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Title: The Lithium/air battery: still an emerging system or a practical reality?

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Lithium/air is indeed a fascinating energy storage system. The effective exploitation of air as a battery electrode has been the long-time dream of the battery community. Air is in principle a no-cost material gifted by a very high specific capacity value. In the particular case of the lithium/air system, energy levels approaching that of gasoline have been postulated. It is then not surprising that in the course of the last decade great attention has been devoted to this battery by various top academic and industrial laboratories worldwide. This intense investigation, however, has soon highlighted a series of issues that prevent a rapid development of the Li/air electrochemical system. Although several breakthroughs have been achieved recently, the question on whether this battery will have an effective economic and societal impact remains. In this review, a critical evaluation of the progress achieved so far is

made, together with an attempt to propose future R&D trends. A forecast on whether Li/air may have a role in the next years' battery technology is also postulated.

1. Introduction

The car industry is currently facing a crisis in the developed world, due to the rising costs associated with car ownership and a growing environmental awareness among the population. New shared mobility concepts like car sharing and car pooling are being developed and offered to people living in densely populated urban areas to counteract the rising costs of oil and gas. At the same time, the penetration of renewable energy sources has opened up the possibility to create a CO_2-neutral mobility system, where electric vehicles are powered by wind, hydro and solar energy.

Broad financial efforts are being made at a governmental and industrial level to fund research into new areas of energy storage. The U.S. Department of Energy has allocated $20M to energy storage research in 2012 and $15M the following year, while the German government has committed itself to €200M between 2011 and 2018;[1] similar schemes are also being promoted in Japan by NEDO. The EU-backed "Horizon 2020" program aims at funding research into energy storage technologies, a field where the European Union lags behind the U.S. and East Asia.[2]

The lithium-ion technology has established itself as a reliable energy storage chemistry over the past 20 years, first being used in camcorders, then mobile phones, laptops and more recently electric cars. However, as the size of the battery pack increases, so does the belief that its cost per kWh and its energy density are not suitable for practical vehicle applications. The Tesla Model S, which sports a 400 km driving range, does so with a whopping 85 kWh battery pack that alone has up to twice the price of a standard economy car. With a current cost higher than 400 $ kWh^{-1}, electric cars have so far only entered a niche, high-end market where users are willing to pay a premium. Resizing the battery pack, and so the total cost of

an electric car, results in a limited driving range (typically 100-150 km) that automatically restricts the use for long-haul journeys and triggers the so-called "range anxiety" feeling. For these reasons, the need to develop energy storage technologies that enable at least a 500 km driving range, while retaining the same battery pack volume at an affordable price, is of primary interest for governments and car manufacturers.

1.1 A brief history of lithium/air batteries

Over the years, the scientific community has focused its interest on advanced lithium-ion and fuel cells with only incremental improvements being made. The lithium-ion technology in particular is predicted to reach an asymptotic limit in specific energy of 250 Wh kg^{-1},[3] due to its intrinsic features. This falls quite short of the 1750 Wh kg^{-1} tank-to-wheel value that is currently achieved with gasoline in the U.S.,[4] therefore it is imperative to look elsewhere for a solution. Primary metal/air batteries were at the center of attention already a few decades ago, with the first review by Blurton and Sammells dating back to 1979.[5] At the time, the authors did not see practical vehicle applications for the Li/air cell chemistry, as opposed to the then more promising Zn/air batteries. They did however recognize the high power density that could be achieved with such a system, thanks to the 3 V open circuit voltage, as well as the very high theoretical gravimetric energy density that could be reached with Li_2O as discharge product (at the time, the optimistic value of 11148 Wh kg^{-1} was provided). The interest in the subject was renewed in the mid-90s, when Abraham *et al.* reported rechargeability for a Li/O_2 system where a lithium metal anode, a carbonate-based PVdF gel electrolyte and a carbon substrate for the O_2 cathode were employed.[6] The two reactions postulated to take place were: [7]

$$2\,Li + O_2 \rightleftarrows Li_2O_2 \quad (2.96\,V) \quad (1)$$
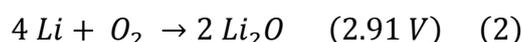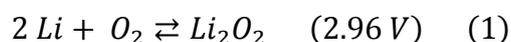
$$4\,Li + O_2 \rightarrow 2\,Li_2O \quad (2.91\,V) \quad (2)$$

Qualitative analyses led to the identification of Li_2O_2 as the main product present in the discharged electrodes. Remarkable specific capacities around 1600 mAh g^{-1}_{carbon} were obtained and a first observation was made on the importance of the air electrode's surface area. Interest in the subject grew steadily with the use of liquid organic electrolytes [8,9] among which ether-based electrolytes were proposed as a solution to the limited O_2 solubility and diffusivity by Read *et al.*;[10] in fact, these two parameters had been found to be a bottleneck for the O_2 electrode in most electrolytes [11,12]. In 2006, Bruce *and coll.* [13] demonstrated the reversibility of Li_2O_2 formation, by making use of a liquid organic electrolyte combined with MnO_2 as catalyst. Since then, the Li/air technology has quickly gained a prominent position among the electrochemical energy storage technologies that are deemed to provide a solution to the low energy density conundrum [14,15]. Many researchers are now focusing on the development of advanced catalysts and cathode substrates to improve efficiency and cycle life using mostly organic electrolytes. Materials used as cathode supports comprise porous carbon,[16–19] graphene,[20] carbon nanotubes (CNT) or carbon nanofibers (CNF)[21,22] with catalysts such as metal oxides (MnO_2,[23–26] Co_3O_4[27,28]), noble metals,[7,29–31] and others.[32,33] At an industrial level, in 2009 IBM launched the "Battery 500" project, which had the ambitious aim of developing a Li/air battery that could ensure a 500 mile driving range,[34] and it was thought that soon enough this technology would make it to practical applications. However, initial excitement soon dwindled down, as scientists realized that the subject was more complex than initially prospected.

2. An academic perspective

Despite having been in the making for the past 40 years, with a steep acceleration in R&D efforts in the last decade, Li/air batteries have to be considered as still in their infancy. Several optimistic claims have already been downsized, while the technology roadmap has been

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extended to a 20 years window because of some yet unresolved challenges, summarized in **Figure 1**. One aspect not to be overlooked is rate capability. So far, only limited current densities have been demonstrated, generally one or two orders of magnitude lower than those exhibited in commercial Li-ion batteries. If higher current densities cannot be achieved, alternative solutions must be found to meet the high flow of O_2 needed for transport applications.

Moreover, it has to be stated that the term "Li/air batteries" is often optimistically adopted to describe devices that in fact are Li/O_2 cells, since oxygen (and not dry air) is supplied to the system in most lithium/air battery studies. The major constituents of ambient air are N_2 (78%) and O_2 (21%) with other gasses making up the rest. CO_2 and moisture in the ambient air can significantly influence the electrochemical performance of a lithium/air cell with a negative impact over cyclability, even in small amounts.[35–37] For instance, lithium metal can react with H_2O traces in the air and generate LiOH and H_2. Aurbach *et al.*[35,36] reported that CO_2 also reacts with the Li^+ ions forming Li_2CO_3 on the electrode surface, while Takechi *et al.*[37] demonstrated that Li_2CO_3 could form from the reaction between CO_2 and Li_2O_2. The higher energy density that can be achieved, if oxygen were harvested from air at a low energy cost, provides with a significant incentive to develop ways to filter out unwanted components, which is why O_2-selective membranes are currently under intense development.
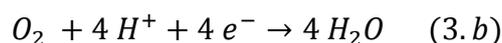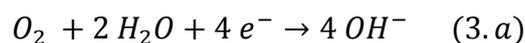
2.1 Electrolytes

So far, the focus of researchers in the academia has mostly revolved around aprotic Li/air cells, where the main discharge product is Li_2O_2. However, the Li/O_2 battery family also comprises "solid-state", "aqueous" (sometimes referred to as *hybrid*) and "dual electrolyte" cells,[4,38] whose main features are portrayed in **Figure 2**.

2.1.1   Solid-state electrolytes

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The all-solid-state lithium/air battery was developed by Kumar *et al.*.[39–42] The electrolyte used in this case was based on lithium aluminum germanium phosphate (LAGP) mixed with polyethylene oxide (PEO). The carbon electrode was made of N-doped Ketjen black and calgon activated carbon.[41] This battery exhibited a high discharge potential and a low charge potential corresponding to 2.8 V and 3.6 V respectively, at an operating temperature of 75 °C. Zhou *et al.*[43] also investigated the solid-state lithium/air battery using a Li/CE (ceramic electrolyte)/LAGP@CNT (carbon nanotube) configuration. Recently, Lu *et al.* [44,45] developed an all solid state lithium/air battery using a lithium phosphorous oxynitride (LiPON) electrolyte with a lithiated $Li_4Ti_5O_{12}$ (LLTO) anode and a vanadium oxide (V_2O_5) cathode substrate. This study confirmed that Li_2O_2 was the main discharge product.

### 2.1.2 Aqueous electrolytes

Aqueous lithium/air batteries have many advantages compared to non-aqueous systems, namely a high discharge potential, a high round-trip efficiency, the absence of solid discharge products that cause electrode pore clogging, and the absence of corrosion of the lithium metal by air moisture. Furthermore, there is no need to use expensive Li salts in the catholyte, as dissociation, solubility and conductivity are higher than the non-aqueous counterpart. Another advantage is that there are known non-noble catalysts, which allow a four-electron transfer at the cathode, leading to:

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \quad (3.a)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 4\,H_2O \quad (3.b)$$

Depending on the pH, a potential of ca. 3.4-4.3 V vs Li metal can be reached.[11] The cathode operates in an aqueous catholyte, separated from the Li anode by additional inorganic and/or organic electrolyte layers. This category was first investigated in the 70's at Lockheed.[46,47] In

this system, a lithium metal anode is immersed into a concentrated LiOH aqueous solution and leads, during discharge, to the formation of LiOH, which is partially soluble in the electrolyte:[48–51]

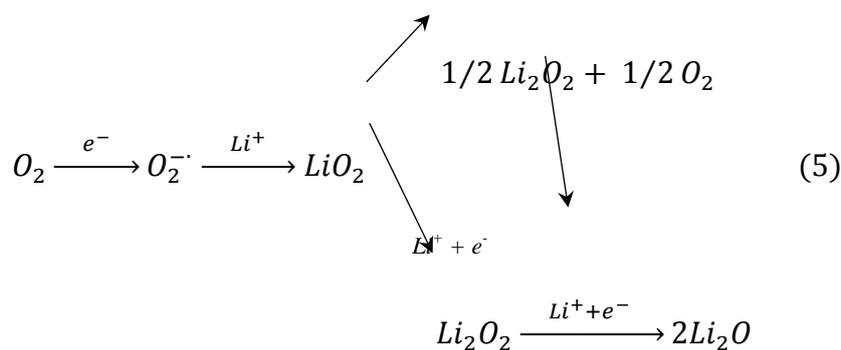$$2\,Li + \frac{1}{2}O_2 + H_2O \; \rightleftarrows 2\,LiOH \quad (4)$$
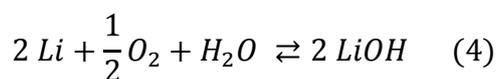
LiOH then precipitates with crystalline water when its concentration exceeds 5.2 M, therefore aqueous Li/air cells face an intrinsic limitation of 477 Wh kg^{-1} in theoretical specific energy,[52] although they might be able to compete with their non-aqueous counterpart in volumetric terms. The solubility of LiOH can be increased if an acidic solution is used,[53–55] which also allows a 3.4 V discharge voltage and ultimately a specific energy of 700 Wh kg^{-1}. Alternatively, the specific energy can be increased by storing and/or precipitating the lithium hydroxide in a reservoir as the cell discharge progresses.[56] Of course, another factor that has to be taken into account when designing such cells is the reactivity of lithium in an aqueous environment. In the first attempts made to passivate the Li electrode, the system suffered from corrosion as well as H$_2$ generation and was soon after abandoned. The development of the aqueous system became possible after Visco et al. developed the lithium conducting solid electrolyte in 2004. [57–60] This electrolyte consists of a lithium-ion conductive interlayer - either lithium nitride (Li$_3$N) or LiPON - between the lithium-conducting electrolyte and the lithium metal anode, and prevents the reaction of lithium metal with water to form LiOH and hydrogen gas. However, the conductivity of this protective solid electrolyte decreases significantly during operation due to the increase of pH of the electrolyte from the dissolution of LiOH. Imanishi *et al.* addressed this issue by effectively lowering the pH of the aqueous electrolyte, thereby stabilizing the glass-ceramic protective electrolyte (LATP) they used.[61] The addition of LiCl in a saturated aqueous solution of 5.12 M LiOH decreased the pH value

to 8.14 and the stability of LATP in aqueous solution was enhanced by a high concentration of Li$^+$ ions. Although reducing the alkaline concentration in the aqueous solution has minimized reactivity with LATP, this solid electrolyte still suffers from degradation in the presence of lithium metal anode. For this reason, PEO-based polymer electrolytes have also been employed [62,63] as the first electrolyte in contact with Li metal, whose flexibility also avoids the loss of contact caused by the volume changes that occur during cycling. To further enhance the performance of lithium/air, Visco *et al.* [57] and Wang *et al.*[64] investigated a dual electrolyte configuration. Wang *et al.*[64] used an ethylene carbonate/dimethyl carbonate electrolyte to separate Li metal and lithium-conducting electrolyte. However, if much higher current densities were reached at the cathode, the system as a whole would present some obvious Li$^+$ mass transport limitations due to the three electrolyte layers used. Although this system has some benefits, its fabrication process is complicated and challenging.

