A critical review on lithium–air battery electrolytes

Moran Balaish, a Alexander Kraytsberg b and Yair Ein-Eli* a,b

Metal–air batteries, utilizing the reduction of ambient oxygen, have the highest energy density because most of the cell volume is occupied by the anode while the cathode active material is not stored in the battery. Lithium metal is a tempting anode material for any battery because of its outstanding specific capacity (3842 mA h g⁻¹ for Li vs. 815 mA h g⁻¹ for Zn). Combining the high energy density of Li with ambient oxygen seems to be a promising option. Specifically, in all classes of electrolytes, the transformation from Li–O₂ to Li–air is still a major challenge as the presence of moisture and CO₂ reduces significantly the cell performance due to their strong reaction with Li metal. Thus, the quest for electrolyte systems capable of providing a solution to the imposed challenges due to the use of metallic Li, exposure to the environment and handling the formation of reactive discharged product is still on. This extended Review provides an expanded insight into electrolytes being suggested and researched and also a future vision on challenges and their possible solutions.

1. Introduction

The worldwide growing demand for energy, which is increasing at an annual rate of ~2.5%,¹ is spurring the search for highly efficient energy sources, as well as for energy storage devices.

Received 2nd October 2013,
Accepted 19th November 2013
DOI: 10.1039/c3cp54165g
www.rsc.org/pccp
The decomposition of aqueous electrolytes, the considerably high rate of Li corrosion and the serious safety concerns due to H₂ formation in the course of Li reaction with water impeded the investigation and development of aqueous Li-air batteries unless the anode is protected from parasitic reactions. One attempt to deal with the last included a mixed electrolyte system where the lithium metal anode (in contact with the aprotic electrolyte) and the porous cathode (in contact with an aqueous electrolyte) are joined together with a lithium ion-conducting ceramic mediator.

The non-aqueous electrolytes have been the widely investigated systems in the past two decades. Initial work on non-aqueous electrolytes for Li–O₂ batteries focused on organic carbonates, which were later found to be unsuitable as they were susceptible to nucleophilic attack by oxygen reduction species. Special attention was given to ethers, which were proven to be more stable than alkyl carbonates. Nevertheless, upon cycling, capacity fading appeared due to instability of the electrolyte caused by its volatility and parasitic reactions between the oxygen reduction species, the organic electrolyte, discharge products and the carbon surface. Low flammability and low vapor pressure electrolytes with a wide electrochemical window such as ionic liquids are necessary in order to support long-term operation batteries. However, ionic liquids still possess several shortcomings, i.e. low Li⁺ transference number, low Li-salt solubility and moisture susceptibility, which prevent their widespread use.

2. General aspects related to Li–air battery components

Finding a suitable solvent that can withstand long-term operation in a highly oxidative environment and support the full formation and decomposition of Li₂O₂ throughout multiple cycles has proven to be of paramount importance. The effect of solvents on the nature of ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) mechanism in the Li–air battery is well acknowledged as solvents play a key role in determining the nature of discharge products and rechargeability. A suitable solvent will be the one which satisfies certain requirements, being extensively discussed in the next sections of this review.

2.1 Anode-related requirements

Generally, all non-aqueous electrolytes react with lithium and form a film on the anode surface. The point is that some electrolytes make up a passivating film on the electrode surface,

After graduating from Bar-ilan University in 1995, Prof. Ein-Eli worked as a post doctoral fellow at Covalent Associates Inc. located in Woburn, MA, U.S.A. (1995–1997), where he eventually headed the Li-ion research group until 1998. He then proceeded and joined Electric Fuel Ltd. and was appointed Director of Research and Battery Technology. In 2001 he joined the Department of Materials Engineering at the Technion. His current research interests involve materials for batteries, solar processing and corrosion inhibitor studies.
which precludes further reaction; the film has to be sufficiently flexible and cohesive to secure the Li-anode protection. An adequate anode film must also have enough Li⁺-conductivity to ensure smooth Li-plating without dendrites (which is a sine qua non condition for a rechargeable cell). The contact of lithium metal with a polar aprotic solvent leads to the spontaneous appearance of a SEI (solid electrolyte interphase) layer formed by the reductive decomposition reactions of organic solvents slowing down the corrosion of lithium metal; some non-aqueous electrolytes allow Li-metal cycling but Li-deposition is often associated with dendrite formation (which ultimately leads to a short between the anode and the cathode). Tackling these issues is a topic of a large body of research; a good review on the history of the problem may be found in ref. 27.

In the case of Li-air cells, the presence of oxygen, water, carbon dioxide and nitrogen may be expected at the electrolyte/lithium surface; these substances may enter the cell through the air cathode and are able to cross over the electrolyte toward the anode. This implies that, in addition to all of the above considerations, the Li-anode may react with these contaminants, and also oxygen and water may be involved in reactions with the electrolyte at the anode. The only detailed study on these reactions is presented in the case of oxygen reactions with ether- and glyme-based electrolytes at the Li-anode; it may be suggested, though, that other non-aqueous electrolytes are also prone to such interaction with oxygen in the presence of lithium. In this context, CSE (ceramic solid electrolyte) and SPE (solid polymer electrolyte) look attractive since these materials can efficiently block oxygen, nitrogen and carbon dioxide crossover toward the lithium anode (these substances are reactive with lithium); most of the CSE are also impermeable to water, a feature which is crucial in the case of Li-air cells with aqueous electrolytes. In addition, CSE are mechanically strong enough (and substantially stronger than polymer electrolytes) to prevent dendrite growth.

2.2 Cathode-related requirements

2.2.1 In-operando chemical and electrochemical stability of non-aqueous electrolytes. The overall reaction at the air cathode may be represented as \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \) in an aqueous Zn–air cell. Whereas oxygen reduction (ORR) is a complicated multistage process, the bottom line is that finally ORR produces electrolyte components. In the case of non-aqueous electrolytes the result is different; it was demonstrated that common electrolyte solvents, which are used for Li-ion batteries, undergo decomposition reactions with, first of all, the intermediate of cathode oxygen reduction reaction – superoxide anion \( \text{O}_2{^*}^- \); the superoxide is a strong nucleophile in aprotic solvents.

Being a strong base \( \text{O}_2{^*}^- \) can also catalyze autoxidation of (weakly) acidic solvents (Scheme 1); it may be suggested that less acidic aprotic solvents, with higher pKa, are more stable. The electrolytes also can react with oxygen and Li-oxides. All of these reactions are (expectedly) irreversible. An adequate Li-air cell electrolyte should be stable against all of the above reactions.

\[
\begin{align*}
\text{O}_2{^*}^- & + \text{HA} \rightarrow \text{HO}_2{^*}^- + \text{A}^- \\
\text{HO}_2{^*}^- & + \text{O}_2{^*}^- \rightarrow \text{HO}_2^- + \text{O}_2 \\
\text{HO}_2^- & + \text{HA} \rightarrow \text{H}_2\text{O}_2 + \text{A}^- \\
\text{A}^- & + \text{O}_2 \rightarrow \text{A}^* + \text{O}_2{^*}^- \\
\text{A}^* & + \text{O}_2 \rightarrow \text{AOO}^- \\
\text{AOO}^- & + \text{O}_2{^*}^- \rightarrow \text{AOO}^- + \text{O}_2 \\
\text{AOO}^- & + \text{O}_2{^*}^- \rightarrow \text{oxidation products}
\end{align*}
\]

Scheme 1 Mechanism of superoxide-induced autoxidation of weakly and moderately acidic C–H acids.

2.2.2 In-operando physical stability of non-aqueous electrolytes. The cathode of a metal–air battery is open to the ambient atmosphere and thus the low evaporation rate of electrolytes is a crucial parameter that dictates the choice of the electrolyte for Li-air cells. Most of the common Li-ion cell electrolytes have considerably high solvent vapor pressure and, accordingly, have a high solvent evaporation rate. Fig. 1 gives an idea of evaporation-related electrolyte losses of coin-type Li-air cells with various electrolytes.

The data demonstrate that the cell with even the least fugitive common organic solvent (butyl diglyme) loses 22% of its electrolyte in a year. Electrolyte loss can be compensated by including excess solvent, but the cost in terms of volume and mass may be too high. Implementation of gel-type electrolytes and ionic liquid-based electrolytes may be beneficial because Li-air cells with these electrolytes would retain the electrolyte substantially longer than cells with common organic electrolytes.
Indeed, saturated vapor pressure of ionic liquids such as 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide \([\text{C}_n\text{C}_{1}\text{im}[\text{Ntf}_2]\] with \(n = 2, 3, 4, 5, 6, 7, 8, 10, 12\) ranges from 7.42 \times 10^{-17} \text{ bar} \) to \(2.45 \times 10^{-14} \text{ bar}\) vs. \(3.48 \times 10^{-5} \text{ bar}\) in the case of butyl diglyme (at 25 °C). Accordingly, the evaporation rates of \([\text{C}_n\text{C}_{1}\text{im}[\text{Ntf}_2]\)-based electrolytes are expected to be several orders of magnitude lower than the evaporation rates of butyl diglyme-based electrolytes.

