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Review

Review on Li–air batteries—Opportunities, limitations and perspective

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ABSTRACT

Li–air batteries are potentially viable ultrahigh energy density chemical power sources, which could potentially offer specific energies up to $\sim 3000 \text{ Wh kg}^{-1}$ being rechargeable. The modern state of art and the challenges in the field of Li–air batteries are considered. Although their implementation holds the greatest promise in a number of applications ranging from portable electronics to electric vehicles, there are also impressive challenges in development of cathode materials and electrolyte systems of these batteries.

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1. Introduction

Electrochemical power sources based on (anode^{metal}|electrolyte|cathode^{oxygen}) configuration have the highest energy density because the cathode active material (oxygen) is not stored in the battery, but can be accessed from the environment. In past, the development of metal/oxygen power systems was mostly focused on aqueous systems; particularly, Zn–air cell has been studied for many years [1] in view of the fact that its specific

capacity is high as compared with cells based on common battery chemistries.

There is a good reason to give a proper attention to lithium as an anode material for metal/air battery on the ground of an outstanding specific capacity of its anode material (3842 mAh g^{-1} for lithium vs. 815 mAh g^{-1} for zinc and 2965 mAh g^{-1} for aluminium), so it comes as no surprise the appearance of the battery design with Li-anode [2,3]. The theoretical values of Li–O₂ couple voltage in aqueous solutions is fairly high ($E_0 = 3.72 \text{ V}$ in case of acidic electrolyte and $E_0 = 2.982 \text{ V}$ in case of alkaline electrolytes [4]) but decomposition of aqueous electrolyte and a considerably high rate of Li-anode corrosion [5,6] practically prohibit the actualization of batteries with a direct anode–aqueous electrolyte contact.

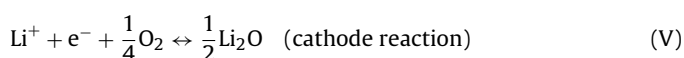
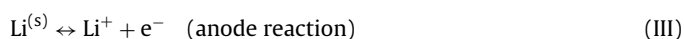
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The first true Li–air system with non-aqueous electrolyte was presented in 1996 by Abraham et al. [7,8]. Such Li–air battery comprises a Li-containing anode (currently Li–metal is used), a non-aqueous electrolyte and an air cathode. Two generally possible energy-producing reactions are



The reversible cell voltage is $E_0^I = 2.959\text{ V}$ for the reaction (I) and $E_0^{II} = 2.913\text{ V}$ for reaction (II) [9,10].

In a real Li–air cell the reactions brake down into anode and cathode parts:



whereas, anode reaction (III) is apparently reversible, the reversibility of cathode reactions (IV) and (V) is not a prerequisite but a condition for the Li–air battery being rechargeable.

The $(\text{Li}^{\text{anode}}|\text{non-aqueous/electrolyte}|\text{oxygen (or air)}^{\text{cathode}})$ arrangement is similar to the common metal–air $(\text{anode}^{\text{metal}}|\text{aqueous/electrolyte}|\text{oxygen (or air)}^{\text{cathode}})$ battery arrangement, but there is also some difference among these two cases; the difference lies in a distinct electrochemistry of the air cathode. Since the discharge products (Li_2O_2 and Li_2O) are insoluble in the non-aqueous electrolyte, and the organic electrolyte easily fills the cathode internal volume, the air cathode is to be considered within the framework of “two-phase reaction zone” instead of a common “three-phase reaction zone” model; this subject is discussed in details below.

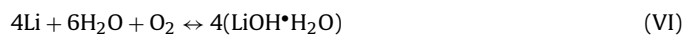
The introduction of non-aqueous electrolytes results in a major suppression of the anode corrosion and also in opening score for a substantial enhancement of Li–air cell voltage (up to a theoretical value), which, in turn, pave the way for a further rise in the cell specific energy. Discussion on Li–air battery design with an electrolyte comprising of two immiscible layers, non-aqueous and aqueous, is followed shortly.

Currently, Li–air batteries are still in the opening development stage, and their actual parameters fall far short of the theoretical values. The highest reported specific energy capacity of a Li–air cell (lab model!) is only 362 Wh kg^{-1} [11] (cp. with 200 Wh kg^{-1} for ordinary market-available Li-ion battery [12]), possessing a specific power of only $\sim 0.46\text{ mW g}^{-1}$ (cp. with 42 mW g^{-1} for ordinary market-available Li-ion battery at 0.2C rate [12]). Also, Li–air cell capacity fades twice after 50 cycles (cp. with 25% capacity fade after 300 cycles for ordinary market-available Li-ion battery [12]). The current status of Li–air batteries suggests that a number of problems would have to be addressed to turn the battery into a viable chemical power source. A good introduction into the principles and current state of development in the field of Li–air batteries was published recently by IBM team [13]. The goals of the present paper are to discuss the specific problems in the field, and to consider possible routes to address these problems.

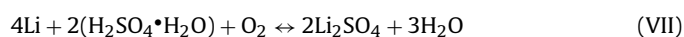
2. Accurate estimate of the actual specific energy and energy density

Whereas Li–air cell capacity is very high per gram of Li (namely, 3861.3 mAh g^{-1} , $11,457\text{ Wh g}^{-1}$ for reaction (I), and $11,248\text{ Wh g}^{-1}$ for reaction (II)), there are factors substantially limiting actual Li–air cell capacity.

