From Lithium-Oxygen to Lithium-Air Batteries: Challenges and Opportunities

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Lithium-air batteries have become a focus of research on future battery technologies. Technical issues associated with lithium-air batteries, however, are rather complex. Apart from the sluggish oxygen reaction kinetics which demand efficient oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalysts, issues are also inherited from the nature of an open battery system and the use of reactive metal lithium as anode. Lithium-air batteries, which exchange oxygen directly with ambient air, face more challenges due to the additional oxidative agents of moisture, carbon dioxide, etc. which degrade the metal lithium anode, deteriorating the performance of the batteries. In order to improve the cycling performance one must hold a full picture of lithium-oxygen electrochemistry in the presence of carbon dioxide and/or moisture and fully understand the fundamentals of chemistry reactions therein. Recent advances in the exploration of the effect of moisture and CO_2 contaminants on Li-O_2 batteries are reviewed, and the mechanistic understanding of discharge/charge process in O_2 at controlled level of moisture and/or CO_2 are illustrated. Prospects for development opportunities of Li-air batteries, insight into future research directions, and guidelines for the further development of rechargeable Li-air batteries are also given.

1. Introduction

The ever-increasing demand for advanced energy storage solutions for the automotive industry, smart grids, and other stationary applications has intensified the research needed on post Li-ion battery technologies, among which lithium-air (Li-air) batteries are known for their ultra-high theoretical specific energy.[1–3] With possible moderations being taken into consideration Li-air batteries would deliver a specific energy of 3–4 times as high as that of the state-of-the-art lithium-ion batteries, based on the inexhaustible oxygen gas from outside of the battery and the high capacity of metal lithium electrodes, whereby oxygen is reduced to form Li_2O_2 ($2Li + O_2 \leftrightarrow Li_2O_2$, 2.96 V vs Li/Li^+).[4] Four types of lithium-air batteries: non-aqueous, aqueous, hybrid, and solid state batteries have been constructed and studied, among which the non-aqueous Li-air battery system (as shown in **Figure 1**) has been the most investigated, and will be the sole focus of this review. In actual cells the main challenges are the limited energy density, poor round-trip efficiency, and unsatisfactory durability. The root cause of these performance limitations could reside in the underperforming materials, non-ideal system design, and insufficient fundamental understanding of the oxygen reaction mechanism on the air electrode, to name a few.

Theoretically, the overall energy density (or discharge capacity) is determined by the amount of insoluble discharge product (Li_2O_2) deposited on air cathode. In practice, however, the discharge capacity is often found to be far lower than its theoretical value, as the porosity feature (pore volume, pore sizes and their distributions) of the air electrode also plays a key role therein. The porous air cathode provides not only the diffusion channel for oxygen gas to reach the electrolyte/electrode interface, but also the space to accommodate Li_2O_2 deposition

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DOI: 10.1002/aenm.201502164

inside the electrode. In most cases the deposition of the discharged product unavoidably creates clogging and restricts the oxygen gas flow, resulting in a notably lower discharge capacity. The effect of pore feature on the discharge capacity of the Li-air batteries is described in some recent works.[5–14]

The round-trip efficiency is largely determined by the catalytic activities of the catalysts toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Unsatisfactory ORR catalytic activity essentially leads to lower discharge potential, while inferior OER catalytic activity results in higher charge potential. The overpotential in both processes contributes to a larger charge–discharge voltage gap, which notably compromises the round-trip efficiency. It is worth noting that poor electric conductivity also increases the polarization, giving a high overpotential on the electrode. The overpotential reduction and efficiency improvement can be achieved through air-electrode engineering, which has been reported and well-reviewed previously.[15–29]

The durability of Li-air batteries can be affected by the performance (activity and stability) of catalysts, and the stability of the electrolyte during the charge–discharge processes.[30] Insufficient catalytic activity and unstable electrolytes, as well as the lithium electrode poisoning due to oxygen crossover will severely shorten the cycle life of the Li-air batteries.[19,21,30–35] Fortunately, some recent research sheds light on the durability issues, giving us a reason to stay optimistic with Li-air battery technology.[36–39] Starting from 2006, more and more understanding has been achieved of electrolytes and cathodes (materials and structures), which in turn accelerated the research on the fundamental problems and improved the Li-air battery system notably. Some significant achievements in the performance improvement of Li-air batteries are summarized in **Table 1**. For instance, the lesson learned from organic carbonate-based electrolytes, i.e., severe decomposition during the operation of Li-O_2 cells, has guided researchers to adopt more chemically/electrochemically stable ether-based, dimethyl sulfoxide (DMSO)-based, and other types of organic electrolytes. Encouragingly, an overpotential of as low as 0.64 V was achievable during charge using DMSO-based electrolytes. As a consequence of the smaller polarization, the cyclability of the lithium-air was notably improved.[40–42] In addition, the upgrade of air electrode from initially simple carbon to the current three-dimensional (3D) porous electrode with bi-functional catalyst was also able to improve kinetics and energy efficiency. For instance, Sun et al. reported Ru nanocrystal-decorated porous graphene as an excellent catalytic air cathode in Li-O_2 batteries, with a highly reversible capacity of 17 700 mAh g^{-1}, a low charge/discharge overpotential (0.355 V), and a long cycle life up to 200 cycles (under the curtaining capacity of 1000 mAh g^{-1}).[41] Li et al. prepared Ru impregnated, multiwalled carbon nanotube paper catalysts (Ru@MWCNTP), which significantly reduces the charge overpotentials of the Li-O_2 battery at a current density of 500 mA g^{-1} and can be discharged and charged over 50 cycles at a cut-off capacity of as large as 5000 mAh g^{-1}.[43] More interestingly, Kang et al. introduced a completely new Li-O_2 cell architecture. Instead of placing the catalyst on the oxygen electrode, the team used a soluble catalyst (LiI) in the electrolyte, which enabled a high reversible capacity of 1000 mAh g^{-1} over 900 cycles with very low polarization (0.25 V).[44]


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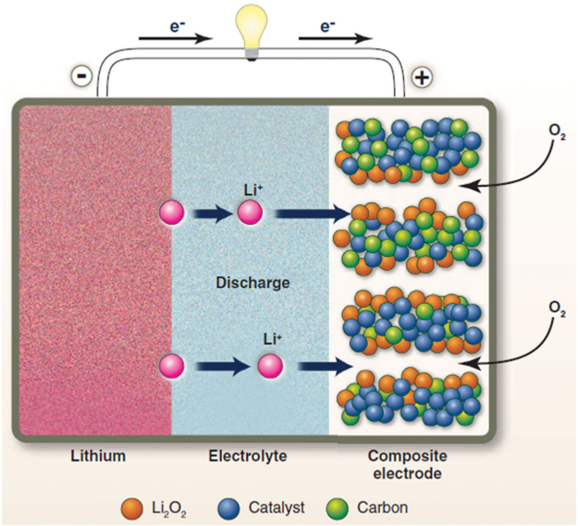

Figure 1. A typical non-aqueous Li-air cell composed of a lithium electrode, an electrolyte consisting of dissolved lithium salt in an organic solvent, and a three-dimensional nanoarchitectured porous O_2-breathing electrode; Reproduced with permission.[3] Copyright 2011, American Association for the Advancement of Science (AAAS).