### 2.2.3 Li⁺ ion and O₂ reagents transport issues

It is substantial that each catalytically active cathode site is to be connected to electronic, ionic and oxygen pathways within the porous air-electrode. In the case of air cathodes in aqueous electrolytes, a three phase pore system is formed in the cathode to secure the access of electrolyte species, air and electrons toward reaction sites; this pore system comprises two inter-penetrating sub-systems of hydrophobic and hydrophilic micro-channels (pores). These two sub-systems are interconnected; oxygen is delivered through gas-filled hydrophobic pores while hydrophilic pores transport metal-ions to and from the reaction sites, enabling the oxygen reduction reaction (ORR) to occur at catalytic sites at the three-phase boundary. However, most organic electrolytes present a significant challenge to the operation of Li–air cells as they easily wet all cathode pores while flooding air channels, and hence only dissolved \(O_2\) participates in the actual ORR charge-transfer reaction, occurring in a two-phase boundary reaction zone. Flooding is an undesirable phenomenon occurring in the non-aqueous Li–air configuration, which decreases oxygen accessibility at the cathode reaction centers, resulting in reduced current density. Lastly, oxygen availability is determined by its diffusion in the electrolyte inside the cathode channels and by its dissolution in the electrolyte (Fig. 2). Thus, the ability of aprotic polar solvents to dissolve and transport oxygen is a crucial parameter. The above circumstances suggest that the electrolyte of choice for Li–air cells should also have outstanding \(O_2\)-transport properties and high Li⁺-conductivity.

### 2.2.4 Charge transfer issues

The insoluble Li-oxides are accumulated within the pores of the air electrode. On the one hand, the oxides clog the cathode pore orifices and thus impede the oxygen and Li⁺-transport inside the air cathode; on the other hand, the oxides deposit onto reaction centers and thus impede ORR because of the inhibition of electron transfer (Li-oxides are insulators).

Since Li–air cell charge reaction (OER) involves these insoluble precipitates, it may take place only at the 1D interface between conductive cathode material, the electrolyte and lithium oxides. This causes a high local charge current density, which, in turn, results in a high OER-overvoltage and high charge resistance.

The implementation of electrolytes enabling dissolution (at least partially) of Li-oxides may increase the charge current rate (and thus decrease charge overvoltage) by substituting 1D OER-interface \([\text{solid product}] / [\text{conductive cathode}] / [\text{electrolyte}]\) for 2D OER-interface \([\text{dissolved product}] / [\text{conductive cathode}] / [\text{electrolyte}]\). Also, such electrolytes may alleviate clogging of the cathode pore system and also decrease deactivation of the cathode/electrolyte interface.

### 3. Current electrolytes employed in non-aqueous Li–air cells

#### 3.1 Alkyl carbonates

Despite having not enough low vapor pressure, organic carbonates were attractive electrolytes to start with because most of the research on Li-metal anodes was conducted using such electrolytes. Different crown ethers have been used as co-solvents in carbonate-based electrolytes to lower the overall electrolyte viscosity, reduce the resistance of ion transport and increase discharge performance. Various additives were developed, which alleviate dendrite formation and prevent the electrolyte reaction with Li-metal by improving the solid electrolyte interface (SEI) layer. But, unlike Li-ion batteries, the oxygen-rich environment in Li-air batteries dramatically influences the stability of carbonate-based electrolytes precluding their practical use. It turned out that organic carbonates are prone to nucleophilic attack by the superoxide radical.

![Fig. 2 Energy density, power density, and specific capacity as a function of the solubility factor $S$ of $O_2$ (left) and the oxygen mobility (right); $S$ is determined as the gas concentration ratio at the gas/electrolyte border, i.e. $C_{O_2}^{E}$, $S$, $C_{O_2}^{E}$; here $C_{O_2}^{E}$ is the concentration of $O_2$ dissolved in the electrolyte at the border and $C_{O_2}^{E}$ is the concentration of $O_2$ in the gas phase at the border. Reproduced with permission from the Electrochemical Society.](image-url)
As the organic solvents are chosen to be aprotic in order to prevent disproportionation of the superoxide anion radical into oxygen and hydroperoxide anion via the hydrogen abstraction mechanism, the superoxide radical is solvated to a lesser extent thereby becoming a highly reactive nucleophile. It is believed that an oxygen molecule is reduced to form a superoxide radical anion (O$_2^-$) (reaction (1)). The superoxide radical anion is solvated by the solvent molecule surrounding it. According to W. Xu et al., the solvated superoxide radical anion can coordinate with a Li$^+$ ion to form LiO$_2$ (reaction (2)) and/or attack a solvent molecule by the nucleophilic mechanism (reaction (3)), as depicted in Scheme 2.

$$\text{O}_2 + e^- \rightarrow \text{O}_2^-$$  \hspace{1cm} (1)

$$\text{O}_2^- + \text{Li}^+ \rightarrow \text{LiO}_2$$  \hspace{1cm} (2)

$$\text{O}_2^- + \text{solvent} \rightarrow \text{(solvent-O}_2^-$$ \hspace{1cm} (3)

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$$  \hspace{1cm} (4)

$$\text{LiO}_2 + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{O}_2$$  \hspace{1cm} (5)

A computational study of the decomposition mechanism of organic carbonate-based electrolytes in the presence of superoxide anion radicals showed that the dominant decomposition pathway is by nucleophilic attack of superoxide on the less-hindered ethereal carbon atom of the organic carbonates rather than the attack on the carbonyl carbon atom. The $S_n2$ addition of the superoxide anion radical results in ring opening of the carbonate and the formation of the peroxo anion (ROO$^-$) species which are expected to be even more reactive than the starting superoxide. The combination of XRD, FTIR, and $^1$H NMR spectroscopy (Fig. 3) provided evidence that the carbonate-based electrolytes decompose to form high molecular weight products including lithium alkyl carbonates, C$_3$H$_6$(OCO$_2$Li)$_2$, Li$_2$CO$_3$, HCO$_2$Li, and CH$_3$CO$_2$Li, with hardly any evidence of Li$_2$O$_2$ for all DOD (from 2.8 V to 2.0 V).

It can be hypothesized that if the formation of Li$_2$O$_2$ does occur first, it will most probably lead to the formation of Li$_2$O$_2$ via chemical reactions (reaction (4)) and/or electrochemical reactions (reaction (5)), despite the fact that Li$_2$O$_2$ is a strong Lewis base able to degrade carbonates activating hydrogen abstraction and nucleophilic-type reactions to form Li$_2$CO$_3$ and lithium alkyl carbonates. As Li$_2$O$_2$ and carbonate molecules are sufficiently stable, no detection of Li$_2$O$_2$ serves as a strong implication that the superoxide radical anion participates in the nucleophilic attack on the carbonate solvent (reaction (3)) at a faster rate than the coordination of the radical with a Li$^+$ ion (reaction (2)).

McCloskey et al. showed with the use of atom labeling and DEMS analysis that during charging carbonate-based cells, not only a small amount of oxygen was initially evolved and CO$_2$ was the dominant species, but also that electrolyte decomposition was the primary source of CO$_2$ formed during charging rather than the oxidation of lithium alkyl carbonates originating from the reaction between Li$_2$O$_2$ and Li$_2$O$_2$ with the carbonate-based electrolytes. In situ GC/MS analysis revealed that Li$_2$CO$_3$ cannot be oxidized even when charged to 4.6 V vs. Li/Li$^+$, while lithium propylenedicarbonate, lithium ethylenedicarbonate and Li$_2$O$_2$ are readily oxidized, with CO$_2$, CO and O$_2$ released, respectively. Even if alkyl carbonates can be oxidized upon charging, it is still based on electrolyte consumption and decomposition, which is a limiting source in the system and will eventually lead to cell failure. Although high cycle numbers have been reported in Li-O$_2$ cells based on carbonate electrolytes, it was evident from spectroscopic characterization of discharged products and from the analysis of

![Scheme 2 Proposed reaction scheme on discharge with carbonate based electrolytes to explain the formation of Li propyl dicarbonate, Li formate, Li acetate, Li$_2$CO$_3$, CO$_2$ and H$_2$O. Reprinted and modified with permission from ref. 8. Copyright 2013 American Chemical Society.](image-url)
the gas evolved upon charging that the carbonate-based electrolytes cannot serve as electrolytes for the Li–O₂ system as they are susceptible to the attack of the superoxide radical anion during discharge and to oxidation of alkylcarbonates during charging.⁷–¹¹

3.2 Esters

Esters could have been considered a good choice as electrolytes in the Li–air battery. High dielectric constant and low viscosity are the minimal criteria to ensure sufficient salt dissolution. While cyclic esters are uniformly polar (ε = 40–90) but rather viscous (η = 1.7–2.0 cP), acyclic esters are weakly polar (ε = 3–6) but fluid (η = 0.4–0.7 cP);⁷⁴ thus the use of a mixed cyclic–acyclic ester electrolyte could have been a good combination as a polar aprotic solvent in the Li–air battery.