The first factor is the electrolyte consumption in course of cathode reaction (in case of two-layer electrolyte design with an aqueous electrolyte being involved), and the second factor is the precipitation of lithium oxides inside the cathode in case of a non-aqueous electrolyte [4]. In alkaline aqueous electrolyte, water molecules are involved in the redox reactions at the air cathode according the equation:



For acidic electrolyte, a conjugate base is involved in the reaction; e.g., in sulphuric acid monohydrate the cell reaction is:



Since the electrolyte is consumed in course of discharge–charge processes, the electrolyte is to be considered as an active material, and it is to be taken into consideration once discussing and defining Li–air cell energy performance. Also, there is no escape from considering weight and volume of the air cathode material, which usually comprises of porous carbon, sometimes with the addition of catalyst.

In alkaline aqueous electrolyte, the maximal Li–air cell specific energy and Li–air cell energy density may be estimated as 1300 Wh kg^{-1} and 1520 Wh L^{-1} , respectively, and in acidic electrolyte, the Li–air cell specific energy and energy density may be estimated as 1400 Wh kg^{-1} and 1680 Wh L^{-1} , respectively (including the electrolyte needed, the carbon cathode with 70% porosity and lithium, but excluding construction materials—current collector, housing, etc.) [4].

Considering a rechargeable Li–air cell with a non-aqueous electrolyte, it is reasonable to assume that only reaction (IV) takes place at the cathode, since reaction (V) is not reversible. As Li–oxide is considered as insoluble in the electrolyte, and precipitating into the air electrode pores occurs, the assumption is made that the discharge terminates if all pore volume of the air cathode turns to be filled or clogged with lithium oxide. The cell capacity in this case may be estimated as 2790 Wh kg^{-1} and 2800 Wh L^{-1} (including carbon cathode with 70% porosity and lithium, but excluding construction materials) [4].

Nevertheless, caution must be exercised in the interpretation of the above maximal energy capacity values for Li–air cell with a non-aqueous electrolyte; these values are calculated with the assumption that lithium oxide is insoluble in the electrolyte and thus, unavoidably precipitate into the air electrode pores. This assumption is not infallible, though, and is open to question. Currently, some electrolyte additives are being suggested, which impart the ability to dissolve (to some extend) Li-oxides in non-aqueous electrolytes [14–18]. It may be speculated that these additives would diminish the adhesion of newly deposited oxide particles to the air cathode material; assuming this, a kind of a Li–air flow cell might be suggested, which may offer the removal of the precipitate from the Li–air cell. By this means, the discharge will not be restricted due to a clogging of the air electrode pores with lithium oxide; therefore, Li–air battery capacity might be extended well over the value of 2790 Wh kg^{-1} . A similar flow design was suggested in Li–air cell design with an aqueous electrolyte (having a film-protected Li-anode), and the air cathode capacity was estimated at $50,000\text{ mAh}$ per gram of carbon at $\sim 3\text{ V}$ [19]. Unfortunately, there is not enough information in the article for calculation of an actual energy performance of this particular Li–air flow system. Up to now, there is no information available regarding kindred flow-type design for Li–air battery with non-aqueous electrolyte. In addition, the energy performance of practical Li–air cells is currently substantially lower than the above numbers, since the weight share of electrolyte is large ($\sim 70\%$ of the whole cell weight), while the weight share of lithium metal and carbon cathode is small ($\sim 11\%$ of the whole cell weight [11]).

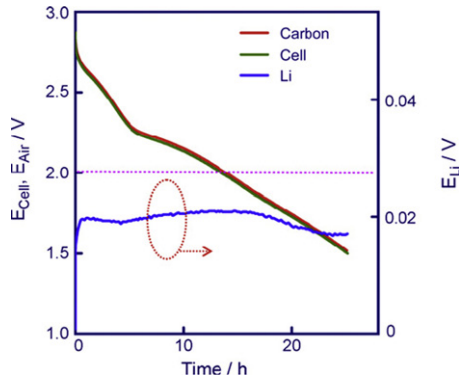


Fig. 1. Li-anode and air cathode potentials vs. Li^+/Li (0.2 mA cm^{-2}) [20]. Li anode potential is shown on the right vertical axes and the corresponding curve is circled; Air cathode potential (left axes) is very close to the overall cell potential (left axes, as well), thus the corresponding curves appear to be fused.

Yet another factor, which restricts Li–air cell energy performance, is that the actual lithium ion activity and the oxygen activity differ from 1, and also that the cell is not under OCV conditions but is delivering a non-zero current to an external load. These issues cause the actual cell specific energy to be lower than the thermodynamically calculated specific energy. Most of the over-voltage is being related to the cathode reaction [20]; the over-voltage, which occurs due to the resistance to mass transfer of reagents to the active sites at the cathode surface, should also be taken into consideration [21]. Giving due consideration for these effects, a noticeable overall cell voltage drops, leading therefore to an additional energy density reduction. As an example, the voltage of a practical Li–air cell drops down from 2.75 to 2.55 V if the current increases from 0.05 to 1 mA cm^{-2} [22].

3. Air cathode challenges

Substantial Li–air cell performance limitations are related to the air cathode. Not only does the cathode reaction deliver the most part of the cell energy, but also most of the cell voltage drop occurs at the air cathode. Fig. 1 presents potential distributions of Li–air cell [20]; the figure shows that the voltage of the anode is constant at a level of about 0.02 V vs. Li^+/Li , while the air cathode contributes to most of the overall voltage drop of Li–air cell. This result suggests that improvement of air electrode is essential for Li–air cell performance enhancement.