More progress has been achieved in the past ten years, covering cycle life, energy efficiency, and rate capability of Li-air batteries. Interested readers can refer to a number of recent reviews presenting technical issues and challenges facing Li-O_2 batteries and the relevant progress, including cathode electrocatalysts and electrochemistry, cathode architecture, and stability of electrolytes.[15,17–20,22,31–33,35,50–55] It should be noted that the term "Li-air battery" is often "abused", as most of actual charge–discharge processes were in fact conducted in a pure oxygen environment whereby the kinetic model was much simpler such that the material aspects could be easily highlighted. The power of a truly high energy density Li-air battery will not be fully released unless it operates in ambient atmosphere. In the journey of making real Li-air batteries practically viable, much effort has to be devoted to understanding how atmospheric contaminants affect the cathode chemistry and electrochemistry therein. The most common air contaminants are H_2O and CO_2, which comfortably react with the conventional discharge product of Li_2O_2 to form LiOH and Li_2CO_3, obscuring or confusing the basic Li-O_2 electrochemistry. In particular, these non-peroxide lithium compounds require higher potentials to be decomposed in the charge, compromising both the energy efficiency and the cycling stability. In this focus review, we make an effort to discuss in depth the impacts of CO_2 and moisture on Li-O_2 electrochemistry and the battery performance. It is anticipated that this review will encourage more research on lithium batteries in ambient air operation, advancing truly rechargeable Li-air batteries toward practical applications.

2. Ambient Air Operation of Li-Air Batteries

The major constituents of dry air include N_2 (78%), O_2 (21%), CO_2 (≈0.03%), and other gases in trace quantities. In ambient air, moisture is inevitable and its content increases with elevated humidity. With the presence of CO_2 and moisture in ambient air, an open system of a lithium-air battery undergoes the following possible reactions:[32,56]

Table 1. Some typical achievements for Li-O_2 batteries in cathode materials, electrolytes, and cycle life etc.

Cathode material	Electrolyte	η_{charge} [V]	Discharge depth [mAh g^{-1}]	Cycling interval [V]	Current density [mA g^{-1} or mA cm^{-2}]	Cycle life [cycle]	Ref.
Nanoporous Au	1 M $LiClO_4$ in DMSO with tetrathiafulvalene	≈0.60	300	2.3–4.0	1 mA cm^{-2}	100	[40]
Au nanoparticles coated Ni nanowires	1.3 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME)	≈1.3	500	2.3–4.3	500	110	[45]
Porous $La_{0.75}Sr_{0.25}MnO_3$ Nanotubes	1.0 M LITFSI in TEGDME	≈1.24	1000	2.2–4.4	0.15 mA cm^{-2}	124	[46]
Ru@nanoporous graphene catalysts	0.1M $LiClO_4$/DMSO	0.64	1000	2.0–4.4	200	200	[41]
TiC	0.5 M $LiClO_4$ in DMSO	≈0.64	500	2.0–4.0	1 mA cm^{-2}	100	[42]
Pd/FeO_x/ordered mesoporous carbon	1.0 M $LiClO_4$inTEGDME	0.48	500	2.0–4.3	100	68	[14]
Ru nanoparticles on MWCNT paper	LITFSI/triglyme (1:5)	≈0.78	5000	2.3–4.6	2000	50	[43]
Hierarchical CNT fibril	1.0 M LITFSI in TEGDME with 0.05 M LiI	0.25	1000	2.0–4.7	2000	900	[44]
Carbon-free $MnCo_2O_4$@ Ni	1.0 M LiTFSI in TEGDME	0.94–1.04	1000	2.0–4.2	500	100	[47]
CoO mesoporous spheres+super P	1.0 M LiTFSI in TEGDME	0.79	1000	2.0–4.3	0.04 mA cm^{-2}	300	[48]
Hierarchical rutile TiO_2 nanowire arrays grown onto carbon textiles	1.0 M $LiCF_3SO_3$ in TEGDME	≈1.54	500	2.0–4.7	100	500	[49]

$$2Li + O_2 \rightarrow Li_2O_2 \quad (1)$$

$$4Li + O_2 \rightarrow 2Li_2O \quad (2)$$

$$4Li + 2H_2O + O_2 \rightarrow 4LiOH \quad (3)$$

$$4Li + O_2 + 2CO_2 \rightarrow 2Li_2CO_3 \quad (4)$$

$$2Li + 2H_2O \rightarrow 2LiOH + H_2 \quad (5)$$

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O \quad (6)$$

$$LiOH + H_2O \rightarrow LiOH \cdot H_2O \quad (7)$$

$$2Li_2O_2 + 2CO_2 \rightarrow O_2 + 2Li_2CO_3 \quad (8)$$

$$2Li_2O_2 + 2H_2O \rightarrow 4\ LiOH + O_2 \quad (9)$$

Here, possible side reactions with N_2 are ignored as N_2 is believed not to be participating in reactions on the air cathode. From the Reactions 1–9 one can easily identify LiOH and Li_2CO_3 as the major byproducts whose formation may be reflected as the change of discharge voltage and capacity. The rechargeability of a Li-air cell depends on whether Li_2O_2, Li_2O, LiOH, and Li_2CO_3 can be electrochemically reversed to Li, O_2, H_2O, and CO_2 (the inversion of Reactions 1–4) within the operating voltage window of a Li-air cathode. Any irreversible process, partially or fully, will cause capacity loss to the matching extent. In the following paragraphs we discuss the effects of moisture (water) and carbon dioxide on the performance of Li-air batteries in detail.