2.1.3 Non-aqueous electrolytes

In aprotic electrolytes, the mechanism of the oxygen reduction process leads to lithium peroxide via a sequence of intermediate steps that include the formation of the oxygen radical $O_2^{-\bullet}$[65]:

$$O_2 \xrightarrow{e^-} O_2^{-\cdot} \xrightarrow{Li^+} LiO_2$$

$$1/2\,Li_2O_2 + 1/2\,O_2$$

$$Li^+ + e^-$$

$$Li_2O_2 \xrightarrow{Li^+ + e^-} 2Li_2O$$

$$(5)$$

This species is highly reactive and, although short-lived, it is active long enough to decompose most of the common electrolytes, such as the organic carbonate solutions commonly used in conventional lithium-ion batteries. These esters, having a very strong electrophile carbonyl group are in fact easily attacked by the nucleophile peroxide and

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superoxide species resulting in the opening of the heterocycle and the subsequent formation of linear carbonates. Indeed, early attempts to operate lithium/air batteries using carbonate electrolytes led to cell failure after a few cycles, due to the overall process being dominated by electrolyte decomposition.[23,66] For this reason, common organic carbonate electrolytes have been now totally abandoned. Consequently, the choice of a suitable, stable electrolyte has been a major challenge in Li/air battery technology. Many solvent systems, whose results are summarized in **Table 1**, have been investigated to reach this goal. Among them, a popular choice is presently lithium triflate ($LiCF_3SO_3$), dissolved into tetraethylene glycol dimethyl ether (TEGDME), due to the poor electrophilic characteristics of glymes, which assure resistance to nucleophilic attacks while the persulphonate salt contributes to the chemical stability.

2.1.4 Carbonate-based electrolytes

The large polarization caused by the oxygen evolution reaction (OER)[19,22–24,26,27,30] and the modest cycling performance of lithium/air batteries have so far made it difficult to reach round-trip efficiencies comparable to lithium-ion batteries. Mizuno et al.[67] reported that the discharge product of lithium/air using organic electrolytes was mainly Li_2CO_3 and lithium alkylcarbonate (RO━(C=O)━OLi) rather than Li_2O_2. These products were mostly the result of the decomposition of the propylene carbonate-based electrolyte. Following this study, several researchers were able to determine the mechanism by which carbonate-based electrolyte decomposition occurs.[66,68–72] For example, Zhang et al. carried out density functional theory (DFT) calculation and determined that the ring opening of PC in the presence of solvated species such as O_2^-, LiO_2, LiO_2^-, and Li_2O_2 has no energy barriers (**Figure 3**). As a result Li_2CO_3 and lithium alkylcarbonate can be easily formed. These materials were confirmed by Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS).[72] Bruce et

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al.[66] also identified the discharge products of the lithium/air cell using a PC electrolyte to be Li_2CO_3, $C_3H_6(OCO_2Li)_2$, CH_3CO_2Li, HCO_2Li, CO_2 and H_2O by using FT-IR, nuclear magnetic resonance (NMR) and surface-enhanced Raman spectroscopy (SERS), together with differential electrochemical mass spectrometry (DEMS). Zhang and co-workers[71] used X-ray diffraction (XRD) and DEMS to confirm the formation of Li_2CO_3 during the discharge process and the evolution of CO_2 during charging.

2.1.5   Ether-based electrolytes

After the confirmation of the decomposition of carbonate-based electrolytes, research efforts were directed to find other stable electrolytes for non-aqueous lithium/air batteries. Among the organic solvents investigated, ether-based electrolytes were found to be the best candidates. In 2006, Read[10] used an ether-based electrolyte in a non-aqueous lithium/air battery for the first time, while Bryantsev *et al.*[73] used density functional theory to calculate the stability of a range of organic solvents against an attack by the $O_2^{-\bullet}$ radical. The calculation showed ether-based electrolytes to be more suitable than carbonate-based ones. Nevertheless, a number of scientists reported mixed results with ether-based electrolytes, with some showing enhanced electrochemical and cycling performance (100 cycles)[72,74–78] and others showing decomposition of the electrolyte. McCloskey *et al.*[79] reported the decomposition of a dimethoxy ethane (DME) electrolyte in a lithium/air cell during cycling. In their study, CO_2 gas evolution was detected by DEMS analysis over the 4 V region. Other researchers also presented evidence of the decomposition of this class of electrolytes.[80–83] Freunberger *et al.*[80] studied the decomposition of DME during the discharge process using XRD and FT-IR analysis and proposed a decomposition mechanism where a progressive formation of Li_2CO_3 takes place. Xu *et al.*[82] demonstrated the decomposition by using XRD, DEMS, NMR, and XPS. In spite of the possible decomposition of ether-based electrolytes, they are still the most studied so far in non-aqueous lithium/air systems,[84–87].

2.1.6   Other non-aqueous electrolytes

Several other non-aqueous electrolytes batteries have been reported for lithium/air, such as acetonitrile (ACN),[88,89] dimethylformamide (DMF),[90] tri(ethylene glycol)-substituted trimethylsilane (1NM3),[72] N-methyl-2-pyrrolidone (NMP),[91] dimethyl sulfoxide (DMSO),[92–94] N,N-dimethylacetamide (DMA),[95] sulfolane,[96] ionic liquids.[97–102] Among these organic electrolytes, DMSO was thoroughly investigated by Feng *et al.*[93], who demonstrated that a solution of 0.1 M $LiClO_4$ in a DMSO electrolyte could give a very stable electrochemical performance. The main discharge product with a DMSO-based electrolyte was Li_2O_2 without any noticeable electrolyte decomposition after 100 cycles. However, the instability of the DMSO electrolyte in the presence of Li_2O_2 has recently been confirmed by in-situ IR and XPS measurements.[103,104]

2.2 The anode

Due to its high electrochemical values, i.e. a plating voltage of -3.05 V vs. SHE, a capacity of 3.86 Ahg^{-1} and 2.06 Ah cm^{-3}, lithium metal is in theory an ideal electrode material. However, its practical use is barred by its tendency to deposit irregularly, resulting in the formation of dendrites that may eventually grow across the cell, ultimately posing a serious safety hazard. It has been shown that both the separation of surface lithium flakes and the continuous growth of an unstable solid electrolyte interphase (SEI) layer lead to reduction in capacity during cycling.[36,53,105–109] Therefore, unless properly protected [4,110] and/or combined with a suitable electrolyte, lithium metal cannot be proposed as an electrode for battery manufacturing. This holds true for lithium/air batteries too. Furthermore, a gradual degradation of the surface of Li metal can also take place due to O_2 crossover, which promotes electrolyte decomposition during charge at the anode and results in the formation of LiOH and Li_2CO_3.[111] Quite surprisingly, this matter is generally ignored since most of the work in the field is still based

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on systems using lithium as anode, and while there are many papers addressing the challenges related to electrolytes and cathode supports, relatively few studies have been conducted on the anode. An attempt to solve this issue has been recently reported by Hassoun *et al.*,[112] who proposed the replacement of lithium metal with a lithiated silicon-carbon composite, LiSi-C, demonstrating one of the rare cases of a "lithium-ion-air battery" configuration. The battery operates reversibly at a capacity of 1,000 mAh g^{-1}_{carbon} for about 15 cycles to then decay, likely because of O_2 crossover with the consequent Si-C composite electrode deterioration (see **Figure 4**).[112] Indeed, oxygen crossover is a serious drawback on the anode side that has so far been underestimated. An obvious solution would be that of protecting the anode with a membrane that is not permeable to oxygen.[111] However, this approach may lead to unwanted additional problems, such as increase in the overall cell resistance and the associated power losses. As an alternate approach, gel-polymer electrolytes have been applied to suppress the Li dendrite formation [113–115] which, however, can still occur and lead to the penetration of the polymer film, to a poor cycling behavior and ultimately cell failure. Aleshin *et al.*[116] tried to solve this problem by coating the lithium metal anode with a protective ceramic layer composed of lithium–aluminum–germanium–phosphorus (LAGP) glass–ceramics. This layer was considered to stabilize the lithium/air performance by preventing anode and electrolyte degradation. However, the cell performance was only tested for ten cycles, making it hard to verify the long term impact of a ceramic protective layer.

2.3 The cathode substrate

The high energy density of lithium/air batteries partly stems from the low mass of its positive electrode, typically composed of conductive substrate, catalyst and binder, as opposed to lithium-ion batteries, where heavy transition metal oxides are used as active materials. Theoretically, the specific capacity of the lithium/air battery is determined by the amount of lithium peroxide (Li_2O_2) formed by the combination of reduced oxygen and lithium ions

during discharge. In practice, the discharge capacity is far lower than the theoretical value in all investigations that have been done to date, and the rate capability is inferior to that of other energy conversion systems. The Li/O_2 cathode structure is typically made up of a porous carbon substrate, a binder and a gas diffusion layer (GDL), usually carbon paper. With this type of substrate and the use of a stable electrolyte (e.g., $LiCF_3SO_3$-TEGDME) the cell can operate well in the discharge step, namely the oxygen reduction reaction (ORR), leading to the formation of Li_2O_2.[76] A pronounced overvoltage is instead usually detected in the opposite charge step, or oxygen oxidation reaction (OER), which results in a poor energy efficiency. Hence, attention is being directed at this issue, through the search for catalysts that can lower the OER overvoltage. To reach this goal, various materials have been tested (see **Table 2**); however, none of them is the ultimate choice and a real effective OER catalyst has still to be identified. Another serious concern at the cathode is the corrosion of carbon occurring during the charging process, with the evolution of CO_2 that ultimately leads to cell failure. [117–119]

A drawback, still associated with the cathode and so far unsolved, is the low power capability of the cell, which is closely correlated to the low current densities attainable, typically in the order of 0.1 mA cm^{-2}.[74,93,120] Alternative, nanostructured carbon configurations, such as graphene, tubes, foams, and nanofibers might bring a solution to this, since their large surface and high electronic conductivity are expected to enhance the kinetics of the electrochemical process.[75,121] On the other hand, this approach may contribute to further decrease the volumetric energy density of the Li/O_2 battery, already considered to be low with the standard carbon substrates.

The reaction at the positive electrode of lithium/air batteries revolves around a triple-phase interaction between the electrode substrate (the solid phase), the lithium ions in the electrolyte (the liquid phase) and molecular oxygen (the gas phase). However, the situation is more complicated for non-aqueous lithium/air cells due to the nature of the discharge products. The

mechanism of the formation/decomposition of Li_2O_2 has not yet been established with certainty.[122–127] The non-conductive solid Li_2O_2 precipitate [11,81,127,128] can accumulate on the porous substrate structure, causing blockage of the available surface area for further formation of Li_2O_2. The transfer pathway for oxygen gas and lithium ions can also be clogged by Li_2O_2 precipitate, resulting in an increase in cell resistance.[6,129,130] When the pore size is too small, such as in micropores ($\leq$ 2 nm), the pore entrance easily becomes blocked, rendering the electrochemically active sites located deeper into the cathode substrate inaccessible. As consequence, poor specific capacities are reached, despite the large surface area.[16] o further complicate things, the performance of lithium/air batteries is not solely determined by the surface area, porosity, or pore size of the air electrode, but by a more complex interplay between these components.[131] Therefore, it remains difficult to determine the most critical parameters that affect performance in lithium/air batteries. In the following sections, we discuss the different materials that have been used at the cathode.

2.3.1 Porous Carbon

The various structures and allotropes of carbon are notable for their low cost, high conductivity, high pore volume, large surface area and facile processing. Carbon is therefore well suited to solve the abovementioned problems, which is why it has become the main choice as substrate and catalyst for the positive electrode. Besides, the catalytic effect of carbon, observed on the ORR and ascribable to its defects, suggests that an additional catalyst for the oxygen reduction may not be necessary. [88,132] Different commercial forms of carbon black (e.g., Super P,[8,10,24] Ketjen Black,[17,18] and Vulcan carbon [133]) have been used as substrates for the positive electrode in lithium/air batteries. Due to the limited success of commercial carbons, many researchers have tried to develop new carbon structures to improve performances. Yang et al. [17] reported that mesocellular carbon foam (MCF-C) with large pore volumes and large mesoporous structures exhibited a higher discharge capacity

than commercial carbon black. Zhai *et al.*[127] showed that two kinds of discharge products, e.g. Li_2O_2 and LiO_2, were formed on pores of the activated carbon and emphasized that the latter can reduce the charge potential. Guo *et al.*[134] highlighted the ability of ordered mesoporous channels to improve the electron transfer process and facilitate Li^+ diffusion. In their structure, macropores, surrounded by ordered mesoporous channels, can provide a space for O_2 diffusion and Li_2O_2 formation/decomposition as shown in **Figure 5**. Carbon nanotubes (CNT) and their derivatives[135,136] have been considered for use in lithium/air batteries because of their unique properties (e.g. high surface area, conductivity, catalytic activity and stability in oxidation).[137–139] Mitchell *et al.*[121] reported carbon nanofibers (CNF) to display an efficient ORR catalytic activity and a high discharge capacity. The fiber was directly grown on a porous substrate using a CVD method, with no need for a binder. CNFs exhibited an exceptionally high discharge capacity of 7200 mAh g^{-1} and gravimetric energies up to 2500 W h kg^{-1}. Treated CNTs showed even better results; for instance, Li *et al.*[138] applied partially cracked CNTs (1513 mAh g^{-1}) to the substrate and found its capacity to be almost twice as large as that of non-cracked CNTs (800 mAh g^{-1}). Mi *et al.*[139] found that the application of nitrogen-doped CNTs to the substrate increased the capacity in both carbonate-based (PC/EC) and ether-based (DOL/DME) electrolytes beyond that of CNTs. Recently, a hierarchical-fibril carbon electrode was developed by orthogonally organizing individual sheets of aligned CNTs.[140] By promoting efficient mass transport in the open framework, this electrode could deliver a high capacity of 1000 mA h g^{-1} with good cycling performance up to 70–80 cycles. Liu and co-workers manufactured a freestanding electrode by applying a hierarchically porous CNT film fabricated via colloidal template-assisted vacuum filtration and post annealing.[141] Although the loading amount of carbon is 7–50 times higher than that reported previously for other free-standing carbon electrodes,[121,140] this electrode still exhibited a high capacity of 4683 mA h g^{-1} and a gravimetric energy of 12830 W h kg^{-1}. On another note, CNTs have been particularly useful in visually analyzing the Li_2O_2 morphology