It appears that a Li–air cell utilizing a fully non-aqueous electrolyte has advantages over a cell, in which the cathode is in contact with an aqueous electrolyte. This is because of the substantially higher cell capacity; nevertheless, there are some problems, which are specific to air electrode contacting a non-aqueous electrolyte.

3.1. Efficiency of air cathode pore volume

In practice, non-aqueous Li–air cell energy performance falls short of the theoretical value, primarily because the discharge terminates well before all pore volume of the air electrode is filled with lithium oxides. The bulk of the data, which are available up to now, suggest that the reason for this predominant discharge termination is that the precipitate blocks the pore orifices. Thus, O_2 intake and Li^+ delivery to the internal pore volume stop, and the discharge process is being terminated, despite the fact that a substantial fraction of pore volume may be still unloaded with products [22]. It has been found that air electrode pores are far from being filled up with lithium oxides at the end of discharge, and that the discharge was terminated when only a fraction of the total pore volume has been filled with the product. The usable pore volume fraction depends

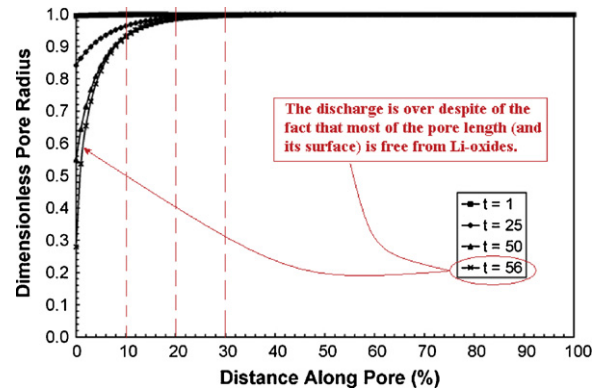


Fig. 2. Dimensionless pore radius vs. pore distance ($i_{\text{geom}} = 0.5 \text{ mA cm}^{-2}$, pore diameter $l_c = 0.07 \text{ cm}$, O_2 pressure = 1.0 atm; the original figure is modified by introducing a textbox and gridlines) [25].

on the conditions and varies from work to work; it was reported that this fraction may be $\sim 47\%$ (1.96 mg cm^{-2} of cathode carbon loading) [23], $\sim 20\%$ (in 14.9 mg cm^{-2} of cathode loading) [11], $\sim 7\%$ [24] and $\sim 3\%$ (12.57 mg cm^{-2} cathode loading) [23]. Calculations demonstrate that under discharge condition, the pores fill up with oxide very unevenly; the bulk of the product precipitate in the area adjacent to the pore orifice, sp., not beyond the distance of 20% of the pore radius from the orifice [25] (see Fig. 2).

The experiments with air electrodes made of carbons with different surface area and with different pore volume but without specially added catalyst, are offering a good reason to suggest that the precipitate is not blocking active charge-transferring centres, but is blocking pore orifices instead. Indeed, it might be expected that the catalytically active centres are evenly distributed over the pore surface area of these carbons, and thus the carbon with larger surface area is expected to have higher filling if the blocking of the active centres is the reason for the discharge termination. The results [24,26–28] have demonstrated, though, that conversely there is no correlation between carbon pore surface area and discharge capacity, whereas there is a strong correlation between average pore diameter and discharge capacity (Fig. 3).

Likewise, the impedance data also support the conclusion that the clogging of the pore orifices is most likely the prime cause for cell discharge termination [29]. The conclusion is also supported

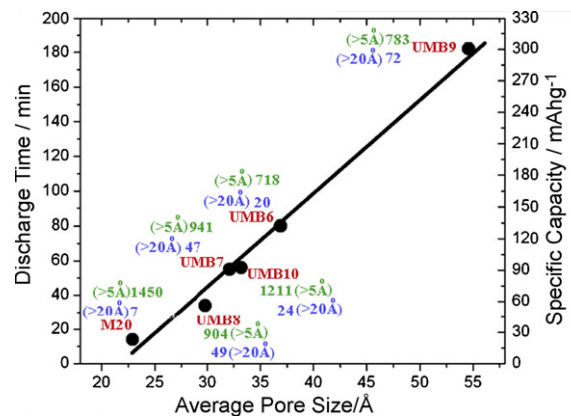


Fig. 3. Discharge time and specific capacity vs. average pores diameter [26]. The original figure is modified by introducing surface area (in $\text{m}^2 \text{ g}^{-1}$) labels; the values are taken from Table 1 in [26]: M20, UMB8, UMB7, UMB10, UMB6 and UMB9 denotes carbon brands; the numbers under the carbon brand labels indicate the pore surface area of the of corresponding carbons; the mark ($>5\text{\AA}$) right after surface area value denotes that this is the surface area of the pores with radii $>5\text{\AA}$ and the mark ($>20\text{\AA}$) right after surface area value denotes that this is the surface area of the pores with radii $>20\text{\AA}$.

with the following reasoning: it may be expected that, in case of active centre blockade, the finer catalytically active centres are dispersed all over the surface, the greater amount of the precipitate needs to block the centres. It was demonstrated that the performance of carbon finely Fe_2O_3 -loaded is similar to the performance of the carbon, just mixed with Fe_2O_3 powder [30]. All things considered, it must not be ruled out, though, that discharge termination may also be linked with the blockade of active reaction sites by the precipitate under some conditions.