2.1. The Effect of Water on the Performance of Li-Air Batteries

2.1.1. The Effect of Water on the Discharge Proces

Luntz et al. studied the effect of H_2O contamination on Li-O_2 battery performance by directly adding small amount of water to the electrolyte prior to the assembly of the cell, and the results are given in **Figure 2**a.[57] Interestingly, the inclusion of 500 ppm H_2O leads to a large increase in cell capacity, as compared to that operated in "pure" electrolyte with 12 ppm H_2O as measured by Karl Fischer titration. A similar result was obtained by Meini et al., where a specific capacity up to 2800 mAh g_{carbon}^{-1} was obtained in dimethoxy ethane (DME) using a "water vapor cell", about 14-fold higher than that using "sealed cell" design (Figure 2b).[58] This seems to suggest that it works for both water in electrolytes and water in O_2. Xia et al. investigated the humidity effect on electrochemical performance of Li-O_2 batteries (Figure 2c,d),[59] where the galvanostatic charge-discharge measurements were carried out in a pure dry oxygen-filled glove box, or oxygen-filled glove box with relative humidity (RH) of 15 wt%. As shown in Figure 2d, the Li-O_2 battery in

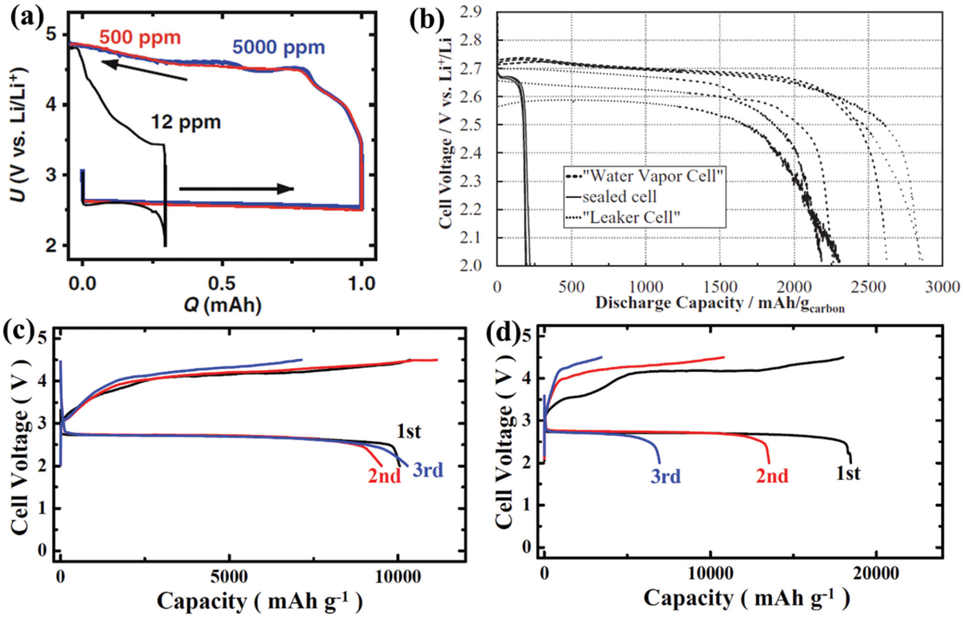

Figure 2. a) Galvanostatic discharge-charge curves for cells with 12 500 and 5000 ppm H_2O contamination in the electrolyte (XC72 carbon-based cathode, 1 M LiTFSI in DME electrolyte, $i = 0.47$ mA cm^{-2}). Reproduced with permission.[57] Copyright 2014, Springer. b) Comparison between discharge capacity (1st cycle) of Li-O_2 cells with 0.1 M $LiClO_4$ in DME using H_2O-free (—) or H_2O contaminated oxygen (100 kPa_{abs}), whereby water was introduced by means of a small leak between the cell and ambient air (—) in the "Leaker Cell" or by connecting a water reservoir to produce H_2O-saturated O_2 inside the cell (···) in the "Water Vapor Cell". Reproduced with permission.[58] Copyright 2012, The Electrochemical Society. c) The discharge/charge curves of Li-O_2 batteries in pure/dry O_2 for initial 3 cycles at a current density of 50 mA g^{-1} with Ketjen Black as the cathode material. d) The discharge/charge curves of Li-O_2 batteries in pure O_2 with an RH of 15% for initial 3 cycles at a current density of 50 mA g^{-1} with Ketjen Black as the cathode material. Reproduced with permission.[59] Copyright 2014, Elsevier, B.V.