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in a clear and distinguishable way. Shao-Horn and co-workers [122,142] investigated the formation and morphological evolution of Li_2O_2 during discharge, confirming the relationship between the Li_2O_2 morphology and the electrochemical performance of lithium/air batteries. Another attractive candidate, graphene, has also received wide consideration especially thanks to its excellent electrical conductivity (higher than that of CNT), high specific surface area, and excellent mechanical strength, resulting from its unique two-dimensional structure. Li *et al.* showed that graphene nanosheets (GNS) could deliver a higher discharge capacity (8,706 mAh g^{-1}) compared to BP-200 (1,909 mAh g^{-1}) and Vulcan XC-72 carbon (1,054 mAh g^{-1}).[143] Sun *et al.* confirmed an improved catalytic effect of GNS for the OER as well as for the ORR, compared to Vulcan XC-72 carbon.[144] In this case, the discharge capacity of GNS is 2,332 mAh g^{-1}, which is higher than that of a Vulcan XC-72 carbon electrode (1,645 mAh g^{-1}). Moreover, the potential difference between the discharge and charge processes of the GNS electrode was 1.22 V, which was significantly lower than that of a Vulcan XC-72 carbon electrode (1.69 V). A 3D hierarchically porous structure with functionalized 2D graphene nanosheets was applied as a porous carbon electrode. The 3D structure which contains inter-connected pore channels on both the micro- and nanometer length scales delivered an exceptionally high capacity of 15,000 mAh g^{-1} (although in good part irreversible) with a plateau at around 2.7 V. Moreover, a DFT calculation revealed that defects and functional groups on graphene would be able to facilitate the formation of isolated nanosized Li_2O_2 particles and therefore help prevent air blocking in the air electrode. [75]

2.3.2   Carbon Decomposition

Although carbon exhibits great potential as substrate material at the cathode, its suitability is being disputed due to chemical stability issues. By employing a carbon-13 isotope (^{13}C) electrode, McCloskey *et al.*[117] showed that oxidation of the carbon electrode contributes to the formation of Li_2CO_3, although electrolyte decomposition is the major source. During

discharge, the reaction of Li_2O_2 with the carbon electrode causes the formation of Li_2CO_3 layer on the carbon surface. Theoretically, this Li_2CO_3 layer can lead to a 10−100 fold decrease in the exchange current density. Thotiyl *et al.*[119] also reported on the stability of the carbon electrode and a non-aqueous electrolyte upon attack by Li_2O_2. They found carbon to be relatively stable below 3.5 V during both the discharge and the charge processes, especially in the case of hydrophobic carbon, but unstable above 3.5 V in the presence of Li_2O_2, which decomposes to form Li_2CO_3. Therefore, the stability of the electrode and the electrolyte cannot be considered separately, and careful consideration is needed if carbon is to be used in a practical lithium/air battery. To avoid stability issues related to carbon, Peng *et al.* used nanoporous gold material as an alternative substrate in lithium/air batteries.[93] Although Au is almost 10 times heavier than the carbon electrode, and not suitable for practical use due to its high cost, it demonstrated improved cycling with 95% capacity retention after 100 cycles with no side reactions. As a result, search for carbon-free electrodes has been actively pursued recently.[28,145–149] Among others, Li *et al.*[147] used a ruthenium nanoparticle/indium tin oxide (Ru/ITO) composite as a carbon free electrode in a lithium/air battery. The Ru/ITO electrode showed much lower charging overpotentials and better cycling behavior than both a Super P (SP) electrode and an SP electrode loaded with Ru nanoparticles (Ru/SP), as shown in **Figure 6**. The necessity and the side effect of carbon electrodes is still under debate [150]. Whether carbon-free electrodes are practically viable is not yet clear, considering the negative weight contribution of the proposed metal oxides. Parallel studies on the advanced carbon-free electrodes and the way of avoiding side effect of carbon should be performed at this stage.

2.3.3 Catalysts

Although many kinds of carbon electrodes have shown catalytic ORR activity, the relatively low catalytic activity of carbon in the OER encouraged the use of additional catalysts for the reversible dissociation of Li_2O_2, some of which have also been used for the reactions at both

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electrodes. While the use of catalysts could enhance the reaction kinetics of lithium/air batteries (i.e. increasing the capacity, lowering the potential gap during discharge-charge cycles and improving the rate capability), it remains unclear whether a catalyst would actually improve the overall performance of lithium/air batteries, due to the possible problem of electrolyte decomposition. Some studies argue that it is not the Li_2O_2 formation-decomposition reactions that are catalyzed during the discharge and charge processes, but rather the Li_2CO_3 formation-decomposition and electrolyte decomposition reactions. [76] Nevertheless, there are many effective electrocatalysts that are currently being used in non-aqueous lithium/air batteries. The use of soluble mediators or *"redox shuttles"* has also been recently proposed to mediate the electron transfer during ORR,[151] OER,[152] or both.[153] In the case of ORR mediators, a clear advantage is that the soluble mediator is reduced at the electrode and then diffuses, avoiding pore clogging by delocalizing the formation of Li_2O_2. Moreover, the diffusion distance for O_2 is shortened, as the shuttle diffuses faster than O_2 and the O_2 reduction occurs closer to the O_2/electrolyte interface. The advantage of OER mediators is the increase in rechargeability and rate, as Li_2O_2 is easily accessible by the soluble mediator. However, the use of redox shuttles can result in parasitic "shuttling" between the two electrodes, with the associated self discharge; thus, this promising new approach still requires further studies, also in terms of cell engineering.

2.3.4   Metal Oxides

To date, metal oxides have been the preferred catalysts for both the ORR and the OER. Manganese oxide, in particular, has attracted great interest because of its good ORR activity based on its high specific capacity and low cost.[8,13,23,25,27,154–156] Bruce and co-workers compared the effectiveness of various crystal structures of manganese oxide and reported α-MnO_2 to have the best catalytic effect for oxygen decomposition and lithium ion coordination.[23] Moreover, they found the catalytic properties of the α-MnO_2 nanowires to be

superior to those of spherical MnO_2, the latter being comparable to the porous carbon substrate. However, one has to be very careful regarding the catalytic behavior of different MnO_2 structures, as most of the studies were made in presence of PC-based electrolytes, which are now known to decompose. Many works have reported on the use of other metal oxides as catalysts in lithium/air batteries (e.g. cobalt oxide,[28,157–159] copper oxide,[27] iron oxide,[160,161] palladium oxide,[30] and others [71,87,162]). More recently, ruthenium oxide[163–165] and iridium oxide,[163,166] have received attention due to their excellent ability to catalyze the OER when used in combination with carbon or other substrate materials.

2.3.5 Metals

Since Lu *et al.*[29] demonstrated the superior catalytic properties of bi-functional platinum-gold nanoparticles ($Pt_{0.5}Au_{0.5}$ supported on Vulcan carbon XC-72), the usage of noble metal catalysts in lithium/air batteries has increased considerably. The same group screened the ORR activity of palladium, platinum, ruthenium, and gold and compared the results with those obtained with glassy carbon (GC).[167] The ORR activity was found to decrease in the order: Pd > Pt > Ru ≈ Au > GC. This trend is consistent with the discharge overpotential in lithium/air batteries, as shown in **Figure 7**. They also observed enhanced oxygen adsorption energy on the surface of these metal catalysts, which resulted in an improved ability to influence ORR activities in lithium/air batteries. Due to their excellent ORR catalytic effects, palladium and platinum have been the preferred choice for catalysts,[168–170] either in the pure form or combined with other catalysts (metals[171,172] or metal oxides[173–175]). Recently, in an attempt to prevent electrolyte decomposition on the carbon surface, Lu *et al.* used a catalyst consisting of palladium nanoparticles on a carbon surface partially coated with alumina to passivate the carbon defect sites.[132] Non-precious metal catalysts have been studied too. Ren *et al.*[33] tested Cu-Fe metal catalysts supported on Ketjen black carbon. These catalysts exhibited an ORR catalytic effect with a significant increase in the discharge voltage and an

improved rate capability. However, they only analyzed the ORR catalytic effect during the discharge process without determining the performance during charge. In addition to these examples, there have been many other studies involving the use of metal catalysts in lithium/air batteries.[86,176–178] As mentioned above, the side reaction such as catalytic electrolyte decomposition can occur in ether based as well as in carbonate-based electrolytes.[79] Further studies are still needed to find suitable ways to develop stable and selective catalysts for desired reactions.

3. A technology perspective

Researchers working on Li/air batteries cannot overlook the end result of their work, namely the development of a stable and functional chemistry for vehicle applications. Therefore, it is important to assess whether the Li/O$_2$ couple can actually reach this goal, or if research on other technologies should be pursued in this respect and other uses be envisioned for the "holy grail" of batteries, i.e. Li/air.

3.1 Defining a cell prototype

Given the fact that the Li/air technology sits somewhere in between Li-ion batteries and fuel cells, several cell designs proposed so far heavily draw inspiration from both fields, in an effort to create a hybrid that can benefit from the lessons learnt in the two branches. In fact, on the one hand there is the need, inherent to Li batteries, to ensure high electrochemical stability to a series of very reactive chemicals; on the other, typical engineering aspects, such as a uniform and optimal reagent feed, have to be taken into account, which represents a central field in fuel cell research. The lack of a standard cell for testing has triggered the creation of a series of designs with the main scope of addressing, from time to time, the issues incurred in the experimental phase. The main problem lies in making a system that is sufficiently shielded from the external while ensuring an oxygen flow in and out of the device

at the same time. The first design by Abraham *et al.* [6] consisted of a pouch cell where a small aperture on the cathode side allowed for uniform oxygen flow. Others have resorted to a modified CR 2032 coin cell design, by perforating the cathode metallic cover with a series of pinholes and then enclosing the cell in an oxygen-filled plastic bag.[179] A similar concept has been applied to Swagelok© cells, where oxygen is provided into the system by flowing it through a perforated cathode.[13] The first problem with such designs is the volatility of the electrolyte, which is free to evaporate during cycling and storage. Secondly, the use of such electrolytes brings up the safety hazard posed by the coexistence of reactive lithium and a pure oxygen atmosphere in contact with a flammable organic electrolyte. Cell drying has to be prevented at all costs, lest the risk of exposing lithium to a strongly oxidizing atmosphere. For this purpose, in addition to their favorable Li cycling performances, alternatives like SPEs,[17] glymes [76,180] and ionic liquids (IL) [99] have been proposed. Glymes and ILs in particular can sport a good ionic conductivity, a wide electrochemical stability window, a negligible vapor pressure, low flammability, good stability versus lithium metal cycling and versus the oxygen superoxide anion.[76,181,182] The flammability risk can be further controlled by feeding the cell with atmospheric air by means of an O_2-selective membrane, which limits the amount of combustive agent present at any time.[183,184] This was also the reason behind the development of a Li/O_2 flow cell, where an oxygen-saturated IL electrolyte is circulated through the electrochemical cell;[12,185] cell operation is ensured by the satisfactory O_2 solubility and diffusivity reached in the IL electrolyte, thanks the forced convection provided by a peristaltic pump.

If progress made on Li-ion batteries can be used to control the chemical aspects, previous research on fuel cells can give a desirable engineering edge over many details. This is particularly true when it comes to ensuring a sufficient oxygen feed that can increase the current density output and guarantee an even and reversible deposition of the discharge products. Researchers at Ford Motor Company have modelled a bipolar plate system based on

PEM fuel cells,[186] where they show that a flow-field plate located on the cathode side can solve some of these problems, at the expense of energy density. This option has been further investigated by the company AVL for an ionic liquid-based circulating electrolyte,[187] showing that electrodes a few millimeters thick and operating current densities of ca. 10 mA cm^{-2} are needed in order to reach a sufficient power density.

Considerable efforts are currently being dedicated to the design of air cathodes, in order to ensure a uniform supply of O_2 throughout discharge. The problem here is that lithium peroxide is an electronic insulator and no current can virtually flow through it once its thickness is above 10 nm.[81] If the pores that make up the cathode substrates are smaller than this size, they will eventually be clogged and block the O_2 flow, thus hindering the total discharge capacity (**Figure 8**). The formation of the discharge products also displaces electrolyte from the pores and recharge is then limited to the regions where Li^+ ions are able to access. Considering the contact losses that might occur during charge, these deposits are often non-rechargeable, therefore two objectives have to be pursued in this respect, namely (a) controlling the discharge product morphology and (b) engineering a cathode structure that allows for extended cycling. Concerning the second point, improvements can be made on the gas diffusion layer (GDL), on the carbon itself, or on both. The most widely used GDLs are carbon fiber mats already found in fuel cells, given their light weight, low thickness and high gas permeability. In addition, such mats are generally treated with a PTFE hydrophobic layer, which prevents the cathode substrate from being flooded thereby increasing the contact area between oxygen and the electrolyte. GDLs can be further teflonized to make them almost impermeable to the electrolyte, thereby allowing current densities up to 2.4 mA cm^{-2} and extended lifetime.[188] Other materials used are carbon cloths,[94] stainless steel and Ti mesh [93,189], inks and slurries directly cast on the separator,[190,191] aluminum foil,[27] graphene nanosheets [192] and porous Ni mesh/foam,[17,26] although the latter has been reported to lead to the electrocatalytic decomposition of the carbonate-based electrolyte.[193] Ein-Eli *et al.* have

proposed an interesting approach of enhancing the O_2 transport by impregnating the GDL with perfluorocarbons;[194] this class of chemicals can dissolve a significant amount of oxygen while not mixing with the electrolyte, due to their low polarity. The emulsion was proposed to allow for a synergistic enhancement of both O_2 and Li^+ transport, thus improving the pore utilization **(Figure 9)**. Control over the degree of wetting by similar means was also carried out by impregnating a GDL with a high/low vapor pressure solvent mixture and then evaporating the former.[195] Finally, carbon nanotubes have also been embedded in an ionic liquid-based gel matrix to create a cross-linked network gel, where O_2 can enter selectively.[98] Free-standing electrodes. i.e. where the cathode support also acts as GDL, have been developed too[28,121,141]. The mass loadings reported for such materials are generally very low (0.1-0.5 mg cm^{-2}), therefore making them appealing for high specific energy applications. However, often these cathode substrates have to be considered as binder-free and not as freestanding electrodes, as heavy metallic substrates are required for the deposition of the carbon. [121] In other works, mass loadings as high as 8 mg cm^{-2} are achieved with metal oxides [28], which might provide with an advantage in volumetric terms, but do not yield good performances if they are not combined with a porous substrate like Ni foam.

