhang, D. Foster, J. Read, *J. Power Sources* 195 (2010) 1235–1240.
- [47] J. Read, *J. Electrochem. Soc.* 153 (2006) A96–A100.
- [48] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, M.A. Hendrickson, *J. Phys. Chem. C* 114 (2010) 9178–9186.
- [49] J. Read, *J. Electrochem. Soc.* 149 (2002) A1190–A1195.
- [50] S.S. Sandhu, G.W. Brutchen, J.P. Fellner, *J. Power Sources* 170 (2007) 196–209.
- [51] Y.C. Lu, Z.C. Xu, H.A. Gasteiger, S. Chen, K. Hamad-Schifferli, Y. Shao-Horn, *J. Am. Chem. Soc.* 132 (2010) 12170–12171.
- [52] S.D. Beattie, D.M. Manolescu, S.L. Blair, *J. Electrochem. Soc.* 156 (2009) A44–A47.
- [53] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, *J. Power Sources* 146 (2005) 766–769.
- [54] D. Zhang, Z. Fu, Z. Wei, T. Huang, A. Yu., *J. Electrochem. Soc.* 157 (2010) A362–A365.
- [55] P. Symons, P. Butler, *Introduction to advanced batteries for emerging applications*, Sandia National Laboratory Report, SAND2001-2022P, April 2010.
- [56] S.J. Visco, B.D. Katz, Y.S. Nimon, L.D. Dejonghe, *US Patent* 7,282,295, October 2007.
- [57] Which comes first: the smart grid or the electric car? Available at http://www.ibm.com/smarterplanet/us/en/smart_grid/article/electric_cars.html?ca=v.electricvehicles (01.03.2011, 4:08 pm).