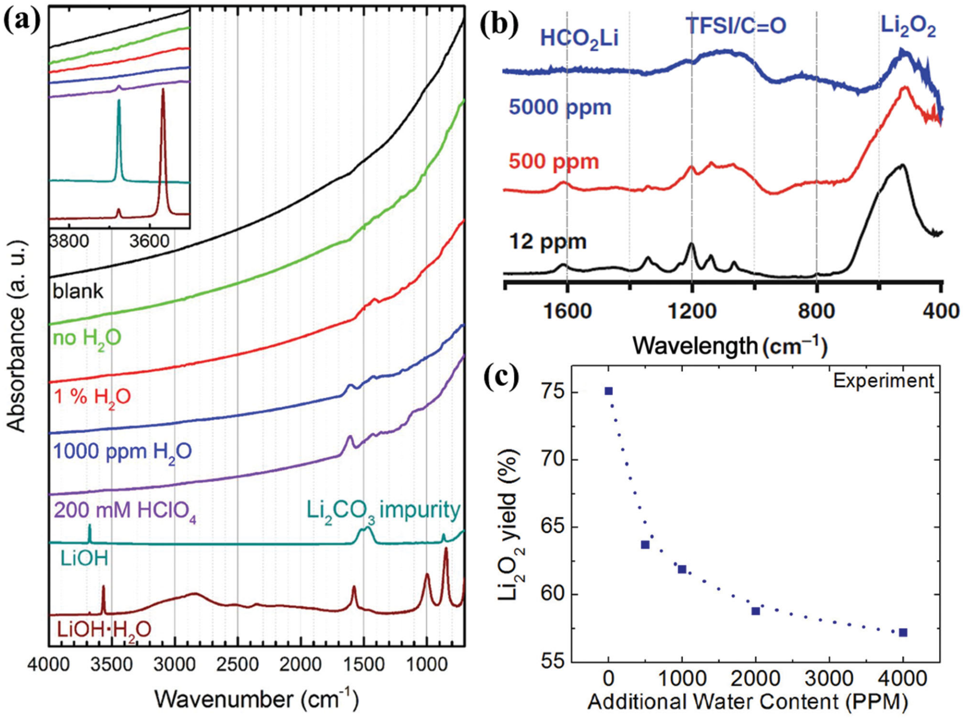

Figure 3. a) FTIR analysis of carbon paper electrodes after washing and drying (black line, "blank"), after discharge in electrolyte without water/acid at 30 µA (green line, "no H_2O"), with 1% water at 30 µA (red line, "1% H_2O"), with 1000 ppm water at 1 µA (blue line, "1000 ppm H_2O"), and with 200 mM $HClO_4$ (including 1% (500 mM) of water) at 30 µA (purple line, "200 mM $HClO_4$"). Reference spectra for LiOH and $LiOH \cdot H_2O$ (absorbance 3x reduced for both salts) are shown in the dark cyan and brown line. It should be noted that the commercial non-hydrated LiOH contains a substantial amount of Li_2CO_3 impurity. The inset shows a ≈5x zoom in the spectrum around 3675 cm^{-1} which is characteristic for the stretching band of the OH group. Reproduced with permission.[61] Copyright 2015, The Electrochemical Society. b) FTIR of extracted P50 cathodes discharged for 5 mAh in the H_2O-contaminated electrolytes. Reproduced with permission.[57] Copyright 2014, Springer. c) A plot of the Li_2O_2 yields obtained from iodometric titration experiments performed on XC72 carbon cathodes. Reproduced with permission.[62] Copyright 2014, Macmillan Publishers Limited.

O_2 atmosphere with an RH of 15 wt% exhibits a capacity of 18 482 mAh g^{-1} on initial discharge, which is about 1.8 times as high as that achieved in pure dry O_2 atmosphere (Figure 2c, ≈10 050 mAh g^{-1}) at the same current density of 50 mA g^{-1}. Clearly, the addition of water into the electrolyte significantly increases the discharge capacity, which has been proven true in three different electrolyte systems, i.e., 1M LiTFSI in DME, 0.1 M $LiClO_4$ in DME, and 1 M LiTFSI in TEGDME. Some apparently contradictory observations in a recent study from Wang et al. showed that the discharge capacity in wet O_2 was not distinctly different from that in dry O_2 . This, however, is believed to be due to the use of a Li-ion conducting solid-state electrolyte, which had more or less eliminated the reaction of lithium to H_2O in electrolyte.[60] Therefore, adding trace amounts of water into electrolytes can be taken as a valid approach to enhance the discharge capacity.

Apart from capacity enhancement, the addition of water was reported to elevate the discharge voltage plateau in a water vapor cell as compared to that in a sealed cell (2.71 V vs. 2.66 V) (Figure 2b). Meini et al. ascribed the effect to the higher reversible potential of Reaction 3 as compared to that of Reaction 1, whereby the discharge electrochemistry may entail the reaction of lithium with water and oxygen to form LiOH. This hypothesis, however, was challenged by Lunz et al. who conducted quantitative analysis on O_2 consumed in the discharge, and O_2 evolved during the charge using differential electrochemical mass spectrometry (DEMS). The obtained ≈2.05 electrons transfer per O_2 molecule in Reaction 1 suggests Li_2O_2 formation as the dominant discharge chemistry, even if water is present in the electrolyte at a concentration of 12–25 000 ppm.[57] The LiOH formation hypothesis was also invalidated by the same group in a recent study, whereby no infrared (IR) absorption bands/peaks were observed for LiOH or its hydrated forms in the discharged cathodes using water-free or water-containing electrolytes (**Figure 3**a).[61] Hence it is believed that water might not be embodied in the Reactions 3 and 9. Moreover, both Fourier-Transform infrared (FT-IR) spectroscopy and iodometric titration experiments (Figure 3b,c) are suggesting a decreased amount of Li_2O_2 formation on the cathode surface with the increase of H_2O content,[57,62] which explains the less electrical passivation of cathode surface thus a higher cell capacity.[63] Further findings indicate that at low discharge current densities even trace amounts of water can induce the formation of Li_2O_2 crystals with varied morphologies and size, which was later validated by Aetukuri et al. on cathodes of Vulcan XC72 carbon, TiC, and AvCarb P50 carbon paper.[62] **Figure 4** shows the typical evolution of the morphology of discharge product in Vulcan XC72 carbon cathode with gradually increased H_2O content. Prior to the addition of H_2O, the discharged XC72 cathode was hardly distinguishable from the pristine cathode, suggesting the formation of Li_2O_2 as thin conformal films of amorphous structure. As H_2O was added, the

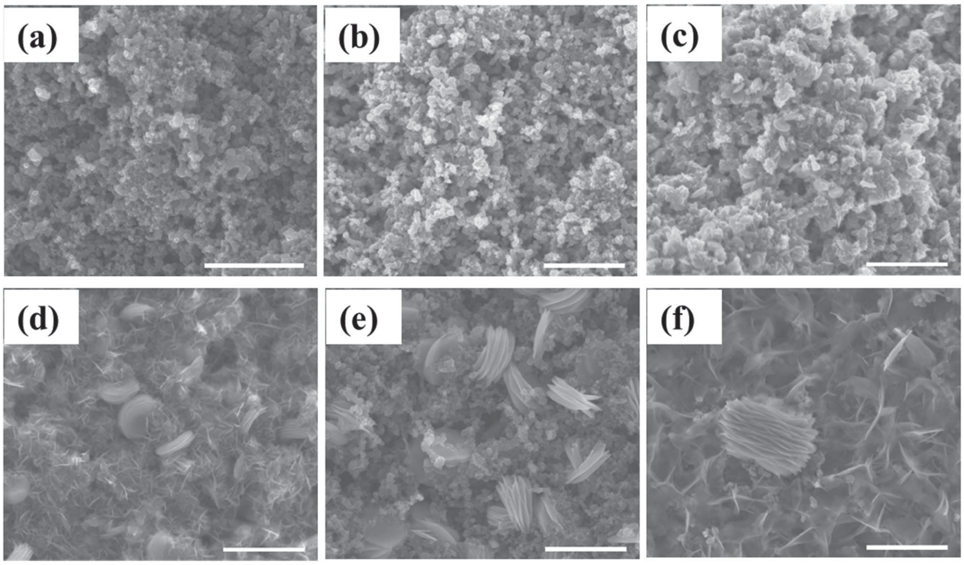

Figure 4. SEM images of Vulcan XC72 carbon cathode before and after discharged to a capacity of 1 mAh at a rate of 50 μA using 1 M LiTFSI in DME as the electrolyte with the various H_2O content. a) without any discharge, b) anhydrous (<30 ppm), c) 500 ppm, d) 1000 ppm, e) 2000 ppm, f) 4000 ppm. All scale bar, 1 μm. Reproduced with permission.[62] Copyright 2014, Macmillan Publishers Limited.