From the above line of reasoning, one avenue of Li–air cell energy performance enhancement is linked with the development of new cathode materials which may be able to accommodate a substantial amount of Li–peroxide without blocking the cathode pore orifices (and thus, compromising oxygen and Li^+ transport). The increase in carbon ability to accommodate the precipitate is related to its pore structure; it was demonstrated that a carbon with meso- and macro-sizes pores may accommodate a substantial amount of Li–peroxide precipitate without compromising oxygen and Li^+ transfer [24,26,27]. The calculations give grounds to expect that dual pore system materials are the most promising in terms of energy capacity: the first pore system of the material serves as an oxidation product storage, and the second (venting) pore system transports oxygen; the products do not clog the second pore system and this secures oxygen transport into the inner regions of the air electrode [31]; basically, this approach has been appreciated in a field of gas electrodes for fuel cells [32,33]. To prevent the decay of the power output in the discharge process, a temporal distribution of reactivity in the air electrode was proposed. When coupled with the dual pore configuration, time-release catalysts application results in better air electrode material utilization [31].

The other avenue of air electrode pore clogging prevention is using non-aqueous electrolyte additives, which render solubility to lithium oxide and lithium peroxide precipitates. It was reported that the addition of such Lewis acids as boron-based anion receptors (BBARs) renders solubility to Li_2O and Li_2O_2 [14–16]. Currently, the experimental results on Li–air with addition of tris-(pentafluorophenyl)-borane (TPFPB) are available [17,18]. The approach is seemingly promising, but the presented results reveal some problems. It was found that whereas the addition of TPFPB promotes the dissolution of lithium oxides formed in course of discharge process (and this is favorable to increasing the cell capacity), this additive also increases air electrode flooding and the electrolyte viscosity, at the same time decreasing oxygen solubility, which impairs the cell performance [18]. Also, it was found that the charge transfer reaction, which is $(\text{Li}_2\text{O}_2)[\text{TPFPB}]_2 \rightarrow \text{O}_2 \uparrow + 2\text{Li}^+ + 2\text{e}^- + 2[\text{TPFPB}]$, requires the dissociation of $\text{Li}_2\text{O}_2[\text{TPFPB}]_2$ complex first. This feature hinders the oxidation of oxygen, and thus impedes the charging of Li–air cell [17]. Therefore, it should be pointed out that this promising approach is still in the opening stage of development.

3.2. Air cathode catalyst and Li–air cell performance

The numerous experimental results demonstrate that the catalyst may have triple functions toward increasing the charge (and thus the energy) capacity of the cell, decreasing the cell charge over-voltage [10,30,34–36] and improving cyclability [37].

In the light of the assumption that the charge capacity is limited by cathode pore volume filling with lithium oxides (and also pore orifice clogging), the dependence of the cathode charge capacity in the presence of catalyst needs a consideration. One approach is that in some cases this effect may be associated with the carbon structure modification, occurring during catalyzed carbon preparation. For instance, mechanical mixing (such as ball-milling) substantially (nearly in 20 times) reduces the pore volume of Ketjen black; the

corresponding Li–air cathode capacity is reduced in accordance with the pore volume reduction [28].

Up to now, MnO_2 -based catalyst is considered as having the most favorable combination of activity and price [34], which makes this catalyst the most appealing. The common way to prepare MnO_2 -catalyzed carbon is the mixing of a manganese salt and potassium permanganate solutions in the presence of suspended carbon substrate ($2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$). The porosity of the carbon substrate does not remain unchanged in course of this process. The substrate undergoes modification due to the reaction between the carbon and permanganate. As a result of this reaction, some of closed pores turn to be opened, and some open pores turn to be widened [38,39]. This effect may be particularly distinct after the catalyzed substrate thermo-treatment. As-deposited MnO_2 particles camouflage the pore orifices, but the oxide particles undergo dehydration being heated, and thus shrink and expose more carbon pore volume. This MnO_2 -catalyzed carbon substrate behavior was demonstrated in the study of Cheng et al. [36], which has revealed that charge capacity of the carbon, catalyzed in $\text{KMnO}_4/\text{MnSO}_4$ -process, was superior to the charge capacity of the same carbon catalyzed by mixing with MnO_2 -powder. Also it was found that the thermo-treatment (300°C) enhanced the charge capacity of the $\text{KMnO}_4/\text{MnSO}_4$ -catalyzed carbon; the latter may be understood as the result of dehydration – and hence shrinking – of $\text{KMnO}_4/\text{MnSO}_4$ -prepared MnO_2 particles ($\text{MnO}_2 \times 1.3\text{H}_2\text{O}_{300^\circ\text{C}} \rightarrow \text{MnO}_2 \times 0.26\text{H}_2\text{O}$) [40].

The other avenue of explanation is that the catalyst may alter the morphology of lithium oxide deposits. Admittedly, the information about precipitate morphology is not yet available; nevertheless, it may be suggested that under some conditions, lithium oxide deposits may be dense and pore free, and under other conditions (e.g., the presence of the catalyst) the deposits may be less dense and porous. In the latter case, the reagents (oxygen and Li^+) may preserve the ability to diffuse into the carbon voids through pore orifices occupied with such a porous deposit, thus increasing the pores filling and the discharge capacity.