This brings us back to the need for a deeper understanding of the charging and discharging mechanisms, a topic that encompasses catalytic and material aspects, e.g. degree of defects on the air electrode,[196] O_2 access to the pores,[188] morphology and stoichiometry of the discharge products.[122,197,198] Li/air hybrid cells perform better in this respect, since more conductive electrolytes can be used on the cathode side, and current densities of 5 mA cm^{-2} have already been reported.[56]

3.2 Theoretical vs. practical specific energy

It is often enthusiastically stated that burning lithium can provide, on a Wh kg^{-1} level, a similar amount of specific energy to gasoline (11680 Wh kg^{-1} vs.13000 Wh kg^{-1},

respectively).[4] The reasoning then follows the principle that internal combustion engines are highly inefficient, since less than 15% of the energy content of gasoline goes into the propulsion of the vehicle, leading to the already mentioned figure of merit of 1750 Wh kg^{-1} for conventional fuel. Electric motors, on the other hand, can sport a typical energy efficiency of 90%, which means that a Li/air battery could in theory largely outperform a gasoline engine. The calculations are however a bit more complex, as Christensen *et al.* have summarized.[128] First of all, looking at the cathode, a purely insulating Li_2O_2 electrode cannot be used, therefore a conductive support has to be factored in, together with a binder and the oxygen consumed during discharge. Secondly, an O_2-permselective membrane should also be added to ensure that no contaminants enter the cell. The main characteristics the latter should have are (a) a high permeability to O_2, (b) blockage of water vapor and CO_2, and (c) electrolyte containment within the cell.[199] After adding electrolyte, O_2 supply and the inactive components, this value quickly drops to around 1000 Wh kg^{-1}, which is definitely an improvement over both the state-of-the-art and possible future Li-ion batteries (150 and 250 Wh kg^{-1}, respectively [3]), but still lower than gasoline. To further complicate things, open Li/air batteries have the peculiarity of increasing in weight while decreasing in volume as the discharge goes on, therefore two values can be given according to the state of charge. The volume variation for a practical cell can be as high as 30%,[200] since lithium peroxide has more than four times the specific weight of lithium metal. Luckily, these drawbacks can be partially offset by the smaller size of electric motors (the BMW i3 has a 650 cc motor). Concerning the need to separate O_2 from unwanted components in air, this can currently only be done temporarily with porous membranes, while allowing a low dry air flow.[183,199,201] Crowther *et al.*[184] investigated the effectiveness of oxygen selective membranes in lithium/air batteries. They protected the cell using Teflon coated fiberglass cloth (TCFC) on the outside of the cathode support, thereby preventing volatilization of the electrolyte and oxidation of the lithium metal by H_2O. In order to keep the cell under constant pressure, the

weight and volume contribution of a gas compressor has to be factored in. For an open system, its function would mostly be that of harvesting O_2 and provide a sufficient pressure inside the cell during operation, but such a device would also negatively contribute to the pack's specific energy. There is speculation as to whether membranes should be abandoned in favor of the addition of an O_2 tank for practical purposes. This would definitely solve the problems deriving from O_2 harvesting, e.g. filtration and purification together with high flow for vehicle uses, but closing the system to the external would add safety concerns (the O_2 has to be stored onboard at high pressures) and lower the practical specific energy .[128] Finally, on the anode side, the low coulombic efficiency typically exhibited by lithium metal electrodes implies that this material has to be added in excess to the cell, further intensifying the decrease in volumetric energy density.

Keeping these parameters and constraints in mind, target values around 500 Wh kg^{-1} and 570 Wh L^{-1} are expected to be met by non-aqueous cells even if they included an O_2 tank, while aqueous cells might fall short of such requirements, despite the higher operational voltage.[200]

3.3 Electric vehicle requirements

Having practical parameters in place, it is now possible to estimate how a hypothetical Li/air battery will look like in an electric vehicle (EV). Provided that high energy densities can be reached, the first figure of merit would be the driving range. The "range anxiety" is the feeling triggered into drivers once the indicator in the fuel gauge reaches the bottom, although typically gasoline-powered cars still have enough fuel to drive for another 100 km after this stage. This value coincides currently with the maximum driving range of most Li-ion EVs; hence, the energy content of the battery pack has to be increased by at least a factor of five. With 140 kWh and a specific energy of 500 Wh kg^{-1},[200] it is reasonable to expect a non-aqueous battery pack that will weigh not more than 300 kg, ancillaries included, and that will drive the vehicle for at least 500 km. In volumetric terms, this amounts to ca. 250 L, which is

well below the combined boot and tank capacity of a regular city car; even if an O_2 tank were added, the volume restrictions would not be too severe. However, reaching 500 Wh kg^{-1} at the pack level is not trivial as postulating 3 Ah g^{-1} of carbon substrate and a 2.7 V discharge voltage leads to a maximum specific energy of ca. 2 kWh kg^{-1} related to Li and carbon substrate only.[181]

Concerning power density, the first step to ensure fast kinetics is the establishment of a triple-phase boundary within the cathode pores, where O_2, the electrolyte and the carbon substrate coexist at the nanoscale. If, for instance, all the porosity in the support were filled with electrolyte, the reaction rate will be limited by the low solubility of O_2 into the solvent, strongly hampering the discharge depth.[8] A "flooded" configuration would be helpful, on the other hand, if the O_2 solubility were sufficiently high, because the deposition of the discharge products would be homogeneous and not limited to the triple-phase boundary interface. However, contrary to Li-ion and Li-metal polymer batteries, which mainly include electrolyte, separator, current collector(s) and packaging as inactive components at the stack level, the O_2 flow required for a use in automotive applications implies additional weight per cell surface area. Indeed, a 500 km range implies a 5h discharge time, corresponding to a consumption of 967 mol of O_2. This amounts to an O_2 flow of ca. 1.2 L s^{-1} if all the O_2 were to be consumed. However, much higher flows are expected to be needed, if we take into consideration that oxygen only makes up about one fifth of the earth's atmosphere and that its effective harvesting could be as low as 20%. For this reason, each cell needs to bear an extra weight in the form of a flow-field plate to feed O_2 to the cathode substrate, as it is already the case with fuel cells. While the solution is realistic for the latter category, where the evacuation of the reaction product (H_2O) from the cell provides with unlimited capacities per cell surface area, this does not hold true for Li/air batteries, as the capacity is limited by the weight of Li and of the Li_2O_2 deposition substrate. Hence, cell inactive components (GDL, flow-field plate, etc.) and the devices able to provide a high O_2 flow must not account for more than 75% of the

pack weight. Li/air batteries for automotive solutions require lightweight inactive materials, as well as electrodes with thicknesses in the millimeter range, and, accordingly current densities in the 1-10 mA cm^{-2} range. Thus, it is unlikely that a Li/air battery, operating in 'breathing mode" (i.e. fed by simple O_2 diffusion through perfluorinated hydrophobic membranes), would enable reaching any significant power. At an engineering level, some mid-term solutions can be envisioned: small current densities are acceptable for cruising speeds, and the peak load shortcomings can be met by the addition of a small Li-ion/supercapacitor pack besides the main Li/air powertrain, as it has already been proposed for fuel cells.[202] In any case, such an improvement in current density might not prove sufficient for keeping up with the increase in battery pack size. Li-ion batteries are already lagging behind gasoline when it comes to charging (refueling) times; with a five-fold increase in capacity, overnight charging will not be sufficient to replenish the battery. An intense infrastructure development in terms of fast-charging stations would still not solve the problem, if higher current densities were not concomitantly achieved.

The final concern that ultimately determines the viability of a Li/air electric vehicle is safety. The presence of a lithium metal anode is definitely the first aspect that comes to mind, since dendritic deposits can form onto the metal's surface, grow through the separator and finally create a short circuit in the cell. This risk is often overstated, since a natural self-recovery mechanism can take place if the dendrites are small enough, with high local currents turning them into electrochemically inactive; also, the use of solid polymer electrolytes has shown to delay their onset.[203]. Another risk is related to the handling of oxygen in the cell: if an O_2 tank is stored onboard, venting systems need to be devised to prevent pressure buildup; also, the materials chosen for the tank have to withstand several hundred bars, while being as lightweight as possible.

3.4 Performance comparison with other technologies

As already stated, the main objective behind current research on Li/air batteries is the development of an electrochemical energy storage technology that has a comparable power density to Li-ion batteries and a specific energy close to that of tank-to-wheel gasoline. With the same scope in mind, other cell chemistries and storage technologies are being investigated alongside, such as fuel cells, lithium/sulfur and fluorine batteries **(Table 3)**.

The first category encompasses a broad family of electrochemical devices, including proton exchange membrane (PEM), direct alcohol and solid oxide fuel cells. For EV applications, the first two are viable options, and companies like Honda and Toyota have already increased their efforts towards the deployment of commercial vehicles by 2015. According to the car manufacturers, a 480 km driving range can be expected,[204] i.e. comparable with the Li/air target; however, the real advantage would lie in the extremely short refueling times (3 minutes), almost two orders of magnitude below that of a battery. The disadvantages comprise the need to use pricey Pt as catalyst and H_2 as fuel, which is still more expensive than regular electricity and cannot boast a comparable distribution infrastructure. Finally, while fuel cell is a clean technology at the tailpipe, the H_2 supply chain is only as clean as its source, which currently relies on natural gas.

Lithium/sulfur batteries have a similar chemistry to Li/air, since they share the same anode (lithium metal) and a conversion reaction as working principle. They are, on the other hand, much closer to commercialization, with companies like Polyplus, Sion Power and Oxis Energy having demonstrated working devices with a practical specific energy of 350 Wh kg^{-1}.[205,206] The rate capability is however comparable to that of Li/air, therefore it is hard to foresee any clear advantages in this chemistry.

3.5 Neighboring metal/air chemistries

If Li/S cells share the same anode with Li/air, a remark can be made by having a look at what is being done by academics if the air cathode remains fixed and the lithium anode is replaced.

As already stated in the introduction, initial efforts focused on zinc/air batteries, due to their theoretical specific energy (1084 Wh kg^{-1}) and their enhanced tolerance to corrosion.[207] Zn/air cells are however still primary and can only be recharged by mechanically replacing the zinc metal anode at the end of discharge.

Al/air batteries sport a higher OCV as well as a higher oxidation number, which together result in a theoretical specific energy of 8135 Wh kg^{-1}.[208] Like Zn/air, this technology only exists in a primary configuration; however, aluminum is the most widespread metal on the earth's crust, therefore it might be economically feasible to develop an infrastructure where the spent anodes are recycled. Both Zn/air and Al/air cells require in most cases a corrosive aqueous electrolyte to avoid passivation, as the layer that forms tends to be impermeable to large cations.

Looking at secondary metal/air cells, sodium has attracted attention for its use in Na/air batteries. Sodium is the closest relative to lithium, having the second lowest standard potential after lithium itself and a relatively small ionic radius. Moreover, it is abundant, equally distributed across the globe and allows for the use of cheaper current collectors. It is not surprising then that growing research is being carried, especially after the recent breakthroughs made in the intercalation chemistry.[209] Sodium has a higher flammability and, unlike Li metal, suffers from its larger weight and higher deposition potential, but Na/air batteries can overcome a series of unresolved issues, such as charge/discharge overpotential and current density. A theoretical specific energy of 1980 Wh kg^{-1} can be reached if we assume Na_2O to be the stable discharge product.[210] Na_2O_2 has also been indicated to form.[211] Unfortunately, the formation of sodium peroxide in carbonate-based electrolytes results in decomposition products.[212] Although not thermodynamically favored, sodium superoxide can also form as a stable compound during discharge, through a one-electron step. This is what Adelhelm et $al.$ [211] observed when using $NaCF_3SO_3$ in DEGDME at room temperature, together with a low overpotential during charge (200 mV) at a current density of

0.2 mA cm^{-2}. Moreover, the conductive nature of NaO_2 enables, in theory, a good cyclability. Even though the specific energy achievable in this way (1108 Wh kg^{-1}) is much lower than that of Li/air, switching to sodium/air is still a reasonable avenue for electric vehicles because it can bring down the cost per kWh, while ensuring a higher specific energy than Li-ion batteries.[213]

Research on magnesium-based batteries has been going on and off for the past 40 years, with early reports deprecating the high self-discharge rate.[5] However, the advantages of magnesium over lithium (widespread availability, low cost, low toxicity [214]), similarly to those of sodium, have kept interest on the subject afloat, to the point that research on Mg-ion batteries has also been undertaken by companies like Toyota.[215] It is of no surprise then that researchers have looked into Mg/air batteries as well, especially considering the high cell voltage (3.1 V) and theoretical specific energy (6800 Wh kg^{-1}).[216] However, this cell chemistry is still restricted to a primary configuration, and problems like Mg corrosion and use of Pt for the ORR have already fuelled research into Mg alloys and non-expensive catalysts, as well as non-aqueous electrolytes that enable rechargeability.[217]

Another recent prospect in the metal/air family is represented by potassium/air. With a voltage gap of only 50 mV between charge and discharge, this battery chemistry exhibits a remarkable round-trip efficiency of 95%, better than any other metal/air cell.[218] This is possible thanks to the relatively high electronic conductivity of KO_2. Unlike Li/air, where LiO_2 is thermodynamically unstable, the authors state that with the appropriate cut-off voltage, KO_2 can be cycled reversibly. With a theoretical specific energy of 935 Wh kg^{-1}, K/O_2, has the potential to become a strong competitor for Li-ion batteries.