discharged cathode underwent morphology changes and grew from small thin toroids to larger toroids, and further to platelets with a layered structure. This phenomenon was recently interpreted by Schwenke et al. using a concept of "solubilization", whereby the cell capacity increase was correlated with some water-induced partial chemical solubilization of Li_2O_2 that formed possible products of H_2O_2 (or LiOOH).[61] Taking these evidences into consideration and combining with the data from quantitative DEMS and Li_2O_2 titration experiments, Aetukuri et al. proposed that with added water the activation of solution-mediated electrochemical Li_2O_2 deposition process was responsible for the formation of large Li_2O_2 toroid and flakes; at the same time water did bring along parasitic chemistry and electrochemistry.[62] Generally, continuous formation of H_2O_2 over the course of the discharge via water-induced disproportionation of the superoxide anion (intermediate species in the formation of Li_2O_2)[64,65] is believed to account for the decreased amount of Li_2O_2 on the cathode surface with the increase in H_2O content mentioned above (Figure 3b,c).

2.1.2. The Effect of Water on the Charge Process

Since H_2O induces parasitic chemistry and electrochemistry, as well as the formation of crystal Li_2O_2 in discharge, it is natural to assume that H_2O impurities affect the charge process and the cycle life. Returning to Figure 2, one sees a higher average charging potential for cells using an electrolyte with added H_2O than that with a "pure" electrolyte (Figure 2a). A similar phenomenon was observed by Xia et al. in 3 consecutive discharge-charge cycles (Figure 2c, d). Usually a charging curve features an initially linear potential increase followed by a voltage plateau for cells in the absence of water. With 1% of water in electrolyte Schwenke et al. found that the charge potential of the cell initially ramped to a much higher value, and fell back to a lower charging plateau eventually.[61] A high voltage plateau was also observed in the charging of electrodes pre-filled with micrometer-sized Li_2O_2 particles,[56,66,67] which was ascribed to the LiOH on commercial Li_2O_2 particles surface as a thin coating that needed to be decomposed first in order to allow for Li_2O_2 to be electrochemically oxidized. Although the two cases showed similar phenomena, they were fundamentally different. As water was introduced to the electrolyte system, the initially higher potential was ascribed to water-induced changes in the size and crystalline structure of the discharge product, Li_2O_2. Lunz et al. also reported a rapid voltage ramp in the charge potential as the H_2O content increased;[57,62] however, O_2 evolved in the charge process solely came out of Li_2O_2 that was formed during the discharge, as evidenced by an oxygen isotopic experiment in which charging a Li-air battery that was discharged under $^{18}O_2$ using $H_2{}^{16}O$ as contaminant released pure $^{18}O_2$. Moreover, the O_2 evolution rate on average was found to decrease with the increase in H_2O content. Higher charge overpotential and poorer O_2 evolution rate suggested that H_2O contamination significantly reduced the cell's rechargeability. Comparing the results in Figure 2c and 2d, one can see that the discharge capacity of Li-O_2 batteries in O_2 atmosphere with an RH of 15% experienced a dramatic decrease (down to 6893 mAh g^{-1}) after 3 cycles, indicating poor cycling performance. However, very recently Zhou et al. demonstrated "water catalysis" at the oxygen cathode side, which helped reduce the charge overpotential to ≈0.24 V, corresponding to a very small discharge/charge potential gap of 0.32 V, by using the different cell system, with $LiFePO_4$ as the anode in the presence of ppm-level of H_2O.[68]

2.2. The Effect of CO_2 on the Performance of Li-Air Batteries

Despite its low concentration in ambient air, CO_2 is believed to have the second most significant impact on the chemistry of the Li-air cell (just after moisture), as it is very soluble in organic electrolytes[69] and highly reactive toward Li, LiOH and Li_2O_2 to form Li_2CO_3 readily (cf. Reactions 4, 6, and 8). In addition, Li_2CO_3 is chemically more stable than Li_2O_2 according to their standard Gibbs free energies of formation,[70] implying conversion of Li_2O_2 to Li_2CO_3 as a thermodynamically favorable process in the presence of CO_2. Some earlier studies have revealed the adverse effects of carbonates formed from the decomposition of cathode/electrolytes during battery operations.[71–77] Studies on discharge products from pre-filled air-cathodes showed that Li_2CO_3 had an adverse impact on the cell performance regardless of its source.[78] Hence, it is critical to understand the reactions involving CO_2 and the chemistry of Li_2CO_3 within a Li-air cell for the further development of Li-air battery technology.[79]

2.2.1. The Effect of CO_2 on the Discharge Process

The CO_2 effect on Li-O_2 batteries has been investigated by different research groups. The results suggested no capacity for Li-air batteries in pure CO_2 atmosphere (**Figure 5**a);[80] however, the introduction of CO_2 with a concentration up to 80% was found to boost the cell capacity significantly (Figure 5b).[81] The specific capacity increased at low CO_2 concentrations, e.g., 1%, but notably decreased when the concentration of CO_2 was high, e.g., 50% (Figure 5c).[82] Basically, the discharge voltage of a Li-O_2/CO_2 battery was about the same as that of Li-O_2 battery, which seemed to imply that the reduced species during cell discharge was only O_2. Moreover, no active Li-CO_2 electrochemistry signal is visible in Figure 5a, b, and c, which tends to rule out the possibility of direct CO_2 reduction. Nevertheless, some recent developments suggested that Li-CO_2 batteries could deliver decent discharge capacities (Figure 5d)[83,84] and enhanced cycle stability,[85] calling for more efforts to look into Li-CO_2 electrochemistry. Takechi et al. proved Li_2CO_3 as the main discharge product using IR spectrum analysis, when the lithium-air battery was discharged in the equal volume mixture of CO_2 and O_2.[81] Here, a natural question to ask is if Li_2O_2 was formed first, while the formation of Li_2CO_3 was just a result of the further reaction of Li_2O_2 with CO_2, i.e., following Reaction 8 above. As seen in Figure 5b, the discharge capacity of the Li-O_2/CO_2 battery (CO_2 concentration of 50%) was 5860 mAh g^{-1} and 2.9 times as high as that of Li-O_2 battery (essentially CO_2-free). This ruled out the likelihood of Li_2CO_3 formation via Reaction 8, as such a pathway cannot explain the much higher battery capacity obtained. Building upon the facts and analysis above, one can deduce the origin of Li_2CO_3 as the reaction of CO_2 with some intermediate(s) produced in the discharge chemistry of Li-O_2. To facilitate the understanding Takechi et al. proposed a