At this time, there is not much information regarding the mechanism of cathode degradation processes. This makes it difficult to discuss the enhancement of cycle life of Li–air cells with catalyzed cathodes; nevertheless, it may be speculated that the reason of cycle degradation may be the irreversible accumulation of the reaction products in the pores. Indeed, it was demonstrated that reaction (IV) is reversible, i.e., Li_2O_2 undergoes electrochemical reduction in course of charge [41], whereas reaction (V) is irreversible, and Li_2O is commonly considered as being not electrochemically active. Keeping in mind that in course of Li–air cell discharge the actual product comprises of the mixture of Li_2O and Li_2O_2 , and that Li_2O_2 share ranges from ~100% to ~0% depending on the electrolyte and carbon employed [22,42], it may be suggested that the accumulation of Li_2O has a bearing on the cycle degradation of a cathode of a Li–air cell. The hypothetical possibility of the influence of catalyst on $\text{Li}_2\text{O}_2/\text{Li}_2\text{O}$ ratio may be supported by the results of Seriani [43], which bring out the significance of the deposit morphology (which, in turn, might be controlled by the catalyst); namely, it was shown that (at the room temperature) Li_2O_2 are the stable type of lithium oxide if the oxide particles are sized less than 2.5 nm; in this relation, it is interesting to note that in the study [44] Li_2O_2 deposit thickness was estimated at 2 nm.

Despite of the conceptual electrochemical reducibility of Li_2O , Li–air cells without cathode catalyst develop charging voltages substantially higher than that on discharge; commonly, these voltages are above 4.2 V vs. Li/Li^+ [10,30,35,41]. This indicates that recharging the cell involves not only a reduction of lithium peroxide but also electrolyte decomposition (propylene carbonate was used as electrolyte in most of the works, where the charge properties of Li–air electrode were studied) [45,46], letting alone apparently low

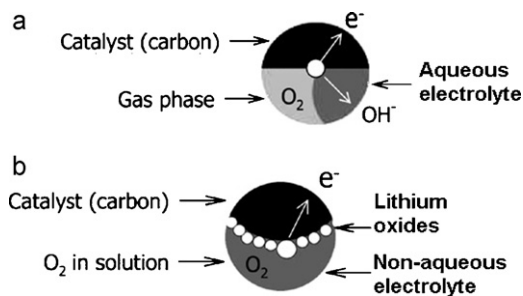


Fig. 4. Models of the reaction zones for catalytic reduction of oxygen: (a) a “three-phase reaction zone” for aqueous electrolyte metal/air battery and (b) a “two-phase reaction zone” for non-aqueous electrolyte Li-air battery (the original figure is insignificantly modified) [20].

energy efficiency of such discharge–charge cycle (the energy cycle efficiency may be roughly estimated as $\eta = V_{\text{charge}}/V_{\text{discharge}}$); typical efficiency was found to be 0.57 for a carbon without catalyst [35].

It was demonstrated that the catalyst implementation provides the possibility of lowering the charge over-voltage (and thus the efficiency enhancement). Up to now, the most serious improvement was attained by implementation of a nano-structured PtAu/C catalyst, which exhibited bi-functional activity. It had not only lowered the charge voltage but had raised the discharge voltage, as well. The resultant discharge voltage was as low as 3.8V and the cycle efficiency was as high as 0.73 at 100 mA g⁻¹ [10,35].

3.3. Non-aqueous electrolyte air cathode flooding

As it was outlined above, air cathode electrochemistry in non-aqueous electrolytes differs significantly from aqueous electrolyte. Common air cathodes for aqueous cells are three-phase systems, which comprise of two interpenetrating sub-systems of hydrophobic and hydrophilic pores. Oxygen diffuses through the gas-filled hydrophobic pores, and hydrophilic pores transport the dissolved ions to and from the reaction sites; flooding of the gas-filled pores reduces the reaction rate substantially because the lesser amount of reaction sites is left accessible for oxygen diffusion. Whereas in case of aqueous electrolytes there are well-developed methods which provide a way to prepare electrodes with hydrophilic catalyst-containing pore sub-system and hydrophobic gas diffusion pore sub-system, most of organic electrolytes may easily wet all electrode pores, thus flooding air channels. The situation suggests that the moderating of air electrode pore flooding may have an impact on Li-air cell performance. There are grounds to believe that electrolytes with high polarity are beneficial for carbon wetting reduction, and that their implementation can moderate, to some extent, the flooding, and can improve air cathode performance [47]; it was demonstrated that the influence of the polarity of electrolyte may even outweigh the influence of viscosity, ion conductivity and oxygen solubility, once these latter properties reach a sufficient level [47].

Recognizing that, most of the carbon pores are flooded while being in contact with a non-aqueous electrolyte, and that the discharge products (Li₂O₂ and Li₂O) are insoluble in these electrolytes and precipitate onto the carbon surface. Thus, such electrodes may be considered within the framework of liquid–solid “two-phase reaction zone” [20], see Fig. 4.

Based on this model, it is clear that only the dissolved oxygen is participating in the charge-transfer reaction, which occurs at the electrolyte–carbon interface and also (to some extent) at the electrolyte–oxide interface [48]. The ability of the electrolyte to transport oxygen toward these interfaces is a feature of prime importance (as long as the air cathode flooding does occur). Such

electrolyte parameters, as oxygen solubility and oxygen diffusion, have a serious effect on the electrolyte ability to secure an adequate rate of oxygen transport, and hence on cell energy capacity (because of pores filling improvement). The implementation of electrolytes with high oxygen solubility and high oxygen diffusivity results in an enhancement of cathode capacity [22,49–51]; these parameters may be adjusted in desirable direction by using mixed solvents and proper lithium salts. Also the quantity of the electrolyte, which the Li-air cell is filled with, substantially affects the capacity of the cell; the dependence of capacity on the electrolyte amount passes through a maximum; the initial cell filling, which support ion conductivity between the anode and the cathode, is about 50 μL per cell, but the maximum capacity is gained if the filling is ~150 μL and then the capacity decreases with further increase of the cell filling [18].