However, the vapor pressure of common esters is considerably high; e.g. γ-butyrolactone has a vapor pressure of ~10⁻³ bar at room temperature⁵⁵ and common esters such as γ-butyrolactone (BL) and methyl formate (MF) are too reactive toward Li metal resulting in low Li cycling efficiency.⁵⁶ A recent computational study on aliphatic esters and lactones¹⁴ revealed that similar to organic carbonate solvents, the superoxide radical nucleophile attacks the ethereal carbon atom in the case of both linear and cyclic esters. Different atomic substitutions were considered to suppress the superoxide nucleophilic attack.¹⁴ The addition of a few methyl groups or other bulkier substituents to the ethereal atom can sterically hinder the nucleophilic attack. However, the stabilizing effect is relatively small and will not prevent solvent decomposition. The attachment of fluorine atoms to the ethereal carbon was considered as a possibility to suppress the nucleophilic substitution on the ethereal carbon, but resulted in lowering of the reaction barrier for the attack at the carbonyl atom. Thus, common organic esters are unstable in the presence of superoxide and could not be used in the Li–air battery.

3.3 Ethers

Ethers and glymes are considered good candidates as solvents for the non-aqueous Li–O₂ battery as they may have a fairly low vapor pressure; e.g. tetraethylene glycol dimethyl ether (TEGME), which is a popular Li–air electrolyte solvent, has a room temperature vapor pressure of ~10⁻⁵ bar.⁵⁷ These compounds also demonstrate substantially higher stability than carbonates as they are less susceptible to nucleophilic substitution by the superoxide anion radical¹⁴ and are stable against oxidation potentials up to 4.5 V versus Li/Li⁺ (but to lower potentials in the presence of Li₂O₂).¹⁰,¹¹,¹⁸ Although ethers were identified as relatively stable electrolytes against nucleophilic attack, the long-term stability is an Achilles heel of these electrolytes as they are prone to autoxidation under oxygenated radicals to be converted into unstable peroxide species (Scheme 3). Furthermore, under ambient atmosphere they are susceptible to slow rate autoxidation⁵⁸–⁶⁰ which could compromise Li–air battery’s cycle life.¹⁸,¹⁹ It is worth considering fluorination at the β-carbon position to improve the autoxidation stability of ethers in order to suppress C–H bond cleavage by O₂, as was indicated by theoretical calculations.⁶⁰,⁶¹

The main product at the first discharge in ether-based electrolytes is Li₂O₂¹¹,¹⁸,²² with negligible amounts of Li₂CO₃, but the proportion of Li₂O₂ diminishes with cycling in favor of a greater share of ether decomposition products.¹¹,¹⁸,¹⁹ to give a mixture of Li₂CO₃, HCO₂Li, CH₃CO₂Li, polyethers/esters, CO₂ and H₂O (Scheme 4), as identified by powder X-ray diffraction,¹¹¹H NMR spectroscopy of the D₂O washed discharged cathode solution, mass spectrometry (MS) and FTIR.¹⁵,²² A recent article²⁰ presented quantitative evidence from isotopically labeled

Fig. 3 (a) Discharge and charge capacity vs. cycle number for a composite electrode (Super P/R-MnO₂/Kynar) cycled between 2 and 4.2 V in 1 M LiPF₆ in PC under O₂. (b) FTIR spectra of composite electrodes. Pristine and after the indicated number of cycles between 2 and 4.2 V at the end of charge. Spectra of Li acetate, formate, and carbonate are shown for comparison. (c) ¹H solution NMR spectrum of a D₂O extract from the composite electrode after 30 cycles at the end of charge. Integration of the areas under the peaks yields a mole ratio of Li propyl dicarbonate–Li acetate–Li formate of 1 : 3 : 1.1 (corresponding to a mass ratio of 1 : 1.09 : 0.32). Reprinted and modified with permission from ref. 8. Copyright 2013 American Chemical Society.
DEMS and XPS studies that during the first discharge Li$_2$O$_2$ was identified as the main product and approximately 5% of the electrochemical deposit was carbonate compounds formed at the cathode interface as a result of the chemical reaction of Li$_2$O$_2$ with the carbon cathode and by the reaction of Li$_2$O$_2$ with the ether electrolyte. These carbonate monolayers cause high interfacial resistance and drive the charging potential to >4 V which leads to electrolyte decomposition and must be eliminated for a feasible rechargeable Li–air battery. This issue can be tackled by controlling the charge and discharge protocol of a Li–O$_2$ cell.

When discharged to 10% DOD at 0.13 mA cm$^{-2}$, the Li–O$_2$ cell demonstrated over 40 cycles during which 100% coulombic efficiency was achieved (Fig. 4).$^{22,62}$ In the protocol, the cells were charged using a constant mode of 4.2 V as a cutoff and discharged at 2.5 V with a discharge capacity limitation of 500 mA h g$^{-1}$.

The influence of the chain length of linear ethers on Li–air cells was investigated by different ex situ characterization methods (FTIR, NMR, PXRD). In the case of diglyme, triglyme, and tetraglyme, PXRD data indicated that Li$_2$O$_2$ was the primary discharge product while FTIR data revealed extensive electrolyte decomposition, with triglyme being more susceptible to polyethers/esters formation. While slight variation in electrolyte decomposition products was observed between different linear-chain ethers, overall, the same products were obtained for different chain length ethers, i.e., Li$_2$O$_2$, Li$_2$CO$_3$, HCO$_2$Li, CH$_3$CO$_2$Li and polyethers/esters. Similar decomposition products were observed by PXRD, FTIR and NMR spectroscopy for cyclic ethers such as 1,3-dioxolane and 2-methyltetrahydrofuran.$^{18}$
The tetraglyme is a preferable choice for cycling studies due to its low volatility as opposed to lower molecular weight linear chain ethers. This polar solvent displays a high lithium salt solubility and a fairly wide electrochemical window.

### 3.4 Nitriles

Oxygen reduction in acetonitrile has been studied for several decades indicating a one-electron reduction reversible diffusion-limited step to the superoxide ion in the presence of 0.1 M n-Bu4NClO4 and further reduction to the highly unstable peroxide species.63–65 Although acetonitrile has a relatively high vapor pressure of $9.7 \times 10^{-2}$ bar at 20 °C,66 CH3CN has been considered as the electrolyte in the Li-air battery. In situ spectroscopic SERS on Au provided evidence that the reduction of O2 in the presence of Li2 ions first forms O2−, which further disproportionates to Li2O2 and O2. Upon oxidation, Li2O2 was found to decompose directly in a one step process to Li+ + e− + O2 and not pass through LiO2, as was indicated by the use of SERS and DEMS.67 Computational studies indicated that nucleophilic substitution at the CH3 carbon is less likely to occur at room temperature than nucleophilic addition at the CN carbon.14 Placing electron-donating groups ortho and para with respect to the cyano group was suggested to increase the nucleophilic stability.61 Although acetonitrile showed sufficient stability towards oxygen reduction species, its high volatility forced the pursuit for alternative nitriles; higher molecular weight aliphatic nitriles, di-nitriles and nitriles with functionalized ether groups were investigated by both computational and experimental techniques.61 Tri-methylacetonitrile (TMA) was identified as a relatively stable electrolyte out of the aliphatic nitrile-based solvents.61 Saying that, the investigation of oxygen reduction in nitrile-based solutions other than acetonitrile is still in its primary stages and the long-term stability of such compounds in the presence of a superoxide ion has not yet been proven.