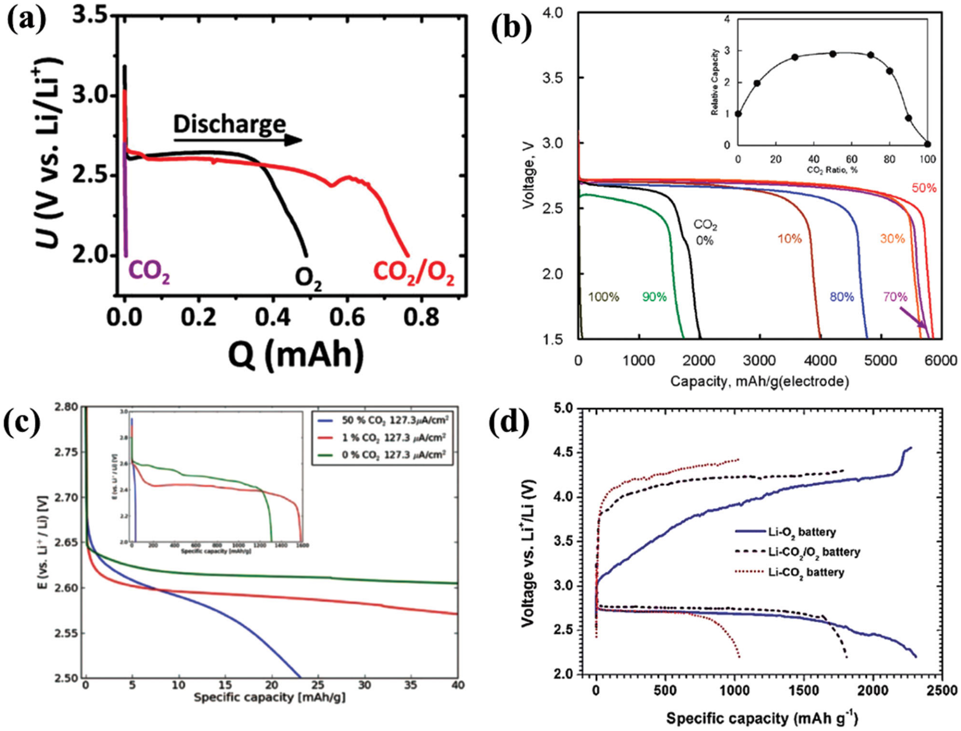

Figure 5. a) Galvanostatic discharge profiles (0.47 mA cm^{-2}) of Li cells discharged under three atmospheres: pure CO_2, pure O_2, and a 10:90 CO_2:O_2 mixture. XC72-based cathodes were used. Reproduced with permission.[80] Copyright 2013, American Chemical Society. b) Discharge curves of the Li-O_2/CO_2 batteries with varied ratio of CO_2 in O_2/CO_2 mixed gas at 25 °C (current density: 0.2 mA cm^{-2}). Inset shows CO_2 ratio dependence on relative capacities as compared with Li-O_2 battery (CO_2 , 0%). Reproduced with permission.[81] Copyright 2011, The Royal Society of Chemistry. c) Galvanostatic discharge profiles (127.3 µA cm^{-2}) at three different atmospheres: 50% CO_2, 1% CO_2, and 0% CO_2. Inset shows the increase in discharge capacity in 1% CO_2. Reproduced with permission.[82] Copyright 2014, AIP Publishing LLC. d) The charge–discharge curves of Li/O_2 battery (solid line), Li/CO_2-O_2 (2:1 in volume ratio) battery (dashed line) and Li/CO_2 battery (dotted line). The current density is 30 mA g^{-1}. Ketjen Black as cathode material. Reproduced with permission.[83] Copyright 2014, The Royal Society of Chemistry.

higher capacity for Li-O_2/CO_2 as a result of controlled reactions below:[81]

$$4O_2 + 4e^- \rightarrow 4O_2^{\cdot -} \quad (10)$$

$$O_2^{\cdot -} + CO_2 \rightarrow CO_4^{\cdot -} \quad (11)$$

$$CO_4^{\cdot -} + CO_2 \rightarrow C_2O_6^{\cdot -} \quad (12)$$

$$C_2O_6^{\cdot -} + O_2^{\cdot -} \rightarrow C_2O_6^{2-} + O_2 \quad (13)$$

$$C_2O_6^{2-} + 2O_2^{\cdot -} + 4Li^+ \rightarrow 2Li_2CO_3 + 2O_2 \quad (14)$$

It is widely accepted that the superoxide anion radical species ($O_2^{\cdot -}$) was the key intermediate for the formation of Li_2O_2. Here, Reaction 11 must be faster than the reaction between $O_2^{\cdot -}$and lithium cations that normally occurs in a Li-O_2 battery. During the process of Reactions 10-14, the intermittent species of peroxydicarbonate ions ($C_2O_6{}^{2-}$) were found to be relatively stable and able to diffuse in electrolytes, resulting in slow precipitation of Li_2CO_3, which filled the void of the cathode.

A counter view held by Gowda et al. claimed Li_2O_2 as the primary discharge product regardless of the presence of CO_2, which was supported by the battery discharge characters and the analytical data obtained on DEMS.[80] Further study using FT-IR to monitor CO_2 consumption in the three sealed cells suggested that Li_2CO_3 in the discharge products was formed via spontaneous reaction of CO_2 with Li_2O_2. A postulate ascribed the higher capacity with CO_2 contaminant to the Li_2CO_3 deposition resultant morphological changes in the cathode, which likely improved the electrode electronic conductivity. This assumption was also supported by Vegge et al. in their density functional theory (DFT) calculations, which showed CO_2 preferentially bound at step valley sites on the Li_2O_2 surface and a low concentration of CO_2 (1%) effectively blocked the step nucleation sites and altered the Li_2O_2 shape via the formation of Li_2CO_3.[82,86] Such an explanation is notably different from what Takechi et al. proposed previously. Nevertheless, it is worth pointing out that the experiments of Gowda et al. were performed using a mixture of CO_2:O_2 (v/v: 10:90) as the "atmosphere"; whereas notably higher concentrations of CO_2 (50%) were adopted by Takechi et al. in their experiments. This perhaps explains the discrepant views, suggesting CO_2 concentration dependent discharge chemistry.