4. Challenges related to the anode and the electrolyte

Lithium metal anodes are anodes of choice for Li-air cells because of their extremely high energy density comparing to common lithium–intercalated carbon anodes; in fact, high energy capacity of Li-air chemistry may be completely compromised once implementation of heavy intercalation anodes is considered. It is a common knowledge that the implementation of lithium metal anodes is associated with dendrite formation (which ultimately may lead to shorts between the anode and cathode), and electrolyte incompatibility (which results in the formation of resistive film barriers onto the anode); these effects compromise cycle life and safety of secondary batteries having Li-metal anodes. Tackling of these problems is a topic of a large body of research (see, e.g., [52–54] and references there; also, Brandt [55] had presented a good review of the history of the problem). The major approach of these studies is the separation of a lithium anode from the liquid electrolyte; the proposed solutions include interfacial or protective layers coated on the metallic lithium; the layers are comprised of polymers, ceramics, or glasses which conduct lithium ions. Other avenue is the implementation of solid polymer electrolyte materials instead of liquid electrolyte; these materials are Li⁺-conductors, being inert toward lithium metal, and prevent dendrites formation. The discussion of the above topic is beyond the scope of this review, and our further consideration is focused on issues, which are particularly related to the practically important ((Li-metal)^{anode}|non-aqueous/electrolyte|(ambient air)^{cathode}) arrangement.

The major challenge is related to the prevention of water and oxygen access to the lithium anode (resulting in anode degradation and posing some serious safety problems). The difficulty stems from the simple fact that most of the common Li-battery grade electrolytes easily absorb a substantial amount of water, and Li-air cells employing such electrolytes may practically have a fair cyclability only being exposed to dry oxygen atmosphere [41]. Electrolyte vapour pressure also plays a substantial role in Li-air cell degradation: since the air electrode is readily permeable for non-aqueous electrolyte, the cell with a volatile electrolyte is prone to desiccating (and, unfortunately, most of the common Li-battery grade electrolytes are substantially volatile).

4.1. The development of hydrophobic electrolytes with low volatility

One way to address the above issue is the implementation of liquid hydrophobic electrolytes, which are based on room temperature ionic liquids (RTIL); such electrolytes also have a fairly low volatility. Up to now, a few considerably hydrophobic RTILs [24] were offered; it was demonstrated that whereas Li-air-cell utilizing

a common Li–battery non-aqueous electrolyte promptly degrades, because of moisture ingress and electrolyte evaporation, the implementation of RTIL-based electrolyte prevents vaporization of the electrolyte and hydrolysis of the anode, and thus delivers a substantial growth of discharge capacity of the cell. Nevertheless, the power performance of Li–air cell employing RTIL-based electrolyte is below the power performance of a cell utilizing a common non-aqueous electrolyte. This may be attributed to low transport and insufficient catalytic properties of the air electrode/RTIL combination.

Other way to address the problem is the implementation of solid (or, at least, gelled) polymer electrolytes—SPE's, which are plasticized by ethylene carbonate/propylene carbonate [7,56] or by RTIL [57,58]. Such electrolytes are expected to be resistant to diffusion of water which penetrates through an air electrode surface from the atmosphere. The conductivity of the implemented SPE lies between 10^{-2} and 10^{-4} S cm⁻¹, which is typical for SPE's commonly used for Li-ion batteries [59].

Thus far, Li–air cells with SPE have not demonstrated a sounding cycle life; this was linked to oxygen crossover from the cathode to the anode through the SPE layer and its further reaction with Li-anode; it was supposed that diminishing of oxygen crossover through the electrolyte toward lithium anode might be helpful in improving the cycle life [58].

4.2. Development of compound electrolytes

It was outlined above, that Li–air cell's energy capacity strongly depends on the electrolyte ability to secure an adequate oxygen flow inside the air cathode, which motivates the implementation of electrolytes having high oxygen solubility and high oxygen diffusivity; this, apparently, is in a conflict with the need to restrict the oxygen access to the lithium anode. The necessity to restrict oxygen access to the anode and yet to maintain an adequate oxygen transport toward catalyst centers of the air cathode have motivated the development of a Li–air cell with a compound electrolyte. In this case, the cell electrolyte compartment comprises of at least two layers with different properties.

The first layer is tight against lithium anode and comprises of thin solid (or gelled) film with adequate Li⁺-conductivity and low water and oxygen permeability. This film may comprise of a SPE with adequate properties [60] and Li⁺-conducting ceramics (LISICON; the NASICON-type ceramics with Li⁺ conductivity) – these types of materials have a favorably low oxygen and water permeability [61,62] – or combination of LISICON and SPE [63–65]. A modification of this approach is to place an additional layer of a non-aqueous liquid electrolyte between the above solid Li⁺-conducting membrane and lithium anode surface [21,66]. The second electrolyte layer is comprised of a fitting aqueous [21,62,65,67], SPE [64,68] or non-aqueous liquid electrolyte [60]. This approach has resulted in designing of Li–air cells which are not subjected to cycle degradation after at least ten cycles [67] and even after 40 cycles [64] have a fair energy capacity.

4.3. Development of compound electrolytes with an aqueous layer

Though, Li–air cell with a non-aqueous electrolyte has theoretically a superior capacity, the implementation of an aqueous electrolyte may also possess some practical merits, because of the better solubility of lithium oxides (and hence, better utilization of the air electrode) and lower air electrode flooding. Generally, considering the implementation of LISICON-type films, there are two major problems to be addressed. First, such materials are not stable enough in alkaline solution in a long-time use [62,65,69]; second, the materials are also not inert enough toward lithium

metal and thus, the LISICON/anode interface conductivity degrades [61,68].