4. Conclusion

In this review, we have shown the most recent and promising advancements on Li/air batteries. Nearly 20 years in the making, most optimistic claims about their specific energy have been

slashed down, and scientists worldwide have adopted a problem-solving strategy to address all the shortcomings as they appeared. Although substantial progress has been achieved in the last few years, the research in this fascinating but intriguing electrochemical system is far from complete and various aspects have not been answered yet. First, substantial research efforts should be devoted to develop lithium/air batteries that offer superior performance in terms of capacity and cycle life to those of conventional systems. Optimistically, a 500 Wh/kg battery can be envisioned, although this would only be 2-3 times better than advanced Li-ion, a technology that is already streamlined and on the market. From an academic point of view, carbon has established itself as the elective cathode substrate, but alternative allotropes like carbon nanotubes are gaining ground thanks to their favorable properties. On the anode side, lithium is still the most widely used electrode, yet its practical applicability is far from viable, mostly due to longstanding safety concerns. As a result, a convincing, fully efficient alternative anode material has not yet been reported. As for the electrolyte, organic carbonates have been abandoned, and more stable alternatives like DMSO, TEGDME and ILs are under intense scrutiny. Particular attention should be placed to the goal of increasing the energy efficiency of the battery. In this respect, the need for catalysts to improve the OER and ORR reactions is debated, and no effective catalyst has been developed yet for the OER charge process, although redox shuttles are an interesting approach. Additionally, the rate capability is not high enough yet. Proper applications for electric vehicles require that charge and discharge rates have to be raised to the 10 mA cm^{-2} level, namely about two orders of magnitude higher than presently. The solution to this issue is not straightforward since it may lead to electrode configurations with a low tap density and a far too large surface area, thus affecting both cell volumetric energy density and safety. Finally, most of the work so far reported is on cells using pure oxygen at the cathode and obvious practical reasons would require its replacement with air. The difficulty here is in feeding the cell with dry air since moisture, even in traces, attacks the lithium metal electrode, thus seriously affecting the

reliability, safety and cycle life of the battery. Carbon dioxide is also an unwanted impurity. The goal may be achieved with the support of ancillary scrubbing elements, however at the cost of the overall cell energy density. A valid alternative is the adoption of cathode-protected designs involving the use of a membrane that exhibits selective and fast O_2 permeability while at the same time blocking the diffusion of organic solvents out of the cell. Efforts on protecting the lithium metal anode from O_2 crossover must also be pursued. With these views in mind, it is clear that a straightforward solution is all but trivial and that a holistic approach, rather than an issue-based one (as it has been done so far) can bring the greatest improvements. Alternative cell chemistries are being evaluated, and even though few of them can compete with the promises held by Li/air, research in these fields can bring a fresh insight into new chemicals to be used, as well as a deeper understanding of the reaction mechanisms that govern metal/air electrochemical cells.

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[1]   E. Borden, W. Schill, *Dtsch. Inst. für Wirtschaftsforsch.* **2013**, 32.

[2]   European Commission, *Horizon 2020   : Boosting Industrial Competitiveness*, **2014**.

[3]   N.-S. Choi, Z. Chen, S. a. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, *Angew. Chemie Int. Ed.* **2012**, *51*, 9994.

[4]   G. Girishkumar, B. D. McCloskey, a. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193.

[5]   K. F. Blurton, A. F. Sammells, *J. Power Sources* **1979**, *4*, 263.

[6]   K. M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1.

[7]   Y.-C. Lu, H. A. Gasteiger, M. C. Parent, V. Chiloyan, Y. Shao-Horn, *Electrochem. Solid-State Lett.* **2010**, *13*, A69.

[8]   J. Read, *J. Electrochem. Soc.* **2002**, *149*, A1190.

[9]   J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, *J. Electrochem. Soc.* **2003**, *150*, A1351.

[10]   J. Read, *J. Electrochem. Soc.* **2006**, *153*, A96.

[11]   I. Kowalczk, J. Read, M. Salomon, *Pure Appl. Chem.* **2007**, *79*, 851.

[12]   S. Monaco, F. Soavi, M. Mastragostino, *J. Phys. Chem. Lett.* **2013**, *4*, 1379.

[13]   T. Ogasawara, A. Debart, M. Holzapfel, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390.

[14]   P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2011**, *11*, 19.

[15]   B. Scrosati, J. Hassoun, Y.-K. Sun, *Energy Environ. Sci.* **2011**, *4*, 3287.

[16]   X. Yang, P. He, Y. Xia, *Electrochem. commun.* **2009**, *11*, 1127.

[17]   S. D. Beattie, D. M. Manolescu, S. L. Blair, *J. Electrochem. Soc.* **2008**, *156*, 126.

[18]   J. Xiao, D. D. D. D. Wang, W. Xu, R. E. Williford, J. Liu, J. Zhang, *J. Electrochem. Soc.* **2010**, *157*, A487.

[19]   Y. Yang, Q. Sun, Y.-S. Li, H. Li, Z.-W. Fu, *J. Electrochem. Soc.* **2011**, *158*, B1211.

[20]   Y. Wang, H. Zhou, *Energy Environ. Sci.* **2011**, *4*, 1704.

[21]   G. Q. Zhang, J. P. Zheng, R. Liang, C. Zhang, B. Wang, M. a. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **2010**, *157*, A953.

[22] Y. Li, J. Wang, X. Li, J. Liu, D. Geng, J. Yang, R. Li, X. Sun, *Electrochem. commun.* **2011**, *13*, 668.

[23] A. Debart, A. J. Paterson, J. Bao, P. G. Bruce, *Angew. Chemie Int. Ed.* **2008**, *120*, 4597.

[24] H. Cheng, K. Scott, *J. Power Sources* **2010**, *195*, 1370.

[25] L. Jin, L. Xu, C. Morein, C. Chen, M. Lai, S. Dharmarathna, A. Dobley, S. L. Suib, *Adv. Funct. Mater.* **2010**, *20*, 3373.

[26] G. Q. Zhang, J. P. Zheng, R. Liang, C. Zhang, B. Wang, M. Au, M. a. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **2011**, *158*, A822.

[27] A. Debart, J. Bao, G. Armstrong, P. G. Bruce, *J. Power Sources* **2007**, *174*, 1177.

[28] Y. Cui, Z. Wen, Y. Liu, *Energy Environ. Sci.* **2011**, *4*, 4727.

[29] Y.-C. Lu, Z. Xu, H. A. Gasteiger, S. Chen, K. Hamad-Schifferli, Y. Shao-Horn, *J. Am. Chem. Soc.* **2010**, *132*, 12170.

[30] H. Cheng, K. Scott, *Appl. Catal. B Environ.* **2011**, *108-109*, 140.

[31] M. Marinaro, U. Riek, S. K. Eswara Moorthy, J. Bernhard, U. Kaiser, M. Wohlfahrt-Mehrens, L. Jörissen, *Electrochem. commun.* **2013**, *37*, 53.

[32] S. S. Zhang, X. Ren, J. Read, *Electrochim. Acta* **2011**, *56*, 4544.

[33] X. Ren, S. S. Zhang, D. T. Tran, J. Read, *J. Mater. Chem.* **2011**, *21*, 10118.

[34] "IBM Battery 500 Project," can be found under http://www.ibm.com/smarterplanet/us/en/smart_grid/article/battery500.html, **2009**.

[35] D. Aurbach, Y. Gofer, M. Ben-Zion, P. Aped, *J. Electroanal. Chem.* **1992**, *339*, 451.

[36] D. Aurbach, I. Weissman, A. Zaban, O. Chusid, *Electrochim. Acta* **1994**, *39*, 51.

[37] K. Takechi, T. Shiga, T. Asaoka, *Chem. Commun.* **2011**, *47*, 3463.

[38] J. Lu, L. Li, J.-B. Park, Y.-K. Sun, F. Wu, K. Amine, *Chem. Rev.* **2014**, DOI 10.1021/cr400573b.

[39] B. Kumar, J. Kumar, *J. Electrochem. Soc.* **2010**, *157*, A611.

[40] B. Kumar, J. Kumar, R. Leese, J. P. Fellner, S. J. Rodrigues, K. M. Abraham, *J. Electrochem. Soc.* **2010**, *157*, A50.

[41] P. Kichambare, J. Kumar, S. J. Rodrigues, B. Kumar, *J. Power Sources* **2011**, *196*, 3310.

[42] J. Kumar, B. Kumar, *J. Power Sources* **2009**, *194*, 1113.

[43]   H. Kitaura, H. Zhou, *Energy Environ. Sci.* **2012**, *5*, 9077.

[44]   Y. Lu, E. Crumlin, T. Carney, *J. Phys. Chem. C* **2013**, *117*, 25948.

[45]   Y. Lu, E. Crumlin, G. Veith, J. R. Harding, *Sci. Rep.* **2012**, *2*, 715.

[46]   W. R. Momyer, J. L. Morris, *Lockheed Missiles Sp. Co. Rep.* **1979**, *1*.

[47]   W. R. Momyer, E. L. Littauer, in *Energy to 21st Century; Proc. Fifteenth Intersoc. Energy Convers. Eng. Conf.*, **1980**, pp. 1480–1486.

[48]   J. P. Zheng, R. Y. Liang, M. a. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **2008**, *155*, A432.

[49]   E. Littauer, K. Tsai, *J. Electrochem. Soc.* **1976**, *123*, 771.

[50]   E. L. Littauer, K. C. Tsai, *J. Electrochem. Soc.* **1976**, *123*, 964.

[51]   E. Littauer, K. Tsai, R. Hollandsworth, *J. Electrochem. Soc.* **1978**, *125*, 845.

[52]   J. P. Zheng, P. Andrei, M. a. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **2011**, *158*, A43.

[53]   N. Imanishi, S. Hasegawa, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* **2008**, *185*, 1392.

[54]   T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, *J. Power Sources* **2009**, *189*, 371.

[55]   T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, *Chem. Commun.* **2010**, *46*, 1661.

[56]   X. J. Chen, a. Shellikeri, Q. Wu, J. P. Zheng, M. a. Hendrickson, E. J. Plichta, *J. Electrochem. Soc.* **2013**, *160*, A1619.

[57]   L. De Jonghe, B. Katz, Y. Nimon, S. J. Visco, *Protected Active Metal Electrode and Battery Cell Structures with Non-Aqueous Interlayer Architecture*, **2007**.

[58]   Y. Nimon, S. J. Visco, *Active Metal/aqueous Electrochemical Cells and Systems*, **2012**.

[59]   L. Puech, C. Cantau, P. Vinatier, G. Toussaint, P. Stevens, *J. Power Sources* **2012**, *214*, 330.

[60]   S. J. Visco, E. Nimon, B. Katz, in *210th ECS Meet.*, **2006**.

[61]   Y. Shimonishi, T. Zhang, P. Johnson, N. Imanishi, a. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, *J. Power Sources* **2010**, *195*, 6187.

[62]   T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, *J. Electrochem. Soc.* **2008**, *155*, A965.

[63] N. Imanishi, Y. Takeda, O. Yamamoto, *Electrochemistry* **2012**, *80*, 706.

[64] Y. Wang, H. Zhou, *J. Power Sources* **2010**, *195*, 358.

[65] J. Hassoun, F. Croce, M. Armand, B. Scrosati, *Angew. Chemie Int. Ed.* **2011**, *50*, 2999.

[66] S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2011**, *133*, 8040.

[67] F. MIZUNO, S. NAKANISHI, Y. KOTANI, S. YOKOISHI, H. IBA, *Electrochemistry* **2010**, *78*, 403.

[68] W. Xu, V. V. Viswanathan, D. Wang, S. a. Towne, J. Xiao, Z. Nie, D. Hu, J.-G. Zhang, *J. Power Sources* **2011**, *196*, 3894.

[69] J. Xiao, J. Hu, D. Wang, D. Hu, W. Xu, G. L. Graff, Z. Nie, J. Liu, J.-G. Zhang, *J. Power Sources* **2011**, *196*, 5674.

[70] G. M. Veith, N. J. Dudney, *J. Phys. Chem. C* **2011**, *115*, 14325.

[71] W. Xu, K. Xu, V. V. Viswanathan, S. a. Towne, J. S. Hardy, J. Xiao, Z. Nie, D. Hu, D. Wang, J.-G. Zhang, *J. Power Sources* **2011**, *196*, 9631.

[72] Z. Zhang, J. Lu, R. S. Assary, P. Du, H.-H. Wang, Y.-K. Sun, Y. Qin, K. C. Lau, J. Greeley, P. C. Redfern, H. Iddir, L. A. Curtiss, K. Amine, *J. Phys. Chem. C* **2011**, *115*, 25535.

[73] V. S. Bryantsev, V. Giordani, W. Walker, M. Blanco, S. Zecevic, K. Sasaki, J. Uddin, D. Addison, G. V Chase, *J. Phys. Chem. A* **2011**, *115*, 12399.