Lim et al. investigated the discharge mechanism of Li-O_2/CO_2 (50%) cells with varied electrolyte conditions using quantum mechanical simulations coupled with experimental verification.[87] The concept of "reaction pathway leveraging using dielectric media" (**Figure 6**) was hence proposed, which suggested that in low dielectric electrolytes (such as DME) the discharge product tended to be primarily Li_2O_2 despite a high CO_2 concentration (50%). Naturally, Li_2CO_3 formation was unavoidable in an environment containing CO_2 due to its superior thermodynamic stability. In high dielectric electrolyte, CO_2 is readily activated electrochemically to directly yield Li_2CO_3. Therefore, it is not difficult to understand why the capacity of Li-O_2/CO_2 (50%) cells was reduced by half as compared to pure Li-O_2 cells when DME electrolyte was used. It is reasonable to deduce that in DME electrolytes, primarily Li_2O_2 will be formed during the discharge process, since CO_2 is notably less electrochemically active than O_2.

Despite the varied views on how CO_2 impacts the battery discharge process, it is rather clear that a higher capacity usually can be obtained with Li_2CO_3 existing as part of, or the only discharge product in cells discharged in CO_2/O_2 (with lower CO_2 concentration), as compared to those discharged in pure O_2.[83] The paths of Li_2CO_3 formation may be electrochemical or thermal reactions, or even decomposition of electrolyte;[74,76,77] whereas a dominating and convincing mechanism is yet to be developed to account for the notably increased discharge capacity discussed above.

2.2.2. The Effect of CO_2 on the Charge Process

The presence of Li_2CO_3 will also affect the charge behavior of the electrochemical cell. Previous studies showed that Li_2CO_3 decomposed only at high voltages (>4.0 V) with a reduced round-trip efficiency for the cell.[74,77] DFT analysis suggested a voltage for Li_2CO_3 decomposition in the range of 4.38–4.61 V.[88] This is also seen in Figure 5d, where Li/CO_2-O_2 (v/v, 2:1) and Li/CO_2 batteries presented charge voltage plateaus of above 4.0 V as a result of high polarization. Furthermore, in the XRD data the disappearance of diffraction peaks of Li_2CO_3 after the first charge clearly suggested a reversible process, which is in agreement with the results obtained by Lim et al. previously.[87] As shown in **Figure 7a**, the flat charge potential at ≈4.2 V in the Li-O_2/CO_2 cell is notably higher than that of conventional Li-O_2 cells, corresponding to the potential for Li_2CO_3 decomposition via an electrochemical pathway. XRD data in Figure 7b further demonstrated that the discharge product, Li_2CO_3, was reversed via an electrochemical oxidation process at 4.5 V.[87] In addition, a rapid rise in charging potential with increased charge capacity was observed for a Li-CO_2/O_2 cell by Gowda et al.,[80] in which the isotopic labeling measurements provided some insights into the mechanism of Li_2CO_3 electrochemical

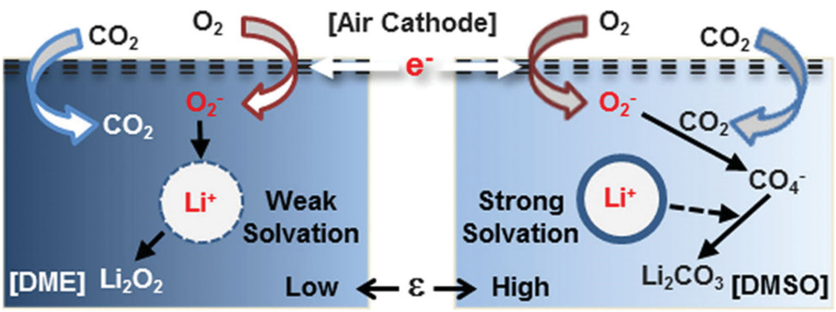

Figure 6. The concept proposed by Lim et al. about "reaction pathway leveraging using dielectric media" for Li-O_2 battery discharged under the existence of CO_2. Reproduced with permission.[87] Copyright 2013, American Chemical Society.

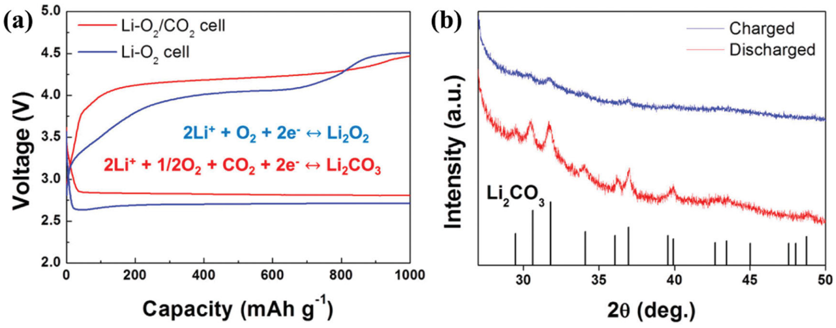

Figure 7. a) The first discharge/charge profiles in each system with DMSO electrolyte. b) XRD patterns after discharge and charge of Li-O_2/CO_2 cell with electrolyte. Reproduced with permission.[87] Copyright 2013, American Chemical Society.

oxidation. The increased concentration of Li_2CO_3 did account for the increase in charge potential; however, Li_2CO_3 formed by spontaneous reaction of CO_2 and Li_2O_2 was not decomposable at even higher charge potential. The CO_2 detected by DEMS at a voltage above 3.8 V was most likely attributed to the Li_2CO_3 from electrolyte mediated decomposition. Therefore, as far as the effect of CO_2 on the charge process of Li-O_2 battery was concerned, Li_2CO_3 formed during discharge gave an increase in the electrode polarization upon charging, which reduced the cell's voltaic cycle efficiency. The actual cause of the increase in overpotential, however, remains debatable. It could be from the intrinsic higher overpotential of Li_2CO_3, or the higher overpotential of the electrochemical oxidation of Li_2O_2 as a result of suppressed kinetics in the presence of Li_2CO_3.[89] In addition, the oxidation of Li_2CO_3 is heavily dependent on the applied charge voltage, electrolyte, cathode material, and the morphology or crystalline structure.[56,57,59,80,82,83,87–91]