The implementation of acidic aqueous solutions, instead of an alkaline electrolyte may be helpful in preventing the degradation of LISICON-type material. However, in course of a long-lasting discharge, the pH of the aqueous electrolyte grows up, and an acidic (and all the more neutral) solution converts into an alkaline solution. Up to now, two approaches are offered to bypass such a circumstance. One approach [70], involves the implementation of a neutral electrolyte (an aqueous solution of lithium chloride) along with restriction of the cell operation in a deep discharge state, thus preventing the electrolyte alkalization. This approach, apparently, results in compromising Li–air cell performance. The second approach involves the implementation of a buffered electrolyte solution to alleviate the electrolyte alkalization [71]. Particularly, a lithium-protecting layer of a water-stable glass–ceramic Li_{1+x}Ti_{2-x}Al_xSi_yP_{3-y}O₁₂ (LTAP) contacted with an electrolyte, which comprises of an aqueous solution of acetic acid and lithium acetate. The electrolyte had considerable buffer ability and had maintained acidity through the whole discharge, with a pH value below 4; cycling properties of this cell were not reported, though. Since the overall cell reaction is $2\text{Li} + 2\text{CH}_3\text{COOH} + (1/2)\text{O}_2 \leftrightarrow 2\text{CH}_3\text{COOLi} + \text{H}_2\text{O}$ ($E_0 = 4.07$ V), acetic acid is to be considered as an active material, and the cell energy capacity depends on the amount of acetic acid in the electrolyte. It should be recognized that in case of non-alkaline electrolytes, the air electrodes are to be comprised of expensive precious metal-based catalysts. In this connection, it is worth noting that air electrodes for Li–air cells with acidic [71] and neutral electrolytes [72] were prepared using Pt-catalyzed carbon. Thereby, increasing stability of LISICON-type ceramics in alkaline media should be the object of much concentrated attention.

Regarding LISICON reactivity toward lithium metal, a common way to manage LISICON/lithium-metal interface is to introduce an interlayer of the material between the LISICON membrane and the anode; the material of such interlayer should have an adequate high Li⁺-bulk conductivity and, in its interface with a metallic lithium, also need to be stable, without presenting any barrier for Li⁺-transport.

Several types of materials were suggested to mediate a contact between LISICON and lithium metal, such as common Li-compatible non-aqueous battery electrolytes [21,66] and also as SPE [64,65,68,70,71]. It was offered to use a thin lithium phosphorous nitride (LiPON) interlayer for mediating LISICON/lithium metal contact; film thickness falls in the range between 1 and 4 μm [69], and in the range between 0.2 and 1 μm [67]. Materials such as Li₃N, Li₃P, LiI, LiBr, LiCl, and LiF were offered for mediating interlayer interface, as well [67].

4.4. Incoming air filtration from water vapors

To prevent water vapor ingress and at the same time to secure a sufficient oxygen inflow, several brands of heat-sealable polymer membrane were used [11]; it was also believed that such membranes can minimize evaporation of electrolyte from the battery. Tested cells were filled with a non-aqueous electrolytes, and their air electrode inlets were protected with 46 μ high-density polyethylene films (HDPE) and 20 μ polyethylene terephthalate-based Melinex[®] 301 (DuPont Teijin) films; the films were tight against air cathode and thus, were in contact with the electrolyte. Performance of the cells with Melinex[®] 301 protecting film was found superior to the performance of the cells with HDPE films. The cells were discharged in ambient air for 33 days and had demonstrated a capacity of 1185.4 mAh; the specific energy of the cell was 362 Wh kg⁻¹ (unfortunately, the comparative example of a similar cell without a protective film was not presented).

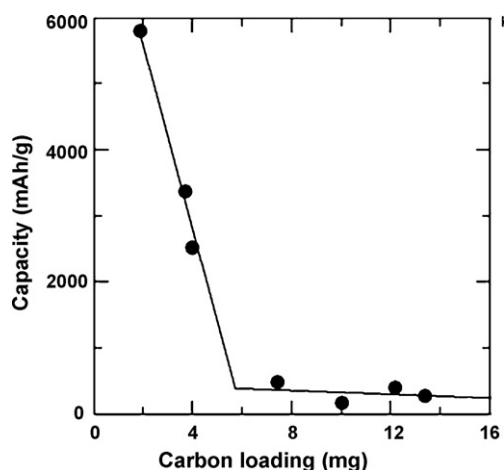


Fig. 5. Capacity vs. carbon loading (horizontal axis—mg of carbon per 0.97 cm^2 of the electrode) [23].

A rough estimation of water amount ingress during the experiment is possible. Water vapor permeability via a dry Melinex[®] 301 is $1.6 \times 10^{-9} \text{ mol cm}^{-2} \times \text{s}$ [73], and thus the total water ingress during the 33 days ($2.8512 \times 10^6 \text{ s}$) discharge through air electrode orifice (total area of 32 cm^2) may be estimated as 0.146 mol of H_2O (this is just a rough estimate, since the permeability of the electrolyte-impregnated film may be somewhat different). Theoretically, it may be suggested that some of these water molecules can be reduced at the air cathode ($2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2\uparrow$); however, in the worst case scenario, this amount of water would consume 0.146 mol of lithium (according to the reaction: $2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2\uparrow$), and the water inflow is equivalent to the current of 0.155 mA cm^{-2} . The numbers suggest that the membrane implemented in [11] may be undoubtedly efficient only if cell currents $i_{\text{Li-air}} \gg 0.155 \text{ mA cm}^{-2}$.