### 3.5 Amides

Straight-chain alkyl amides, such as N,N-dimethylacetamide (DMA), are one of the few classes of polar, aprotic solvents that can withstand the highly reactive oxygen reaction species in the O2-electrode. N,N-Dialkyl amides are more stable against oxygen reduction species than organic carbonates and ethers/glymes.64,68,69 and have a wide electrochemical stability window up to ~4.2 V in the case of 1 M LiTFSI in DMA.69 But, one should bear in mind that typical amide’s vapor pressure is not low enough (e.g. n-methyl trifluoro acetamide has a vapor pressure of $3.8 \times 10^{-3}$ bar at 25 °C70 and n-methylacetamide has a vapor pressure of $0.5 \times 10^{-3}$ bar at 40 °C71). Dimethylformamide (DMF) was investigated as the basis of an electrolyte for the Li-O2 battery. Although DMF was capable of forming Li2O2 upon discharge and it decomposed upon charge, it was revealed that the degree of side reactions increases upon cycling with the accumulation of Li2CO3, HCO2Li and CH3CO2Li in the cathode (Scheme 4). Li2CO3 is not completely oxidized on charging and accumulates upon cycling, sealing the cathode orifices causing capacity fading.68 No difference in the nature of electrolyte decomposition was observed, even when different lithium salts were investigated in DMF and when the Super P carbon cathode was replaced with nano-porous gold. Similar results were obtained in the case of DMA and N-methyl-2-pyrroliodine (NMP).68 At the anode, a stable SEI film is acute for the operation of the Li electrode in a rechargeable Li-O2 cell; however the high reactivity of N,N-dialkyl amides towards Li-based negative electrodes led to an unstable solid-electrolyte interphase (SEI) on the anode resulting in a rapid solvent decomposition. A vigorous reaction between the electrolyte and the Li metal electrode results in the formation of soluble decomposition products that are oxidized at the cathode surface upon charging. The above-mentioned reasons prevented the application of such promising solvents in Li–O2 batteries. Different approaches have been taken in order to enhance the interfacial stability of the straight-chain alkyl amides with Li anodes. The usage of lithium nitrate (LiNO3) as an electrolyte in DMA stabilized the SEI on the Li metal surface and demonstrated low overpotential (~10 mV) for plating and stripping Li in the LiNO3/DMA electrolyte with little drift in the voltage profile. In addition, it sustained reversible cycling for over 2000 h (>80 cycles) at a rate of 0.1 mA cm$^{-2}$, retaining >95% capacity (Fig. 5).69 The discharge products in the 1 M LiNO3/DMA electrolyte were identified as Li2O2 by XRD.

The addition of fluorinated amides for SEI stabilization was found to be a promising method for improving the stability of the unprotected Li anode.72 Different types of fluorinated solvents were investigated in order to improve the lithium/electrolyte interface. Partially fluorinated organic solvents have shown higher cycling efficiencies in lithium batteries as the surface film formed on Li metal in these solutions was found to be homogeneous and uniform.73,74 A recent study61 showed that an electrolyte comprised of 0.5 M LiTFSI in 98% DMA and the addition of 2% of fluorinated amide, i.e. N,N-dimethyl-trifluoroacetamide (DMTFA), supported the formation of a SEI.
layer with low interfacial resistance under static (storage) and dynamic (deposition/dissolution) conditions and good Li cycling properties. However, as opposed to the fairly stable DMA, DMTFA was found to be unstable in the highly oxidative environment of the O₂ electrode. Quantum chemical calculations showed that initial decomposition of γ-fluorinated amides leads to the formation of LiF with little or no activation energy, and hence cannot be considered as the primary electrolyte component for long-term cycling. In addition, the amount of H₂ evolved upon discharge and charge in the case of adding 2% DMTFA was larger indicating Li corrosion.

3.6 DMSO

Recently, several groups have presented results on DMSO-based electrolytes, which demonstrate fair stability of the electrolytes. Although a reversible behavior for ORR and OER in DMSO was demonstrated via the gold electrode in EQCM measurements, different side products (DMSO₂, Li₂SO₃ and Li₂SO₄) were accumulated onto the cathode surface with cycling, when carbon cathodes were used. DMSO decomposition is small but not negligible, especially with increased cycles, which can lead to poor cell performance. It should be taken into account that although DMSO-based electrolytes have demonstrated fair stability against oxygen reduction species, these electrolytes interact with the Li-metal anode and do not demonstrate high Li-cycling efficiency. Also, DMSO vapor pressure is not low enough to guarantee a long battery operation (PᵥaporDMSO ~ 0.56 × 10⁻³ bar). Thus, DMSO seems to be a less suitable solvent for a rechargeable Li–air cell.

3.7 Sulfones

Quantum-chemical calculations suggest that sulfones are stable against O₂ attack and thus are promising electrolytes for Li–air cells; recent experimental studies on sulfolane confirm this suggestion. The issue is that although sulfolane has a fairly low vapor pressure (1.24 × 10⁻⁵ bar at the melting point), it is solid at room temperature (sulfolane m.p. ~ 27 °C; sulfolane-based electrolytes may have lower m.p., though), which is not convenient for Li–air application. It may be rewarding to focus future research on low-melting sulfones, such as e.g. ethylmethoxyethyl sulfone (m.p. 2 °C) and ethylmethoxyethyl sulfone (m.p. < 0 °C).

3.8 Ionic liquids

The first Li–air battery based on a hydrophobic ionic liquid (IL) was reported by Kuboki et al. and introduced new possible classes of tailored electrolytes, which offered a great deal of advantages over traditional non-aqueous electrolytes. Apart from having a negligible vapor pressure, low flammability, high ionic conductivity and superior hydrophobicity, ionic liquids are well known for their wide electrochemical window, since alkyl groups bounded to the N atom are very poor leaving groups making them less prone to O₂ attack (Scheme 5).

Although ionic liquids possess attractive features, they have several shortcomings, as common ILs such as EMIMTFSI have poor Li⁺ solubility and relatively low conductivity. Lithium salt dissolution in ILs is of the utmost importance for the formation of a stable SEI on lithium metal, otherwise the electrochemical window of ILs is narrowed and they become prone to decomposition; common ILs become susceptible to moisture when lithium salt is dissolved in them, eliminating their use for prolonged Li–air battery operation. In order to prevent the tarnishing of lithium in the presence of moist air, a hydrophobic ionic liquid-silica-PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene)) polymer composite electrolyte, which served both as an electrolyte and as a moisture barrier, was investigated. While the polymer composite resulted in a membrane which effectively protected lithium from moisture invasion, the addition of silica enhanced the ionic conductivity by creating a higher amorphous phase. The construction of an ionic liquid-composite electrolyte, as opposed to the pure ionic liquid, resulted in a 50% increase in discharge capacity to 3000 mA h g⁻¹ at a current density of 0.02 mA cm⁻² (Fig. 6). The research on ionic liquids as electrolytes in Li–air batteries is still in its primary stages, but the electrochemical behavior of the oxygen/superoxide ion couple in pure room
temperature ionic liquids has been studied for more than a decade.\textsuperscript{90–92} These studies reported different ILs which were capable of supporting the electrochemical generation of a stable superoxide ion when no impurities were present. Recently, a deeper understanding of the oxygen reduction reactions in the presence of Li\textsuperscript{+} ions in ionic liquids was gained by Abraham et al.\textsuperscript{93,94} This study investigated the oxygen reduction reaction mechanism in two different ionic liquids, 1-ethyl-3 methyl imidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI). The reaction mechanism as determined by cyclic voltammetry suggests that Li\textsubscript{2}O\textsubscript{2} is formed from the chemical decomposition reaction shown in Scheme 6 and not from electrochemical reduction of LiO\textsubscript{2}.\textsuperscript{93} This mechanism can be explained by the hard soft acid base (HSAB) theory of Pearson.\textsuperscript{95} Li\textsuperscript{+} is a hard Lewis acid in ionic liquids while O\textsubscript{2} and O\textsuperscript{2} are soft and hard Lewis base, respectively. Thus the chemical decomposition of the unstable LiO\textsubscript{2} to form LiO\textsubscript{2}, \textit{i.e.} hard (Li\textsuperscript{+})–hard (O\textsuperscript{2}) is favorable.\textsuperscript{93}

However, one should take into account that imidazolium-based ILs are not enough at the air cathode,\textsuperscript{96,97} whereas electrolytes based on pyrrolidinium and piperidinium IL-families are fairly stable against peroxide radical attack.\textsuperscript{77,97–100} ILs of the piperidinium and pyrrolidinium families also demonstrate excellent Li-metal cyclability\textsuperscript{101–103} (imidazolium-based ILs are not stable against reduction at Li-deposition potentials and thus cannot be used along with Li-metal anodes\textsuperscript{104}).

On the cathode side, the choice of cathode material for the Li–air battery is crucial. While conventional Super P cathodes show capacities that can be compared to the aprotic Li-air system, cathodes based on SWCNTs and cross-linked network gel (CNG)\textsuperscript{105,106} can obtain a capacity as high as 10 730 mA h g\textsuperscript{–1} at 50% RH (relative humidity). Although the low carbon weight in the case of SWCNT can be pointed out as the reason for significant capacity difference, the π–π interactions between imidazolium ions and the surface of the nanotubes lead to the formation of a hydrophobic gel air cathode which can allow high passage of electrons through the SWNT, high conduction of lithium ions through the IL anchored to the SWNT and passage of oxygen through the cross-linked SWNT/IL network.\textsuperscript{106} The structure of the SWNT/IL cathode can allow the transition from Li–O\textsubscript{2} to Li–air without hampering cell capacity or discharge product type. A recent study based on the SWNT/IL gel cathode with the use of a solid conductor ([Li\textsubscript{1.35}T\textsubscript{1.75}Al\textsubscript{0.25}P\textsubscript{2.7}Si\textsubscript{0.3}O\textsubscript{12}]) delivered a high discharge capacity of 56 800 mA h g\textsuperscript{–1} and 95% coulombic efficiency for charging during one cycle and 2000 mA h g\textsuperscript{–1} discharge–charge capacity for 30 cycles.\textsuperscript{107} However, in this Li–air system, operating in ambient air, the Li\textsubscript{2}O\textsubscript{2} reacted chemically with H\textsubscript{2}O to form LiOH which further reacted with CO\textsubscript{2} to produce Li\textsubscript{2}CO\textsubscript{3}, causing a much higher charging overpotential.