[74] C. O. Laoire, S. Mukerjee, E. J. Plichta, M. a. Hendrickson, K. M. Abraham, *J. Electrochem. Soc.* **2011**, *158*, A302.

[75] J. Xiao, D. Mei, X. Li, W. Xu, D. Wang, G. L. Graff, W. D. Bennett, Z. Nie, L. V Saraf, I. a Aksay, J. Liu, J.-G. Zhang, *Nano Lett.* **2011**, *11*, 5071.

[76] H.-G. Jung, J. Hassoun, J.-B. Park, Y.-K. Sun, B. Scrosati, *Nat. Chem.* **2012**, *4*, 579.

[77] S. Oh, R. Black, E. Pomerantseva, J. Lee, L. Nazar, *Nat. Chem.* **2012**, *4*, 1004.

[78] Z.-L. Wang, D. Xu, J.-J. Xu, L.-L. Zhang, X.-B. Zhang, *Adv. Funct. Mater.* **2012**, *22*, 3699.

[79] B. D. McCloskey, R. Scheffler, A. Speidel, D. S. Bethune, R. M. Shelby, A. C. Luntz, *J. Am. Chem. Soc.* **2011**, *133*, 18038.

[80] S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bardé, P. G. Bruce, *Angew. Chemie Int. Ed.* **2011**, 8609.

[81] V. V. Viswanathan, K. S. Thygesen, J. S. Hummelshøj, J. K. Nørskov, G. Girishkumar, B. D. McCloskey, a C. Luntz, *J. Chem. Phys.* **2011**, *135*, 214704.

[82]   W. Xu, J. Hu, M. Engelhard, *J. Power …* **2012**, *215*, 240.

[83]   H. Wang, K. Xie, *Electrochim. Acta* **2012**, *64*, 29.

[84]   H.-D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K.-Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Lepró, R. Ovalle-Robles, R. H. Baughman, K. Kang, *Angew. Chemie Int. Ed.* **2014**, *53*, 3926.

[85]   J. Shui, F. Du, C. Xue, Q. Li, L. Dai, *ACS Nano* **2014**, *8*, 3015.

[86]   G. Zhao, R. Mo, B. Wang, L. Zhang, K. Sun, *Chem. Mater.* **2014**, *26*, 2551.

[87]   K. Guo, Y. Li, J. Yang, Z. Zou, X. Xue, X. Li, H. Yang, *J. Mater. Chem. A* **2014**, *2*, 1509.

[88]   C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, M. a. Hendrickson, *J. Phys. Chem. C* **2010**, *114*, 9178.

[89]   C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, M. a. Hendrickson, *J. Phys. Chem. C* **2009**, *113*, 20127.

[90]   Y. Chen, S. A. Freunberger, Z. Peng, F. Bardé, P. G. Bruce, *J. Am. Chem. Soc.* **2012**, *134*, 7952.

[91]   H. Wang, K. Xie, L. Wang, Y. Han, *J. Power Sources* **2012**, *219*, 263.

[92]   D. Xu, Z.-L. Wang, J.-J. Xu, L.-L. Zhang, X.-B. Zhang, *Chem. Commun.* **2012**, 6948.

[93]   Z. Peng, S. A. Freunberger, Y. Chen, P. G. Bruce, *Science* **2012**, *11*, 19.

[94]   M. J. Trahan, S. Mukerjee, E. J. Plichta, M. a. Hendrickson, K. M. Abraham, *J. Electrochem. Soc.* **2012**, *160*, A259.

[95]   W. Walker, V. Giordani, *J. Am. Chem. Soc.* **2013**, *135*, 2076.

[96]   Z.-K. Luo, C.-S. Liang, F. Wang, Y.-H. Xu, J. Chen, D. Liu, H.-Y. Sun, H. Yang, X.-P. Fan, *Adv. Funct. Mater.* **2014**, *24*, 2101.

[97]   T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, *J. Power Sources* **2005**, *146*, 766.

[98]   T. Zhang, H. Zhou, *Angew. Chemie Int. Ed.* **2012**, *51*, 11062.

[99]   L. Cecchetto, M. Salomon, B. Scrosati, F. Croce, *J. Power Sources* **2012**, *213*, 233.

[100] H. Wang, N. Imanishi, a. Hirano, Y. Takeda, O. Yamamoto, *J. Power Sources* **2012**, *219*, 22.

[101] H. Nakamoto, Y. Suzuki, T. Shiotsuki, F. Mizuno, S. Higashi, K. Takechi, T. Asaoka, H. Nishikoori, H. Iba, *J. Power Sources* **2013**, *243*, 19.

[102] H. Ye, J. Xu, *ECS Trans.* **2008**, *3*, 73.

[103] N. Mozhzhukhina, L. P. Méndez De Leo, E. J. Calvo, *J. Phys. Chem. C* **2013**, *117*, 18375.

[104] R. Younesi, P. Norby, T. Vegge, *ECS Electrochem. Lett.* **2014**, *3*, A15.

[105] D. Aurbach, B. Markovsky, M. . Levi, E. Levi, a Schechter, M. Moshkovich, Y. Cohen, *J. Power Sources* **1999**, *81-82*, 95.

[106] D. Aurbach, E. Zinigrad, Y. Cohen, H. Teller, *Solid State Ionics* **2002**, *148*, 405.

[107] J. Yamaki, S. Tobishima, K. Hayashi, Y. Nemoto, M. Arakawa, *J. Power Sources* **1998**, *74*, 219.

[108] R. Younesi, M. Hahlin, M. Roberts, K. Edström, *J. Power Sources* **2012**, *225*, 40.

[109] J. Steiger, D. Kramer, R. Mönig, *J. Power Sources* **2014**, *261*, 112.

[110] I. S. Kang, Y.-S. Lee, D.-W. Kim, *J. Electrochem. Soc.* **2013**, *161*, A53.

[111] R. S. Assary, J. Lu, P. Du, X. Luo, X. Zhang, Y. Ren, L. a Curtiss, K. Amine, *ChemSusChem* **2013**, *6*, 51.

[112] J. Hassoun, H.-G. Jung, D.-J. Lee, J.-B. Park, K. Amine, Y.-K. Sun, B. Scrosati, *Nano Lett.* **2012**, *12*, 5775.

[113] J. H. Shin, W. A. Henderson, S. Passerini, *J. Electrochem. Soc.* **2005**, *152*, A978.

[114] M. Dollé, L. Sannier, B. Beaudoin, M. Trentin, J.-M. Tarascon, *Electrochem. Solid-State Lett.* **2002**, *5*, A286.

[115] G. B. Appetecchi, F. Croce, B. Scrosati, *Electrochim. Acta* **1995**, *40*, 991.

[116] G. Yu. Aleshin, D. a. Semenenko, A. I. Belova, T. K. Zakharchenko, D. M. Itkis, E. a. Goodilin, Y. D. Tretyakov, *Solid State Ionics* **2011**, *184*, 62.

[117] B. D. McCloskey, A. Speidel, *J. Phys. Chem. Lett.* **2012**, *3*, 997.

[118] B. Gallant, R. R. Mitchell, *J. Phys. Chem. C* **2012**, *116*, 20800.

[119] M. M. Ottakam Thotiyl, S. A. Freunberger, Z. Peng, P. G. Bruce, *J. Am. Chem. Soc.* **2013**, *135*, 494.

[120] J.-B. Park, J. Hassoun, H.-G. Jung, H.-S. Kim, C. S. Yoon, I.-H. Oh, B. Scrosati, Y.-K. Sun, *Nano Lett.* **2013**, *13*, 2971.

[121] R. R. Mitchell, B. M. Gallant, C. V. Thompson, Y. Shao-Horn, *Energy Environ. Sci.* **2011**, *4*, 2952.

[122] B. M. Gallant, D. G. Kwabi, R. R. Mitchell, J. Zhou, C. V. Thompson, Y. Shao-Horn, *Energy Environ. Sci.* **2013**, *6*, 2518.

[123] B. D. McCloskey, R. Scheffler, *J. Phys. Chem. C* **2012**, *116*, 23897.

[124] 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.* **2010**, *132*, 071101.

[125] S. W. Lee, C. Carlton, M. Risch, Y. Surendranath, S. Chen, S. Furutsuki, A. Yamada, D. G. Nocera, Y. Shao-Horn, *J. Am. Chem. Soc.* **2012**, *134*, 16959.

[126] F. Mizuno, K. Takechi, S. Higashi, T. Shiga, T. Shiotsuki, N. Takazawa, Y. Sakurabayashi, S. Okazaki, I. Nitta, T. Kodama, H. Nakamoto, H. Nishikoori, S. Nakanishi, Y. Kotani, H. Iba, *J. Power Sources* **2013**, *228*, 47.

[127] D. Zhai, H.-H. Wang, J. Yang, K. C. Lau, K. Li, K. Amine, L. a Curtiss, *J. Am. Chem. Soc.* **2013**, *135*, 15364.

[128] J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, *J. Electrochem. Soc.* **2012**, *159*, R1.

[129] M. Mirzaeian, P. J. Hall, *J. Power Sources* **2010**, *195*, 6817.

[130] M. Eswaran, N. Munichandraiah, L. G. Scanlon, *Electrochem. Solid-State Lett.* **2010**, *13*, A121.

[131] R. Black, B. Adams, L. F. Nazar, *Adv. Energy Mater.* **2012**, *2*, 801.

[132] J. Lu, Y. Lei, K. C. Lau, X. Luo, P. Du, J. Wen, R. S. Assary, U. Das, D. J. Miller, J. W. Elam, H. M. Albishri, D. A. El-Hady, Y.-K. Sun, L. a Curtiss, K. Amine, *Nat. Commun.* **2013**, *4*, 2383.

[133] Y.-C. Lu, H. A. Gasteiger, E. Crumlin, R. McGuire, Y. Shao-Horn, *J. Electrochem. Soc.* **2010**, *157*, A1016.

[134] Z. Guo, D. Zhou, X. Dong, Z. Qiu, Y. Wang, Y. Xia, *Adv. Mater.* **2013**, *25*, 5668.

[135] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, *106*, 1105.

[136] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787.

[137] X. Guo, N. Zhao, *Adv. Energy Mater.* **2013**, *3*, 1413.

[138] J. Li, B. Peng, G. Zhou, Z. Zhang, Y. Lai, M. Jia, *ECS Electrochem. Lett.* **2012**, *2*, A25.

[139] R. Mi, H. Liu, H. Wang, K.-W. Wong, J. Mei, Y. Chen, W.-M. Lau, H. Yan, *Carbon N. Y.* **2014**, *67*, 744.

[140] H.-D. Lim, K.-Y. Park, H. Song, E. Y. Jang, H. Gwon, J. Kim, Y. H. Kim, M. D. Lima, R. Ovalle Robles, X. Lepró, R. H. Baughman, K. Kang, *Adv. Mater.* **2013**, *25*, 1348.

[141] S. Liu, Z. Wang, C. Yu, Z. Zhao, X. Fan, Z. Ling, J. Qiu, *J. Mater. Chem. A* **2013**, *1*, 12033.

[142] L. Zhong, R. R. Mitchell, Y. Liu, B. M. Gallant, C. V Thompson, J. Y. Huang, S. X. Mao, Y. Shao-Horn, *Nano Lett.* **2013**, *13*, 2209.

[143] Y. Li, J. Wang, X. Li, D. Geng, R. Li, X. Sun, *Chem. Commun.* **2011**, *47*, 9438.

[144] B. Sun, B. Wang, D. Su, L. Xiao, H. Ahn, G. Wang, *Carbon N. Y.* **2012**, *50*, 727.

[145] A. Riaz, K.-N. Jung, W. Chang, S.-B. Lee, T.-H. Lim, S.-J. Park, R.-H. Song, S. Yoon, K.-H. Shin, J.-W. Lee, *Chem. Commun.* **2013**, *49*, 5984.

[146] M. M. Ottakam Thotiyl, S. A. Freunberger, Z. Peng, Y. Chen, Z. Liu, P. G. Bruce, *Nat. Mater.* **2013**, *12*, 1050.

[147] F. Li, D.-M. Tang, Y. Chen, D. Golberg, H. Kitaura, T. Zhang, A. Yamada, H. Zhou, *Nano Lett.* **2013**, *13*, 4702.

[148] J.-J. Xu, D. Xu, Z.-L. Wang, H.-G. Wang, L.-L. Zhang, X.-B. Zhang, *Angew. Chemie Int. Ed.* **2013**, *52*, 3887.

[149] H. Huang, Y. Meng, A. Labonte, A. Dobley, S. L. Suib, *J. Phys. Chem. C* **2013**, *117*, 25352.

[150] G. A. Elia, J.-B. Park, B. Scrosati, Y.-K. Sun, J. Hassoun, *Electrochem. commun.* **2013**, *34*, 250.

[151] M. J. Lacey, J. T. Frith, J. R. Owen, *Electrochem. commun.* **2013**, *26*, 74.

[152] Y. Chen, S. A. Freunberger, Z. Peng, *Nat. Chem.* **2013**, DOI 10.1038/NCHEM.1646.

[153] D. Sun, Y. Shen, W. Zhang, L. Yu, Z. Yi, W. Yin, D. Wang, Y. Huang, J. Wang, D. Wang, J. B. Goodenough, *J. Am. Chem. Soc.* **2014**, DOI 10.1021/ja501877e.

[154] D. Zhang, R. Li, T. Huang, A. Yu, *J. Power Sources* **2010**, *195*, 1202.

[155] S. Ida, A. K. Thapa, Y. Hidaka, Y. Okamoto, M. Matsuka, H. Hagiwara, T. Ishihara, *J. Power Sources* **2012**, *203*, 159.

[156] Q. Li, P. Xu, B. Zhang, H. Tsai, J. Wang, H.-L. Wang, G. Wu, *Chem. Commun.* **2013**, *49*, 10838.