5. Specific power issue

Specific power and power density are important parameters for a practical application of a power source. It was outlined above that the specific power of current Li–air cells is too low for most of practical applications (e.g., specific power of 0.46 mW g^{-1} [11], contrasting a value of 42 mW g^{-1} for ordinary market-available Li-ion batteries (at $0.2C$ rate)). Such low specific power value is mainly related to the low power per unit of Li–air cell electrode area. The point is that the feature, innate to Li–air cell, is the necessity of air access to all cathode surfaces. This feature renders the counterbalancing act of low surface-specific electrode power with a jelly-roll type design, and the only addressing design may be a stack-type design (similar to the design of a PEM fuel cell); such design assumes the introduction of bipolar plates, which electrically connect electrodes of the adjacent cells and also provide the air access to the gas cathode of the particular cells. The introduction of bipolar plates entails a serious build up of both battery weight and volume; by way of illustration, bipolar plates commonly make up nearly 80% of the total fuel cell weight [74]. The above consideration suggests that an important task it to increase the power of Li–air cell per electrode area unit.

Since Li–air cell discharge voltage is governed by battery chemistry, and in most of the studies it is in the range of $2.5\text{--}2.8 \text{ V}$, the per-area-unite power depends on the electrode current density; whereas, Li–air electrode current density per gram of (carbon + catalyst) may be maintained at fairly high values (up to 250 mA g^{-1} [10]), the discharge currents are commonly in the range of $0.05\text{--}1 \text{ mA cm}^{-2}$. The issue stems from the fact that the energy

capacity (and hence the energy) of Li–air cell is very sensitive to the carbon loading in the cathode, in such way that the higher is the loading the lower is the energy capacity [23] (see Fig. 5); this circumstance causes the implementation of a very low carbon loading, which in turn, results in low discharge current densities.

On the one hand, it was shown [50] that at a given current density and a given carbon loading, the increase in oxygen mobility in the electrolyte results in increase of cell capacity. On the other hand, the growth in cathode carbon loading is apparently attended by a growth in the air electrode density and/or electrode thickness [8], i.e., growth of loading retards oxygen access to the inner layers of the air electrode. Combining these provisions, it may be suggested that the clue to high cathode loadings (and hence, to high discharge densities) is the enhancement of the oxygen access toward the inner carbon/catalyst layers. It may be speculated that the problem may be solved by compiling an electrolyte with high oxygen mobility, by preparing carbons with an adequate pore systems, or by developing an adequate active electrolyte flow system design.

6. Conclusions and perspective

Li–air batteries are potentially viable ultrahigh energy density chemical power sources, which may be used in a number of applications, ranging from portable electronics to electric vehicles. Currently, Li–air batteries are still in the initial stages of development; this statement is true for a theoretical understanding of the processes inside the cell, as well as for the development of a practically viable design of Li–air battery. The reader can find below a list of the key areas of development, which will assist evolving Li–air cell into a valuable chemical power source.

- Further investigation of the electrochemical processes at the two-phase interfaces (dissolved oxygen/non-aqueous electrolyte|carbon/catalyst) and (dissolved oxygen/non-aqueous electrolyte|Li-oxide); understanding of these processes will pave the way to attaining high cathode charge capacity and current capacity, and will guide a development of efficient cathode catalysts.
- Research and development of cathode catalysts, which will be able, first of all, to control the redox process at the cathode surface in a way that lithium oxidation will be reversible; this is a clue to attaining of high charge efficiency in a discharge–charge cycle and a long cycle life. The research should also be focused on the development of the catalyst, which will reduce the charge over-voltage. The latter will enhance the cycle efficiency and, which is particularly important, prevent possible electrolyte oxidation and thus, will secure a long cycle life.
- Development of air cathodes with hierarchical, several levels pore structure, which will maintain adequate transport of oxygen and Li^+ toward the active, electron-conducting surfaces, and at the same time provide enough room for accommodating solid lithium oxides. Such structure is important for achieving high cathode carbon loading and thus high capacity at higher power densities.
- Development of electrolyte system; the system should offer high oxygen transport ability and low volatility and, at the same time, it should offer an adequate barrier for oxygen and moisture diffusion (and, probably, carbon dioxide diffusion) toward the battery anode. What is more, the system should maintain high lithium-metal anode cyclability. It may be suggested that the successful electrolyte system will most likely be comprised of several layers; the layer adjacent to the anode will protect lithium metal from degradation, and also will inhibit dendrite growth whereas, the layer adjacent to the air cathode (and inside it) will maintain the adequate oxygen transport.

- Parallel to electrolyte development, it would make sense to conduct a development of some mechanisms enabling filtering out H₂O (and possibly CO₂) from the incoming air; an example of such a mechanism is a high throughput air-breathing O₂-selective membrane.
- Concurrently with the above electrolyte and air-cathode design development, development of flow-type Li-air batteries should receive a proper attention. The design may offer a route to store lithium oxide products outside the battery, and thus seriously increase the Li-air battery energy capacity. Also, the design may be helpful in bypassing the low-carbon-loading problem, and thus, it may be an alternative to the sophisticated cathode structure design. Apparently, the flow-type design may be viable only in case of large scale power sources, e.g., in case of vehicle-powering batteries.

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