Having the above-mentioned attractive features, IL-based electrolytes have some serious drawbacks, which are to be tackled. Namely, most of ILs have low Li\textsuperscript{+}-transfer numbers (<0.12\textsuperscript{108}), and many ILs have low Li-salt solubility and low conductivity (which substantially restricts current rates\textsuperscript{99}). These issues are to be addressed.

4. Compound/engineered electrolytes

Up to now, the above-mentioned electrolytes cannot satisfy all of the above requirements. Although carbonate-based and ether-based electrolytes may offer adequate Li\textsuperscript{+}-transport properties, good Li-salt solubility and Li-anode compatibility, these electrolytes are not sufficiently chemically and electrochemically stable against air cathode processes, and also not sufficiently physically stable. IL-based and sulfone-based electrolytes may offer a fair stability against superoxide species attack and good physical stability but are not always compatible with the Li-anode, often do not have sufficient Li\textsuperscript{+}-conductivity and are frequently solid at room temperature. Also, all of the above electrolytes do not offer practically significant Li-oxide solubility and satisfactory high oxygen and superoxide transport properties.\textsuperscript{106} These circumstances have stirred up interest in the implementation of compound electrolytes (engineered electrolytes, mixed electrolytes, electrolytes with additives, \textit{etc.}); this approach is retracing the development of the Li-ion cell electrolytes from the methodological point of view.

4.1 Blended electrolytes – an attempt to combine the best features, while alleviating components’ drawbacks

It is emphasized above that generally many ILs have outstanding superoxide stability but unsatisfactory conductivity, Li\textsuperscript{+}-transfer number, and too low Li-salt solubility; at the same time many common Li-ion cell organic electrolytes have good conductivity and Li\textsuperscript{+}-transfer number but are not stable against superoxide attack (this is particularly true in respect of carbonates). These circumstances have stirred up interest in the implementation of the blended electrolytes (engineered electrolytes, mixed electrolytes, electrolytes with additives, \textit{etc.}), which contain ILs and common organic electrolytes combining the useful properties of both components; this approach is retracing the development of the Li-ion cell electrolytes from the methodological point of view.
The attempts to combine useful electrolyte features by blending IL and carbonates bear some fruits: the electrolyte, which is the mix of IL [N-propyl-N-methylpyrrolidinium bis[trifluoromethanesulfonyl] imide, PYR14(TFSI) and propylene carbonate in the ratio of 1:1, has demonstrated nearly threefold increase of conductivity (when compared with pure IL), and at the same time IL substantially mitigated PC decomposition (the tested Li–air cell with such a blended electrolyte demonstrated good cycle life but very modest charge performance, though).119 Similarly, the mix of ether and IL (tetraethylene glycol dimethyl ether and PYR14(TFSI) demonstrates satisfactory conductivity and improved electrolyte stability (when compared with a TEGDME-based electrolyte).111

4.2 Electrolytes enabling dissolution of Li-oxides

There are several attempts to prepare electrolyte additives that would be able to dissolve products such as Li2O2 and/or Li2O. Some boron compounds, such as boron esters of general formula Y-C((CH2O)(Z1O)(Z2O))B, Y → CH3 or NO2 and Z1,2 → CH2 or CO, 112 tris(pentafluorophenyl) borane (TPFPB) and its derivatives113,114 were tested. It was found that the introduction of these compounds imparts the ability to dissolve Li-oxides in non-aqueous electrolytes. There is not much information on the behavior of such compound electrolytes in Li-air cells. It was found that although TPFPB enhances the Li-oxide solubility it decreases air cathode accessibility for oxygen and increases electrolyte viscosity.40 Recently it was demonstrated that the addition of TPFPB also has a positive impact on ORR and OER. It substantially reduces the charge voltage of the Li–air cell by rendering solubility to Li2O2. It was found that oxygen transport effectively occurs in TPFPB-containing electrolytes in the course of charging and Li2O2 again appears on the Li-electrode, ORR usually involves the dissolved oxygen.37 At the same time, oxygen solubility and diffusivity are insufficiently low in most of the common organic electrolytes and ionic liquids11,14,167–119 and these low values compromise power performance and also indirectly degrade cathode energy performance because low oxygen transport results in non-homogeneous pore filling with Li-oxide and thus clogging of cathode pore orifices.43,120,121 The importance of oxygen solubility and oxygen mobility is clearly illustrated in Fig. 7 and 8.

The first approach involves IL modification so as to increase O2-solubility; the driving force behind the attempt is the well-known stability of IL against O2•−. It was demonstrated that O2-solubility of IL may be enhanced by choosing a suitable anion (at the expense of a decline in oxygen mobility, though; see Scheme 7).119 The authors of this study have suggested that the reason for the increase in O2-solubility is the increase in fluorne content in the IL anion (in an allusion to perfluoro-carbons – the excellent O2-solubilizers119); there is a possibility, though, that in this case the improvement in O2-solubility originates from the increase in the size of anions124 (the sizes of the anions are in the order IM14 > BETI > TFSI).

The second approach attempts to improve oxygen solubility and diffusivity by mixing electrolyte solvents in anticipation that one component would maintain the oxygen transport-related properties and another would maintain the blend conductivity and stability. The approach also has borne fruit; e.g., the O2-transport properties of propylene carbonate were enhanced by mixing it with tris(2,2,2-trifluoroethyl) phosphate (TFP),125 with the best results received for 1.5 ≤ PC/TFP ≤ 2.3. The oxygen transport properties of IL (which is stable against O2•− attack but has low O2-transport properties) were enhanced by mixing it with DMF; the resulting blend had larger O2-mobility than precursor IL.126
The third approach is to blend the electrolyte-forming solvents with materials that are not polar (and thus cannot be the basis of an electrolyte) but have high oxygen mobility and solubility. It looks particularly promising to employ perfluorinated additives (PFCs) because it has been long known that oxygen is very soluble and mobile in these solvents.127,128 Fluorocarbons and their derivatives are well-known for their thermal stability, chemical inertness, and extreme hydrophobicity. The PFC’s low polarizability translates into low van der Waals interactions between PFC molecules, making the liquid PFCs behave like nearly ideal gas-like fluids, easily dissolving gases.129 Indeed, oxygen solubility in perfluorocarbons is 3–10 times higher than the value observed for parent hydrocarbons or in water, respectively.130,131 Saying that, polar electrolyte-forming solvents do not dissolve PFCs, and the blend makes up an emulsion; such electrolytes may be considered as engineered, compound electrolytes. These emulsions demonstrate excellent oxygen absorption and oxygen mobility.132,133 Deyang Qu et al. demonstrated the implementation of even very thin (0.5%) perfluorotributylamine (FTBA) emulsion as an additive for increasing O2-solubility in the [propylene carbonate + LiPF6] electrolyte.134 By the introduction of such compounds the diffusion-limited current of oxygen reduction on the gas diffusion electrode was increased, as well as the operating voltage and discharge capacity (Fig. 9). The electrochemical window of the dual electrolyte incorporating the PFC additive was investigated and no additional electrochemical reaction took place within the voltage windows; unfortunately, the study was conducted using an O2*-− unstable PC-based electrolyte.134

It may be suggested that high O2-diffusion and solubility are useful only inside the air cathode. O2, which is transported toward the Li-anode, reacts with the Li-anode, thus impairing the cell cyclability and increasing anode overvoltage. This suggests that the use of [polar solvent]/[PFC] emulsions as electrolytes is not the most promising approach for applying liquid PFCs. The next approach lies with the idea of a dual cathode pore system with a two-component electrolyte, which is illustrated in Scheme 8. One sub-system of the cathode is to be filled with a highly oxygen-conducting electrolyte component (PFC) and another with a Li+-conducting electrolyte component.

Such a two-component electrolyte system was prepared in Ref. 121 and has resulted in substantial enhancement of the cell capacity (it increased ~50%, see Fig. 10); it was suggested that a dual pore system favors more complete pore filling with oxides because of the prevention of clogging of orifices. An additional advantage of this design is that it does not increase the oxygen diffusion toward the Li-anode.