[157] D. S. Kim, Y. J. Park, *J. Alloys Compd.* **2013**, *575*, 319.

[158] W.-H. Ryu, T.-H. Yoon, S. H. Song, S. Jeon, Y.-J. Park, I.-D. Kim, *Nano Lett.* **2013**, *13*, 4190.

[159] Y. Yang, Q. Sun, Y.-S. Li, H. Li, Z.-W. Fu, *J. Power Sources* **2013**, *223*, 312.

[160] M. M. Thackeray, M. K. Y. Chan, L. Trahey, S. Kirklin, C. Wolverton, *J. Phys. Chem. Lett.* **2013**, *4*, 3607.

[161] J. Lu, Y. Qin, P. Du, X. Luo, T. Wu, Y. Ren, J. Wen, D. J. Miller, J. T. Miller, K. Amine, *RSC Adv.* **2013**, *3*, 8276.

[162] C. An, G. Liu, Y. Wang, L. Li, F. Qiu, Y. Xu, C. Xu, Y. Wang, L. Jiao, H. Yuan, *RSC Adv.* **2013**, *3*, 15382.

[163] Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2012**, *3*, 399.

[164] H.-G. Jung, Y. S. Jeong, J.-B. Park, Y.-K. Sun, B. Scrosati, Y. J. Lee, *ACS Nano* **2013**, *7*, 3532.

[165] E. Yilmaz, C. Yogi, K. Yamanaka, T. Ohta, H. R. Byon, *Nano Lett.* **2013**, *13*, 4679.

[166] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **2013**, *135*, 16977.

[167] Y. Lu, H. A. Gasteiger, Y. Shao-Horn, *J. Am. Chem. Soc.* **2011**, *133*, 19048.

[168] Y. Shen, D. Sun, L. Yu, W. Zhang, Y. Shang, H. Tang, J. Wu, A. Cao, Y. Huang, *Carbon N. Y.* **2013**, *62*, 288.

[169] Y. Yang, M. Shi, Q.-F. Zhou, Y.-S. Li, Z.-W. Fu, *Electrochem. commun.* **2012**, *20*, 11.

[170] Y. Lei, J. Lu, X. Luo, T. Wu, P. Du, X. Zhang, Y. Ren, J. Wen, D. J. Miller, J. T. Miller, Y.-K. Sun, J. W. Elam, K. Amine, *Nano Lett.* **2013**, *13*, 4182.

[171] F.-S. Ke, B. C. Solomon, S.-G. Ma, X.-D. Zhou, *Electrochim. Acta* **2012**, *85*, 444.

[172] R. Choi, J. Jung, G. Kim, K. Song, Y.-I. Kim, S. C. Jung, Y.-K. Han, H. Song, Y.-M. Kang, *Energy Environ. Sci.* **2014**, *7*, 1362.

[173] D. Oh, J. Qi, Y.-C. Lu, Y. Zhang, Y. Shao-Horn, A. M. Belcher, *Nat. Commun.* **2013**, *4*, 2756.

[174] A. K. Thapa, T. Ishihara, *J. Power Sources* **2011**, *196*, 7016.

[175] A. K. Thapa, Y. Hidaka, H. Hagiwara, S. Ida, T. Ishihara, *J. Electrochem. Soc.* **2011**, *158*, A1483.

[176] Q. Li, P. Xu, W. Gao, S. Ma, G. Zhang, R. Cao, J. Cho, H.-L. Wang, G. Wu, *Adv. Mater.* **2014**, *26*, 1378.

[177] D. Wu, Z. Guo, X. Yin, Q. Pang, B. Tu, L. Zhang, Y.-G. Wang, Q. Li, *Adv. Mater.* **2014**, *26*, 3258.

[178] W. Fan, X. Guo, D. Xiao, L. Gu, *J. Phys. Chem. C* **2014**, *118*, 7344.

[179] S. S. Zhang, D. Foster, J. Read, *J. Power Sources* **2010**, *195*, 1235.

[180] M. Marinaro, S. K. Eswara Moorthy, J. Bernhard, L. Jörissen, M. Wohlfahrt-Mehrens, U. Kaiser, *Beilstein J. Nanotechnol.* **2013**, *4*, 665.

[181] L. Grande, E. Paillard, G. Kim, S. Passerini, *Int. J. Mol. Sci.* **2014**, *15*, 8122.

[182] M. Marinaro, S. Theil, L. Jörissen, M. Wohlfahrt-Mehrens, *Electrochim. Acta* **2013**, *108*, 795.

[183] D. Wang, J. Xiao, W. Xu, J.-G. Zhang, in *218th ECS Meet.*, **2010**, p. 2010.

[184] O. Crowther, D. Keeny, D. M. Moureau, B. Meyer, M. Salomon, M. a. Hendrickson, *J. Power Sources* **2012**, *202*, 347.

[185] D. Bresser, E. Paillard, S. Passerini, *J. Electrochem. Sci. Technol.* **2014**, *5*.

[186] J. Adams, M. Karulkar, *J. Power Sources* **2011**, *199*, 247.

[187] T. Traußnig, R. Reichelt, V. Wettengel, G. Rauth, M. Dohr, P. Krabb, P. Urch, A. Lukacs, H. Stütz, V. Hennige, in *Kraftw. Batter.*, **2014**.

[188] L. Xu, J. Ma, B. Li, F. Kang, *J. Power Sources* **2014**, *255*, 187.

[189] S. Sunahiro, M. Matsui, Y. Takeda, O. Yamamoto, N. Imanishi, *J. Power Sources* **2014**, *262*, 338.

[190] S. Meini, M. Piana, H. Beyer, J. Schwammlein, H. A. Gasteiger, *J. Electrochem. Soc.* **2012**, *159*, A2135.

[191] Y. Li, J. Wang, X. Li, D. Geng, M. N. Banis, Y. Tang, D. Wang, R. Li, T.-K. Sham, X. Sun, *J. Mater. Chem.* **2012**, 20170.

[192] E. Yoo, H. Zhou, *ACS Nano* **2011**, *5*, 3020.

[193] G. M. Veith, N. J. Dudney, *J. Electrochem. Soc.* **2011**, *158*, A658.

[194] M. Balaish, A. Kraytsberg, Y. Ein-Eli, *ChemElectroChem* **2014**, *1*, 90.

[195] C. Xia, C. L. Bender, B. Bergner, K. Peppler, J. Janek, *Electrochem. commun.* **2013**, *26*, 93.

[196] R. Black, S. H. Oh, J.-H. Lee, T. Yim, B. Adams, L. F. Nazar, *J. Am. Chem. Soc.* **2012**, *134*, 2902.

[197] R. R. Mitchell, B. M. Gallant, *J. Phys. Chem. Lett.* **2013**, *4*, 1060.

[198] Y.-C. Lu, D. G. Kwabi, K. P. C. Yao, J. R. Harding, J. Zhou, L. Zuin, Y. Shao-Horn, *Energy Environ. Sci.* **2011**, *4*, 2999.

[199] O. Crowther, M. Salomon, *Membranes (Basel).* **2012**, *2*, 216.

[200] N. Imanishi, A. C. Luntz, P. G. Bruce, *The Lithium Air Battery : Fundamentals*, **2014**.

[201] J.-G. Zhang, D. Wang, W. Xu, J. Xiao, R. E. Williford, *J. Power Sources* **2010**, *195*, 4332.

[202] B. Wu, M. a. Parkes, V. Yufit, L. De Benedetti, S. Veismann, C. Wirsching, F. Vesper, R. F. Martinez-Botas, A. J. Marquis, G. J. Offer, N. P. Brandon, *Int. J. Hydrogen Energy* **2014**, *39*, 7885.

[203] T. Osaka, T. Homma, T. Momma, H. Yarimizu, *J. Electroanal. Chem.* **1997**, *421*, 153.

[204] Toyota, "Toyota Fuel Cell Cars: Introducing Toyota's fuel cell technology," can be found under http://www.toyota.com/fuelcell/, **n.d.**

[205] Y. V. Mikhaylik, in *Int. Batter. Assoc. Hawaii Batter.*, **2006**.

[206] R. Van Noorden, *Nature* **2013**.

[207] J. S. J.-S. Lee, S. Tai Kim, R. Cao, N. S. N.-S. Choi, M. Liu, K. T. K. T. Lee, J. Cho, *Adv. Energy Mater.* **2011**, *1*, 34.

[208] J.-G. Zhang, P. G. Bruce, X. G. Zhang, in *Handb. Batter. Mater.*, **2011**, pp. 757–795.

[209] D. Buchholz, A. Moretti, R. Kloepsch, S. Nowak, V. Siozios, M. Winter, S. Passerini, *Chem. Mater.* **2013**, *25*, 142.

[210] E. Peled, D. Golodnitsky, R. Hadar, H. Mazor, M. Goor, L. Burstein, *J. Power Sources* **2013**, *244*, 771.

[211] P. Hartmann, C. L. Bender, M. Vračar, A. K. Dürr, A. Garsuch, J. Janek, P. Adelhelm, *Nat. Mater.* **2013**, *12*, 228.

[212] Q. Sun, Y. Yang, Z.-W. Fu, *Electrochem. commun.* **2012**, *16*, 22.

[213] R. Van Noorden, *Nature* **2014**.

[214] S. Sathyanarayana, N. Munichandraiah, *J. Appl. Electrochem.* **1981**, *11*, 33.

[215] J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Zajicek, Y. Kotani, *Energy Environ. Sci.* **2012**, *5*, 5941.

[216] T. Zhang, Z. Tao, J. Chen, *Mater. Horizons* **2014**, *1*, 196.

[217] T. Khoo, P. C. Howlett, M. Tsagouria, D. R. MacFarlane, M. Forsyth, *Electrochim. Acta* **2011**, *58*, 583.

[218] X. Ren, Y. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 2923.

[219] Y. Wang, S. C. Cho, *J. Electrochem. Soc.* **2013**, *160*, A1847.

[220] R. Bernhard, A. Latini, S. Panero, B. Scrosati, J. Hassoun, *J. Power Sources* **2012**, *226*, 329.

[221] B. D. McCloskey, D. Bethune, R. M. Shelby, T. Mori, R. Scheffler, A. Speidel, M. Sherwood, A. C. Luntz, *J. Phys. Chem. Lett.* **2012**, *3*, 3043.

[222] H. Wang, Y. Yang, Y. Liang, G. Zheng, Y. Li, Y. Cui, H. Dai, *Energy Environ. Sci.* **2012**, *5*, 7931.
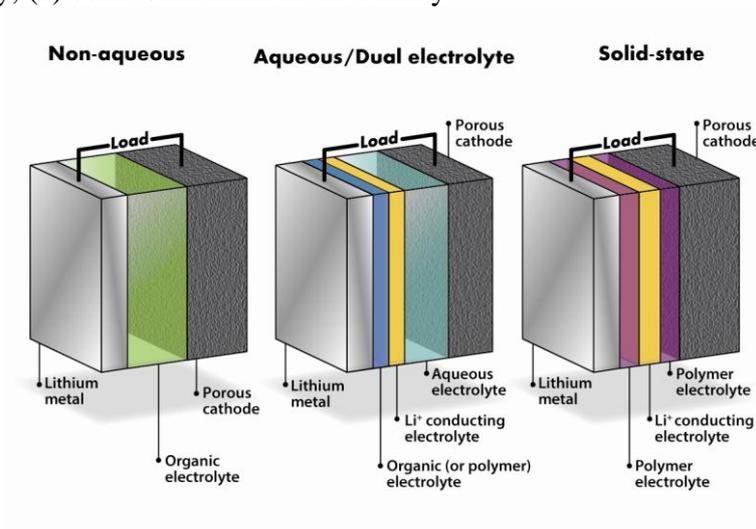
Figure 1: graphical summary of challenges currently faced by Li/air batteries
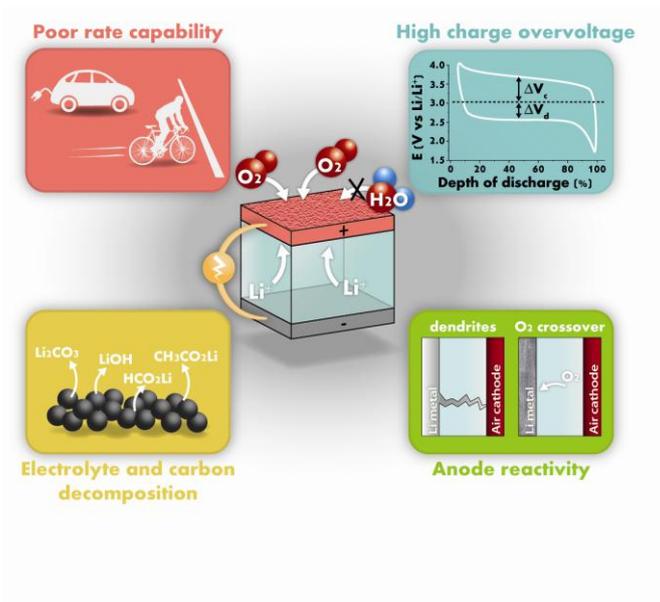
Figure 2: Schemes of a (a) non-aqueous lithium-air battery, (b) aqueous/dual electrolyte lithium-air battery, (c) solid-state lithium-air battery.