It is worth mentioning that a comparable two-component electrolyte system was recently offered for an aqueous air cathode; in this case one cathode pore sub-system was filled with air-transporting PFC and another with an aqueous electrolyte.135 This approach may also be related to the attempts at enhancing O2-transport by creating a non-aqueous air cathode with dual pore systems by means of nano-engineering.136,137
5. Solid state electrolytes

All-solid-state batteries are considered competitive alternatives to liquid electrolytes as they offer safe, low cost, durable, flexible and thin profile batteries with a wide operational temperature range, the ability to prevent lithium dendrite formation and possibly longer cycle life batteries. There are two general classes of materials used as solid state electrolytes in Li-air batteries: Li⁺ ion conducting inorganic ceramics and organic polymers. In the solid configuration, not only the electrolyte has high electrochemical stability and is safer with no volatility issues but it can also sustain a 3 phase reaction zone, which is highly important in order to withstand high current rates in Li-air batteries. In the case of Li-air cells, the additional advantage of solid electrolytes is that they provide a substantial barrier against diffusion of ambient gases and moisture toward the Li-anode; also, the cell with a solid electrolyte is resistant against desiccation. These attractive features are the main driving force behind the development of Li-air cells with solid electrolytes. Generally, relatively low conductivity is the most important disadvantage of solid electrolytes for Li-air cells; the implementation of solid electrolytes for Li-air cathodes has additional problems, though. Among these problems are stability against oxygen reduction species, oxygen transport issues and product (lithium oxide) accumulation.

5.1 Solid polymer electrolytes (SPE)

Polymer as an ion conductive medium has been studied since the work of P.V. Wright in the early 1970s but the technological interest in polymers stemmed after M. Armand et al. proposed them as a new class of solid electrolytes in rechargeable solid state batteries. Although numerous polymer systems have been offered for lithium batteries, solid polymer based on poly(ethylene) oxide, PEO, hosting a lithium salt, LiX, e.g. lithium trifluoromethanesulfonate, LiCF₃SO₃, is far the most researched one. While aprotic solvents suffer from limited electrochemical stability and dendrite growth upon lithium deposition, polymers are expected to react slowly due to the absence of convection and diffusion selectivity, thus minimizing the hazard when dealing with the energetically attractive metallic lithium. The polymer–salt complex allows the use of lithium metal as lithium stripping/plating tests indicated excellent interfacial compatibility observed upon lithium oxidation and deposition. However, high internal resistance at room temperature prevents their wide practical use unless inorganic fillers such as ZrO₂, Al₂O₃, SiO₂, TiO₂ and/or anion traps are used in order to increase polymer ionic conductivity, lithium transference number and electrochemical stability.

One should take into account that when incorporating a solvent-free solid polymer as an electrolyte, the reaction takes place at a three phase reaction zone composed of gas (O₂)–solid (electrode)–solid (polymer electrolyte). The only fly in the ointment is the poor contact between the solid electrolyte and the carbon substrate, which can be reconciled by forcing an intimate contact between them through the production of a composite cathode, consisting of the polymer electrolyte and high surface area carbon thus further reducing the internal resistance. In addition, it is worth considering the operation of a high temperature Li-air battery with a solid state polymer electrolyte especially if it is directed to automobile applications where temperature may not be a critical factor. Although solvent-free polymer electrolytes have been incorporated extensively in Li-ion batteries, their implementation in the Li-air system is still in its early stages. Scrosati et al. reported a Li-air system with a high molecular weight PEO-LiCF₃SO₃ based solid state electrolyte. ORR and OER were only 400 mV, the smallest overvoltage achieved so far without the use of a catalyst. A meticulous examination of the electrochemical reactions occurring using potentiodynamic cycling with galvanostatic acceleration (PCGA) revealed that the high stability PEO based electrolyte could have stabilized the new triplet oxygen intermediate (Li₂O₃⁺), which has a much lower potential (2.91 V) than the singlet oxygen (3.9 V).

Although solid polymer electrolytes seem to be a promising alternative for the volatile, low electrochemical stability and poor cycling efficiency organic solvents, the electrochemical...
stability of the very long molecular chain glymes is still questionable as short chain glymes (i.e. TEGDME) were proven to react with lithium oxide species 58–60 and the rechargeability of a solvent-free solid polymer electrolyte system has not been proven, yet.

5.2 Ceramic solid electrolyte (CSE)

Alternative approaches use Li-ion conducting glass ceramic materials as solid state electrolytes especially for high temperature operation. A high Li\(^+\) ion conductivity, high thermal and chemical stability when in contact with lithium metal and high stability in the atmospheric environment are some of the important features ceramic solid electrolytes need to possess in order to allow the operation of an all-solid-state long cycle life Li–air battery. Numerous types of solid state electrolytes based on sulfides, oxides and phosphate compounds were investigated widely in Li-ion batteries. An extensive listing of possible CSE (including monocrystal Si) may be found in ref. 150–153. Only a few of these materials were employed for CSE air cathodes; the most fitted CSE belong to Li–Al–Ge–PO\(_4\) (LAGP) and Li–Al–Ti–PO\(_4\) (LATP) systems, which possess ionic conductivity in the range of \(10^{-4.5} \times 10^{-3}\) S cm\(^{-1}\).\(^{154}\) Some phosphate compounds such as LiGe\(_2\)(PO\(_4\))\(_3\)-based solid solutions are promising candidates to meet the demands described above. The NASICON-type LiGe\(_2\)(PO\(_4\))\(_3\) consists of both GeO\(_6\) octahedra and PO\(_4\) tetrahedra linked by their corners to form a three-dimensional rigid \([\text{Ge}_2(\text{PO}_4)_3]\)\(^{-}\) skeleton structure with cavities and tunnels which support Li\(^+\) ion migration.\(^{152,155,156}\) One of its derivatives is Li\(_{1-x}\)Al\(_x\)Ge\(_{2-x}\)(PO\(_4\))\(_3\) (LAGP) which has relatively high Li\(^+\) ion conductivity (\(\sim 10^{-3}\) S cm\(^{-1}\)) at room temperature and good atmospheric stability.\(^{152,155–158}\) Kumar et al.\(^{157}\) investigated a superionic conductive membrane (glass ceramic) with a chemical composition of Li\(_{1-x}\)Al\(_x\)Ge\(_{2-x}\)(PO\(_4\))\(_3\) (x = 0.5) (LAGP) as a solid state electrolyte for lithium air batteries. It was also suggested that LAGP-type SCE are not mere Li\(^+\)-conductors but also catalyze oxygen ionization and thus Li-peroxide formation, in the following manner; the LAGP can support the adsorption of oxygen molecules on to its surface (reaction (6)), followed by the reduction of oxygen (reaction (7)) and the formation of lithium peroxide (reaction (8)) as suggested by Kumar:\(^{155}\)

\[
\begin{align*}
2\text{LAGP–Li}^+ + \text{O}_2 & \rightarrow 2\text{LAGP–Li}^+\text{:O} \quad (6) \\
2\text{LAGP–Li}^+\text{:O} & \rightarrow 2\text{LAGP–Li}^+ + 2\text{O}^- \quad (7) \\
2\text{Li}^+ + 2\text{O}^- & \rightarrow \text{Li}_2\text{O}_2 \quad (8)
\end{align*}
\]

The mechanism has not yet been validated by spectroscopic means.\(^{134}\) Although the conductivity of the glass ceramic (GC) membrane was as high as \(4.48 \times 10^{-3}\) S cm\(^{-1}\) at 23 °C and \(\sim 4\) S cm\(^{-1}\) at 310 °C,\(^{157}\) the highest conductivity achieved for any solid lithium ion conductor, the high interfacial resistance between Li/GC and GC/cathode prevented the practical use of the solid state ceramic. A polymer ceramic (PC) material with Li\(_2\)O and boron nitride (BN) as dopants inserted on both sides
of the GC electrolyte was found to be suitable for cell impedance reduction and electrochemical compatibility with lithium metal as it served as an anodic charge transfer reaction catalyst, a SEI stabilizer and good media for lithium ion transport (Scheme 9). The polymer electrolyte doped with Li2O between the Li metal and the GC plate prevented the reaction between Li and GC, while the boron nitride (BN) polymer between the GC and the composite air cathode enhanced their contact and prevented the penetration of moisture and CO2. One should take into consideration (1) that in some cases, an increase in the internal resistance of the Li–air battery was observed when a polymer buffer layer was used; (2) the electrochemical stability of the polymer buffer layer especially in high oxidative environments; (3) that the Li2O and BN dopants may react with H2O and CO2 in air. A further decrease in GC/cathode interfacial resistance was achieved with the fabrication of a solid-state composite air cathode prepared from high surface area carbon and ionically conducting LAGP powder as a major component (up to 81.10 wt%) in the cathode, improving the overall cell performance.