Figure 3: Calculated decomposition pathway for propylene carbonate molecule by LiO_2^- from density functional theory. The first step A→B is barrierless. The enthalpy of activation is 23.6 kcal mol^{-1} for C→D but is much below the starting reactants. Note that the addition of Li^+ either in position (a) or (b) results in the formation of structure C.
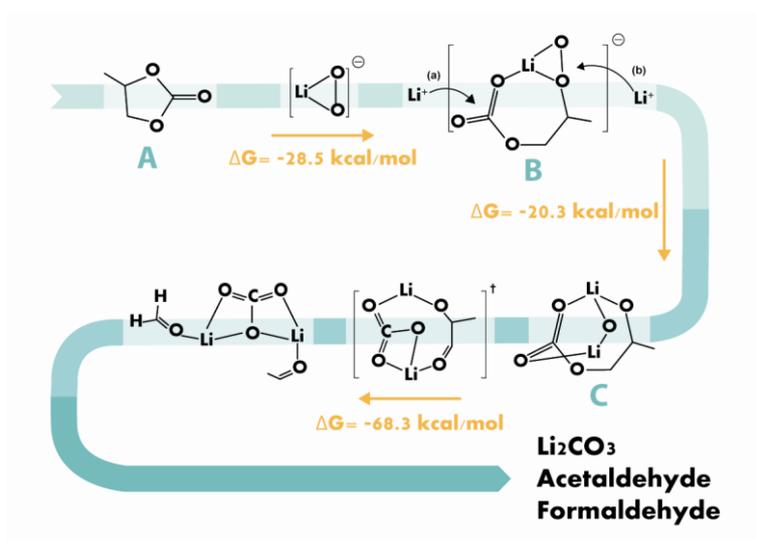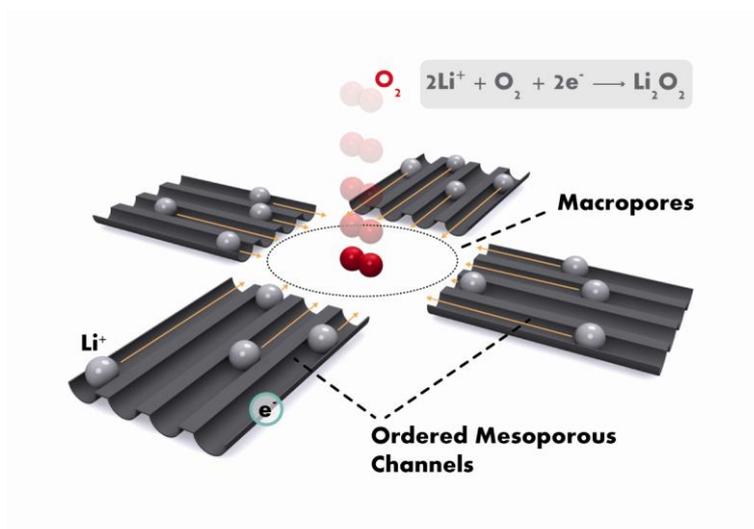

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Figure 4: Voltage profiles of the lithiated-silicon/carbon-oxygen battery at room temperature in a TEGDME-LiCF$_3$SO$_3$ electrolyte. Cycling current: 200 mA g$^{-1}_{carbon}$.
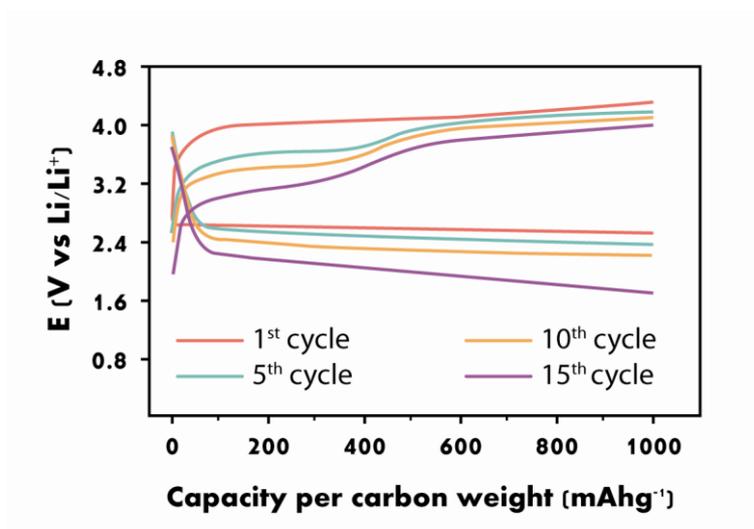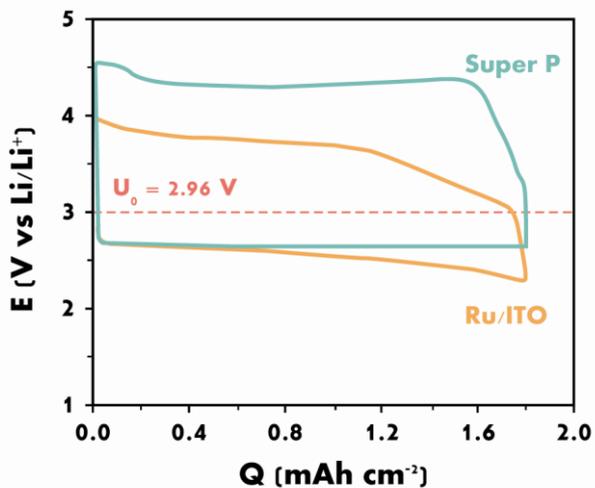

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Figure 5: Schematic illustration of O_2/Li_2O_2 conversion in an ordered hierarchical mesoporous/macroporous carbon catalyst.
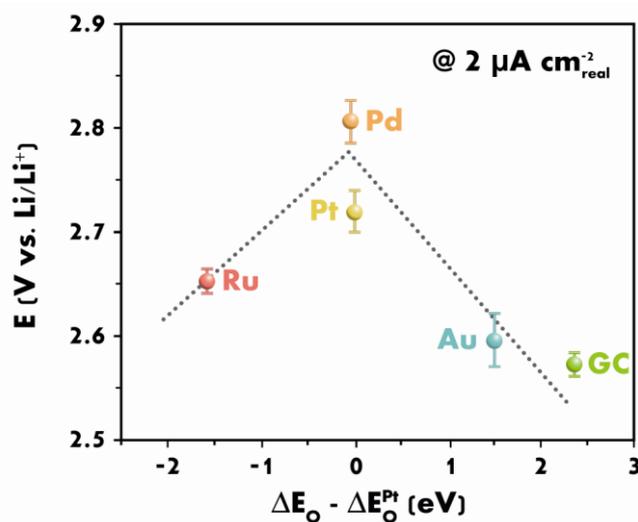

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Figure 6: First discharge-charge curve of Ru/ITO and Super P with an identical limiting capacity of 1.81 mAh cm^{-2} and a 2.3– 4.65 V potential window.


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Figure 7: Nonaqueous Li+-ORR potentials at 2 µA cm^{-2} real as a function of calculated oxygen adsorption energy, ΔE_O (per oxygen atom relative to an atom in the gas phase), relative to that of Pt.
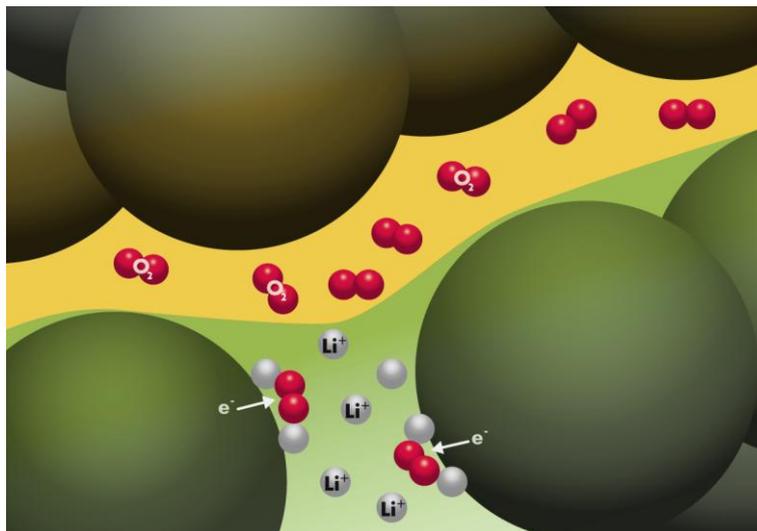

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Figure 8: Scheme of the effect of discharge products on the oxygen flow path upon discharge
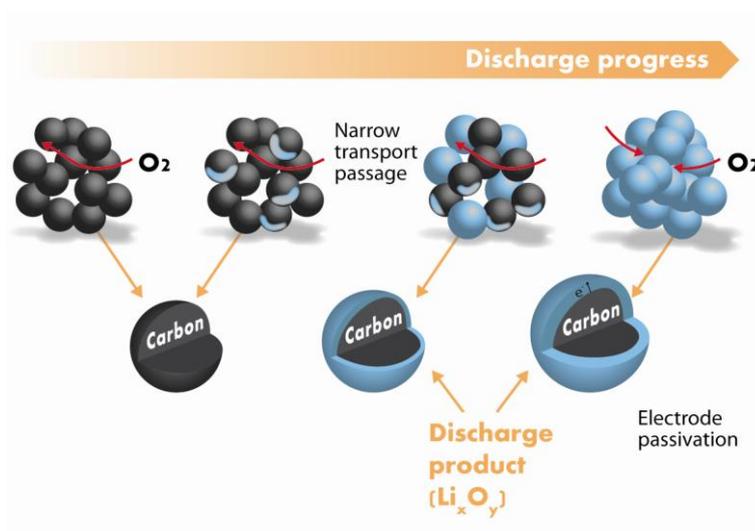
Redrawn from [219] 2013, The Electrochemical Society.

Figure 9: Proposed distribution of perfluorocarbons (yellow) and electrolyte (blue) within the carbon substrate porosity.

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Table 1. List of common solvents in relation to their use as electrolyte media in Li/O$_2$ cells.

Solvent	Stable	Unstable	Ref.
DMSO	√		[88]
ACN	√		[88]
TEGDME	√		[76]
PEGDME	√		[220]
PEO	√		[65]
EC		√	[66]
PC		√	[66]
DMC		√	[66]
EMC		√	[66]
DME		√	[221]
DOL		√	[80]

Table 2. List of materials investigated as catalysts for the OER in Li/O$_2$ cells.

Material	η_{charge} (V)	Discharge depth (mAh g^{-1})	Cycling interval (V)	Current density (mA g^{-1})	Ref.
Pt	0.8	800	2 – 4	250	[7]
Fe$_2$O$_3$	1.3	2700	2 – 4.3	70	[27]
Fe$_3$O$_4$	1.3	500*	2.3 – 4.5	100	[161]
CuO	1.3	1000	2 – 4.3	70	[27]
Pt-Au/C	0.8	1200	2 – 3.8	100	[29]
Nanoporous Au	0.3 - 1	300	2.3 – 4	500	[93]
α-MnO$_2$ wires	1.1	3000	2 – 4.15	70	[23]
Ru-rGO	0.7	5000	2.5 – 4.5	500	[164]
Nanocrystalline pyroclore	1	10000	2 – 4.5	70	[77]
RuO$_2$/CNT	0.6	1700	2.4 – 4.5	10	[165]
MnCo$_2$O$_4$/graphene	1.1	3000	2.4 – 4.3	200	[222]
Co$_3$O$_4$/Ni	0.7	1000	2 – 4.5	12.5	[28]

* specific capacity indicated as per gram of carbon+catalyst

Table 3. Summary of alternative cell chemistries to Li/air for EV applications.

Chemistry	Discharge reaction	Cell voltage (V)	Theoretical energy density (Wh kg^{-1})
Fuel cells	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	1.23	1,000
Li/S	$2\,Li + S \rightleftarrows Li_2S$	2.1	2,567
Zn/air	$2\,Zn + O_2 \rightarrow 2\,ZnO$	1.65	1,084
Al/air	$4\,Al + 3\,O_2 + 6\,H_2O \rightarrow 4\,Al(OH)_3$	2.71	8,135
Na/air	$4\,Na + O_2 \rightleftarrows 2\,Na_2O$	1.95	1,691
	$2\,Na + O_2 \rightleftarrows 2\,Na_2O_2$	2.33	1,605
	$Na + O_2 \rightleftarrows NaO_2$	2.27	1,108
Mg/air	$2\,Mg + O_2 + 2\,H_2O \rightarrow 2\,Mg(OH)_2$	3.1	6,800
K/air	$K + O_2 \rightleftarrows KO_2$	2.48	935
Li/air	$2\,Li + O_2 \rightleftarrows Li_2O_2$	2.96	3,458

Prof. Dr. Stefano Passerini

After graduating from Sapienza University in Rome, he acquired a wide international experience in the lithium battery field as senior scientist at the University of Minnesota and at ENEA in Italy, and as visiting scientist in Japan (Waseda University) and Brazil (University of Sao Paulo). His research efforts have focused on the understanding and development of ionic liquids, polymer electrolytes and electrode materials for lithium batteries. He is co-author of over 240 peer-reviewed publications, several book chapters and patents. He is European Editor of "Journal of Power Sources" and is now Full Professor at the Helmholtz Institute Ulm.

Prof. Dr. Bruno Scrosati

Formerly Full Professor at Sapienza University, he has been Visiting Professor at the Universities of Minnesota, Pennsylvania, Hanyang and at the Helmholtz Institute Ulm. He has received honorary degrees from the Universities of St. Andrews, Chalmers and Ulm. Formerly President of the Italian Chemical Society and of the Electrochemical Society, European Editor of "Journal of Power Sources", he is presently member of the Editorial Boards of various international journals and affiliated with the Italian Institute of Technology. Professor Scrosati is author of more than 500 scientific publications; 30 books and book chapters, and 18 patents. His H-index is 61.

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The recent, large-scale deployment of electric vehicles has fuelled research into high energy density electrochemical storage. However, the question remains as to whether Li/air cells, often termed as the "Holy Grail of batteries", can already put up with the automotive industry requirements. This review will address the matter from an academic and a technological standpoint.

Lithium/air, metal/air, energy storage, electric vehicles.

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The Lithium/air battery: still an emerging system or a practical reality?