Kitaura and Zhou took it one step forward and sintered the composite cathode onto the GC membrane directly to improve the interfacial contact and reduce the impedance of the cell (see Scheme 10).

Although the improved configuration using polymer buffer layers on both sides of the GC electrolyte reduced significantly the overall cell impedance, the rechargeability of this system was reported but hardly proven. More intimate contact (with larger CSE/cathode/oxygen border) may be suggested in the case of cathodes based on carbon nanotubes (CNT); Zhou et al. replaced the high surface area carbon within the composite air cathode with CNTs to make continuous electron conduction pathways and take advantage of their reported catalytic activity. The cell constructed from a Li metal, LAGP and the CNT-ceramic composite cathode operated in ambient atmosphere, showed poor current density, high polarization at moderate current densities and poor cycling performance.

Until now, the solid state Li–air battery is still in its infancy, suffering from low current densities and high overpotential. However, this battery has the potential to operate at moderate and high temperatures, which can be considered as an advantage for electric vehicle applications and can potentially enable better kinetics, resulting in high current densities and lower overpotential. A comprehensive investigation of the solid electrolyte stability (polymer or ceramic) throughout multiple cycles, in the presence of the superoxide radical anion, is still lacking.

6. Li–air with a two-sectional electrolyte compartment

The first Li–air battery based on an aqueous electrolyte was reported in 1976 by Galbraith. However, low practical specific energies owing to severe Li corrosion in aqueous electrolytes and serious safety issues in the course of Li reaction with water led to the abandonment of the aqueous Li–air battery concept. Saying that, the aqueous Li–air battery is a promising system with high solubility of discharge products making the aqueous configuration anode-limited with high practical discharge potential (3–3.3 V). In order to take full advantage of the aqueous electrolyte while minimizing the hazard of lithium when in contact with water, a hybrid electrolyte configuration was suggested (Scheme 11).

Under the proposed scheme, a non-aqueous electrolyte is located at the anode side, an aqueous electrolyte is located at the cathode side, where water soluble discharge products are produced, and a Li-ion conducting glass ceramic membrane is situated between the two different electrolytes. In this

![Scheme 10](image1)

**Scheme 10**  Schematic representation of a CSE-based lithium–air battery with a lithium anode, an intermediate layer (which facilitates Li⁺-transport between CSE and the lithium anode), CSE, which is placed between the anode and the cathode, and a porous SCE–air cathode comprised of a carbon current collector (which may also serve as a catalyst substrate) and CSE particles (adapted and modified from ref. 160).

![Scheme 11](image2)

**Scheme 11** Schematic illustration of an aqueous Li–air battery. Reproduced with permission from the Electrochemical Society.
configuration $O_2$ diffuses into the porous carbon cathode where the oxygen reduction takes place. Simultaneously, lithium metal is oxidized to lithium ion which diffuses through a non-aqueous solution into an aqueous solution through the membrane. As one of the challenges in the aqueous configuration is the elimination of parasitic and dangerous reactions between metallic lithium and water, the protection of the Li metal anode from water is a critical issue for the long term stability of aqueous Li-air batteries. In order to do so, the lithium anode is protected with a water-stable Li$^+$ conducting solid state ceramic glass plate based on NASICON structure. The plate prevents the contact of $H_2O$ and $O_2$ with the lithium metal anode. This configuration showed an extremely long discharge time (~ 500 h) with a capacity of 50 000 mA h g$^{-1}$ (based on the mass of carbon, catalyst and binder) under 0.5 mA cm$^{-2}$ (Fig. 12).\(^{164}\)

The conducting solid state ceramic plate based on NASICON structure of the type $Li_1_x$M$_x$Ti$_2$O$_7$(PO$_4$)$_3$ [(M = Al, Sc, Y, La) (LATP)] with $x \sim 0.3$ and $y \sim 0.2$ was first proposed by Visco et al. in 2004.\(^{167}\) This ceramic plate possesses high water impermeability and good lithium ion conductivity on the order of $10^{-4}$ S cm$^{-1}$ at room temperature.\(^{163,168}\) In addition to LATP, different possible materials have been suggested for the Li$^+$ conducting solid state ceramic glass plate, such as lithium titanium phosphate $LiTi_x$(PO$_4$)$_3$ (LTP) and lithium lanthanum titanates, $Li_{3+x}$La$_{2-3x}$TiO$_3$ (LLTO), in particular $Li_{0.3}$La$_{0.7}$TiO$_3$, which showed superior stability in distilled water and conductivity compared to LATP.\(^{169,170}\) As the LATP plate can react when in contact with lithium metal to produce an insulator phase,\(^{168}\) different materials have been proposed as a solid state interfacial layer between the ceramic plate and lithium metal, such as lithium nitride ($Li_3N$), lithium phosphorous oxyxinitride (LiPON)\(^{168,171,172}\) or polyethylene oxide (PEO) with $Li(CF_3SO_2)_2$.\(^{163,173,174}\)

The addition of LiTFSI:PEO$_{20}$ (or LiTFSI:PEO$_{18}$) was found to be a promising barrier between the Li metal and LATP as the formation of dendrites during lithium deposition, which limits the use of lithium metal as the anode, occurs to a lesser extent in polymer electrolytes as opposed to liquid electrolytes.\(^{173}\) However, the Li-air cell resistance is still mainly due to the interface resistance between the lithium anode and the buffer layer as well as the interface resistance between the buffer layer and LATP.\(^{163}\) In the case of the polymer protective layer, in order to increase the room temperature conductivity ionic liquids have been added to the polymer leading to an increase in its conductivity to ~ $10^{-3}$ S cm$^{-1}$ at room temperature, i.e. one order of magnitude higher than that without the addition of ionic liquids.\(^{173,175}\) Alternatively, finely dispersed nano-sized BaTiO$_3$ can be added to the polymer between the lithium anode and the polymer electrolyte.\(^{176}\)

The LIPON-coated LATP plate (electrical conductivity at 25 $^\circ$C was about $10^{-6}$ S cm$^{-1}$, ref. 168) was suggested by West et al.\(^{172}\) as a chemically stable layer that can suppress the reaction of LATP and Li metal. The LIPON film was shown to passivate the LATP plates in contact with the lithium metal. However, the addition of a thin film LIPON increased the chemical stability of LATP at the cost of increasing cell resistance.\(^{172}\) The conductivity of the passivated solid electrolyte plates (LATP) was measured to be $10^{-3}$ S cm$^{-1}$ with an electrochemical stability window of 0–5.0 V versus Li/Li$^+$. The plates were capable of supporting electrochemical plating and stripping of Li metal,\(^{172}\) even when an Al thin film was sputtered on the LIPON and LATP plate surfaces in order to make a good contact between the Li metal foil, the LiPON film and the LATP plate.\(^{168}\)

The aqueous Li-air battery can be divided into two categories depending on the type of electrolyte used at the cathode side. In the case of basic electrolytes (eqn (10)) the LiOH discharge product is deposited at the cathode surface and dissolved in water. The solubility of LiOH in water is 12.5 g of LiOH/100 g of $H_2O$.\(^{161}\) Above this concentration LiOH will precipitate at the cathode, eventually blocking all cathode pores, unless additional $H_2O$ is introduced to the system. In both acidic and basic electrolytes, the higher the solubility of discharge products, the higher the energy density of the battery.

\[4Li + O_2 + 4H^+ \rightarrow 4Li^+ + 2H_2O \text{ (acidic media)} \quad (9)\]

\[4Li + O_2 + 2H_2O \rightarrow 4LiOH \text{ (alkaline media)} \quad (10)\]

In the case of basic electrolytes, the $OH^-$ concentration in the electrolyte is increased at a higher depth of discharge, impairing the long term cycling of the LATP plate, which is not stable in strong alkaline or acidic media. In alkaline solutions (pH $\geq 10$), a high resistance phase segregates at the LATP plate’s grain boundary and the electrical conductivity decreases significantly.\(^{177}\) High concentration of Li$^+$ ions leads to low dissociation of LiOH resulting in pH values which are less than 10 and to high stability of the LATP plate. For long-term operation of the aqueous Li-air system, LATP should have high chemical stability in saturated basic/acid aqueous solutions as well as in organic solutions. Although LATP was found to react with water when immersed in water for 1 month and
form a resistive layer, the conductivity degradation by the reaction with water was not significant.\textsuperscript{168} Extensive research has been conducted on the stability of LATP in neutral (LiCl, LiNO\textsubscript{3}), alkaline (LiOH), acidic (HCl) and buffer acidic (CH\textsubscript{3}COOH–H\textsubscript{2}O–LiCH\textsubscript{3}COO) environments.\textsuperscript{169,173,178} It was found that the stability of LATP depends on the pH value of the solutions. Whereas in acidic and basic environments the LATP corrodes rapidly, at pH values from \(\sim 4\) to \(10\) the lithium conducting solid electrolyte shows high stability.\textsuperscript{163,169,173,177,178} Although acetic acid and formic acid are considered as weak acids, acetic acid was found to be a good candidate for an electrolyte in the aqueous Li–air system while formic acid was found to decompose at low potentials.\textsuperscript{178}

Imanishi et al. reported a Li–air battery consisting of a Li|PEO\textsubscript{18}LiTFSI|LATP|HOAc–H\textsubscript{2}O–LiOAc (saturated)|Pt catalyst–air cathode with a discharge–charge capacity of 250 mA h g\textsuperscript{-1} (based on the weight of HOAc) within 15 cycles with a low overpotential of 0.75 V (they reported a rechargeable Li–air battery with an expected practical energy density of more than 400 W h Kg\textsuperscript{-1}, twice the practical energy density established for graphite/LiCoO\textsubscript{2} batteries).\textsuperscript{163} During long term operation of the battery through multiple discharge–charge cycles, the evolution of O\textsubscript{2} can destroy the porous catalytic electrode; hence Zhou et al. employed an additional positive electrode in the charge process.

![Scheme 12 Structure and operating principle of the proposed rechargeable lithium–air battery, with an aqueous/LISICON/non-aqueous hybrid electrolyte design.\textsuperscript{165} Copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

Table 1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl carbonates</td>
<td>PC, EC, DMC</td>
<td>(~10^{-3} - 10^{-2})</td>
<td>1</td>
<td>Prone to nucleophilic attack</td>
<td>7, 8, 10, 11, 13, 17, 44–52</td>
</tr>
<tr>
<td>Ester (lactones)</td>
<td>(\gamma)-Butyrolactone ((\gamma)-BL)</td>
<td>(~10^{-5})</td>
<td>2</td>
<td>Not suitable for a rechargeable Li–air system</td>
<td>14, 54–56</td>
</tr>
<tr>
<td>Ethers</td>
<td>Tri/tetraethylene glycol dimethyl ether</td>
<td>(~10^{-5})</td>
<td>1</td>
<td>Relatively stable against nucleophilic attack</td>
<td>10, 11, 14, 18, 19, 57–62</td>
</tr>
<tr>
<td>Nitriles</td>
<td>Acetonitrile (ACN)</td>
<td>(~10^{-1})</td>
<td>3</td>
<td>High volatility</td>
<td>61, 63–66</td>
</tr>
<tr>
<td>Amides</td>
<td>(N,N)-Dimethylacetamide (DMA)</td>
<td>(~10^{-3})</td>
<td>2</td>
<td>- Withstand the highly reactive oxygen reaction species</td>
<td>61, 68–74</td>
</tr>
<tr>
<td></td>
<td>Dimethylformamide (DMF)</td>
<td></td>
<td></td>
<td>- Stable solid-electrolyte interphase (SEI) unless fluorinated amides are used</td>
<td></td>
</tr>
<tr>
<td>Sulfoxides</td>
<td>DMSO</td>
<td>(~10^{-3})</td>
<td>2</td>
<td>- Solvent experiences oxidation by oxygen reduction species and lithium oxides</td>
<td>21, 75–82</td>
</tr>
<tr>
<td>Sulfones</td>
<td>Ethyl methyl sulfone (EMS)</td>
<td>Negligible</td>
<td>—</td>
<td>According to computational studies: stable against O\textsubscript{2}^{-1}</td>
<td>14, 83–85</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Based on imidazolium,</td>
<td>Negligible</td>
<td>—</td>
<td>- Usual solids at room temperature</td>
<td>77, 88, 89, 93, 94, 96–100, 104–108</td>
</tr>
<tr>
<td></td>
<td>pyrrolidinium and piperidinium</td>
<td></td>
<td></td>
<td>- Low Li-salt solubility</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Moisture susceptibility</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- SWCNTs are a promising cathode material in this system</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Low ionic conductivity</td>
<td>146–149</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Long-term stability is questionable</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Rechargeability has not been proven yet</td>
<td>138, 157, 159, 160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Low ionic conductivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- High internal resistance</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Rechargeability has not been proven yet</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- High internal resistance</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Long term stability of LATP at (4 \geq \text{pH} \geq 10) is poor</td>
<td>163–178</td>
</tr>
</tbody>
</table>

Although acetic acid and formic acid are considered as weak acids, acetic acid was found to be a good candidate for an electrolyte in the aqueous Li–air system while formic acid was found to decompose at low potentials.\textsuperscript{178}

Imanishi et al. reported a Li–air battery consisting of a Li|PEO\textsubscript{18}LiTFSI|LATP|HOAc–H\textsubscript{2}O–LiOAc (saturated)|Pt catalyst–air cathode with a discharge–charge capacity of 250 mA h g\textsuperscript{-1} (based on the weight of HOAc) within 15 cycles with a low overpotential of 0.75 V (they reported a rechargeable Li–air battery with an expected practical energy density of more than 400 W h Kg\textsuperscript{-1}, twice the practical energy density established for graphite/LiCoO\textsubscript{2} batteries).\textsuperscript{163} During long term operation of the battery through multiple discharge–charge cycles, the evolution of O\textsubscript{2} can destroy the porous catalytic electrode; hence Zhou et al. employed an additional positive electrode in the charge process.
where during the charge process O₂ evolution takes place via the additional electrode (Scheme 12). However, as the solubility of LiOH is low and the concentration of LiOH increases during discharge, Wang and Zhou suggested developing a rechargeable Li-air battery with a cycle operation model, in which the generated LiOH is separated from the system during the discharge process.¹⁶⁴

7. Summary and future vision

There is a long way to go... The possibility of buying off the shelf Li-air batteries within 10–20 years does not seem realistic at the moment. However, the research community should direct efforts towards establishing safe and robust components for such advanced metal–air batteries. The efforts should be mounted in such a way that all of the five major components (anode, separator/membrane, electrolyte, air cathode, and packaging) of the Li-air cell will be investigated and developed concurrently.

Here, we presented the current state of Li-air battery electrolyte development; this overview comprises two parts, summarized and presented in Table 1: non-aqueous electrolytes and aqueous (two-compartment) systems. Up to now, the employed non-aqueous organic electrolytes cannot meet all of the requirements imposed by the rechargeable Li-air cell environment. Whereas carbonate-based and ether-based electrolytes may offer adequate Li⁺-transport properties, good Li-salt solubility and are compatible with the Li-anode, these electrolytes are not sufficiently chemically and electrochemically stable against air cathode processes, and also they are not sufficiently physically stable. IL-based and sulfone-based electrolytes may offer a fair stability against superoxide species attack and good physical stability, but are not always compatible with the Li-anode, often do not have sufficient Li⁺-conductivity and are frequently solids at room temperature. Also, all of the organic electrolytes do not offer practically significant Li-oxide solubility and sufficiently high oxygen transport.

These circumstances have stirred up interest in the compound electrolytes (engineered electrolytes, mixed electrolytes and electrolytes with additives); this approach is retracing the development of Li-ion cell electrolytes from the methodological point of view. It may be suggested that this “engineering approach” would lead to development of hybrid electrolytes comprised of IL-organic solvent mixtures (for safety reasons, the implementation of nonflammable fluoro-organics is preferable); such electrolytes are expected to combine the beneficial features of both components.

When considering two-compartment Li-air cells with an aqueous electrolyte and a solid membrane, particular attention has to be paid to the stability of this solid membrane, which is comprised of Li⁺-conducting material and protects the anode. The other crucial feature is the ability of this membrane to secure congruent Li stripping/deposition upon cell cycling, since the modification of the anode surface (in the course of cycling) may substantially diminish Li anode/electrolyte interface conductivity. The membrane material should be able to conform to the changes of the anode shape and size in the course of the lithium stripping/plating process.

7.1 Food for thought...

Up to now, the studies on the safety of Li-air cells and Li-air battery systems are scantly, where safety should be the highest priority. One would hesitate to introduce to the market a battery system where Li metal and oxygen are brought together, while water may penetrate in... In this relation, it may be useful to change the research paradigm and allocate the safest electrolyte systems first, and then focus on the investigation of chemical/electrochemical/physical properties of these compounds (it is expected that such compounds may be found in the group of nonflammable hybrid IL-fluoro organic mixtures).

Acknowledgements

This research was partially financially supported by The Nancy & Stephen Grand Technion Energy Program (GTEP), the EU FP7 InnoEnergy Program and the Israel Science Foundation (ISF) and Israel National Research for Electric Propulsion (INREP).

References

1 BP GROUP, BP statistical review of world energy, 2012.
This journal is © the Owner Societies 2014 Phys. Chem. Chem. Phys., 2014, 16, 2801--2822 | 2819

PCCP Perspective