2.3. The Effect of O_2 Partial Pressure on Battery Performance

Besides the environmental contaminants, the change of oxygen partial pressure when oxygen is replaced with air could also have an impact. Li-oxygen batteries have been mostly investigated in pure oxygen with O_2 partial pressure ranging from 0.2 to 25 atm.[92–94] The results clearly showed higher discharge capacity and rate capability as the oxygen partial pressure increased (**Figure 8**). Oxygen partial pressure is about 0.21 atm in the dry air, which is on par with the lower end of those previous experimental conditions. Hence, there is not any significant concern in this regard, as the battery operation environment is switched from "pure oxygen atmosphere" to ambient dry air. Moreover, the rate of oxygen reduction reaction is known to depend on the concentration of dissolved O_2 molecules and their diffusion in the electrolyte apart from the catalysts. A slightly lower O_2 partial pressure in dry-air may reduce the solubility and transport of O_2 in the electrode but only to a very limited extent. Some other reports suggested that the concentration of dissolved O_2 molecules and their diffusion can be notably elevated if the right electrolyte is chosen,[33,95,96] which is a very positive sign for practical Li-air batteries. Zhang et al. presented a detailed study that recommends the selection of organic electrolytes based on their polarity, viscosity, ion conductivity, and oxygen solubility for primary Li/air batteries operated in dry air conditions.[95] Ishigawa et al. tested and compared Li-O_2 battery performance in pure O_2 and in dry air. The results suggested only a slight decrease in both the potential plateau and the discharge capacity, as the operation environment of the battery was switched from O_2 to dry air.[97] All these results have unambiguously pointed out that the partial pressure of oxygen in the ambient atmosphere is sufficient to support electrochemical reactions in Li-air battery. More effort should hence be directed to other remaining issues, including the electrolyte, the catalysts, or the design and integration/stacking of the cells.

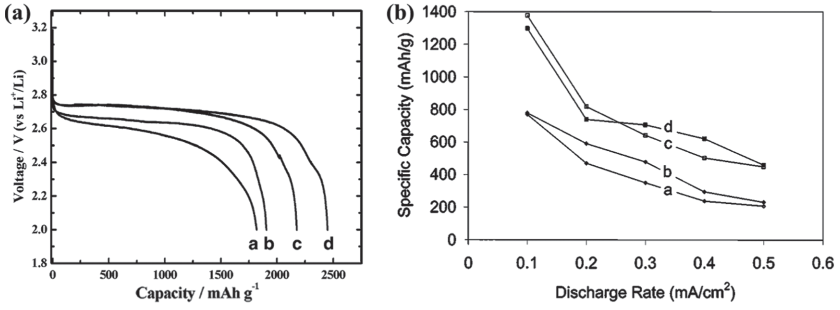

Figure 8. a) Discharge curves of the lithium air cell at a fixed current density of 0.1 mA cm^{-2} in 1, 3, 5, and 10 atm of oxygen for a-d curves. Reproduced with permission.[92] Copyright 2010, Springer. b) Specific capacity of carbon vs discharge rate in 0.8 atm O_2, 4 atm air, 2 atm O_2, and 11 atm air for a–d curves. Reproduced with permission.[94] Copyright 2003, The Electrochemistry Society.

3. Summary and Outlook

In this review, we make no attempt to cover all the inherent challenges in the field of Li-O_2 batteries, but focus on the issues that become more prominent if the operating atmosphere of the cell is switched from pure O_2 to ambient air. As real Li-air batteries are the ultimate goal, one has to identify and address all emerging issues when the system is switched from Li-O_2 to Li-air. One critical issue is the effect of the trace amounts of H_2O and CO_2 from air on the performance of Li-O_2 cell, above all, the discharge/charge behavior and cycling life, which are crucial for practical batteries. At the same time, reactions at the anode side should not be ignored, as environmental contaminants (e.g., O_2, CO_2, H_2O, N_2) entering the cell through the air cathode may cross over the electrolyte, reaching the anode and start side reactions with lithium metal. The process sees further complications when oxygen and water are involved in reactions with electrolyte at the anode. As reported by Amine et al., in Li-air cells the crossover of O_2 from the cathode to the anode resulted in various decomposition reactions at the Li-anode.[98] The practical use of lithium metal as an anode is still a great challenge, especially in an open air environment.[98,99] As a good start, some clues have been obtained on how to alleviate short-circuit of batteries caused by dendrite growth on Li metal anode.[33,100,101] Moreover, good stability of lithium is proven to be achievable in a number of nonaqueous solvents via the formation of a passivation layer (a.k.a. solid electrolyte interface, SEI) on its surface, which blocks the further reactions with the electrolyte. For instance, a stable SEI film formed on an Li anode via the reaction with additives of vinylene carbonate, $LiNO_3$, even O_2 or trace of H_2O, has notably improved the cycling efficiency of Li-air batteries.[102,103] A stable SEI on Li anode can also help to protect lithium from reacting with environmental contaminants crossing over from the cathode side. Effective protection is likewise attainable from a dense Li^+-conductive ceramic membrane, e.g., lithium-aluminum-germanium-phosphorus (LAGP), pressing onto one side of Li metal (with the other side fully sealed) to only allow for the transportation of Li^+, but block possible crossover of any contaminants to the Li anode.[104] With the Li anode protected by an artificial ceramic SEI, Visco et al. demonstrated smooth operation of an aprotic Li-Air battery over 60 discharge-charge cycles at 0.4 mA cm^{-2} in air of 50% relative humidity.[105] Further Li anode protection approaches came from the angle of minimizing Li corrosion, e.g., surface-coating Li with tetraethoxysilane[106] or crosslinked gel polymer electrolyte,[107] or forming a passivation layer of Li_3N via reaction with N_2 at specific conditions.[108] Instead of surface engineering the Li anode, it is also possible to switch to solid electrolytes of ceramic or polymers, so that the crossover of oxygen, nitrogen, and carbon dioxide toward the Li anode can be effectively blocked.[33,101,109] The related progress has been summarized in some recent reviews.[99,110] The unavailability of lithium cells using Li metal anodes in the market to date, despite their various significant advantages, is a clear indication for the immaturity of the currently available lithium protection techniques. Developing a reliable and cost-competitive approach for lithium anode protection remains a high priority. In addition, as extensively discussed in this review, the traditional view on the detrimental effects of H_2O and CO_2 on the performance of Li-air battery is facing challenges. It at least remains debatable if the elimination of H_2O and/or CO_2 is necessary for, or even helps, a practical Li-O_2 battery.[111,112] Importantly, the comprehensive account we present here on how H_2O or CO_2 affected the cathode electrochemistry of Li-O_2 in both the discharge and charge processes, is paving the path for the advancement of real rechargeable Li-air battery technologies towards practical applications.

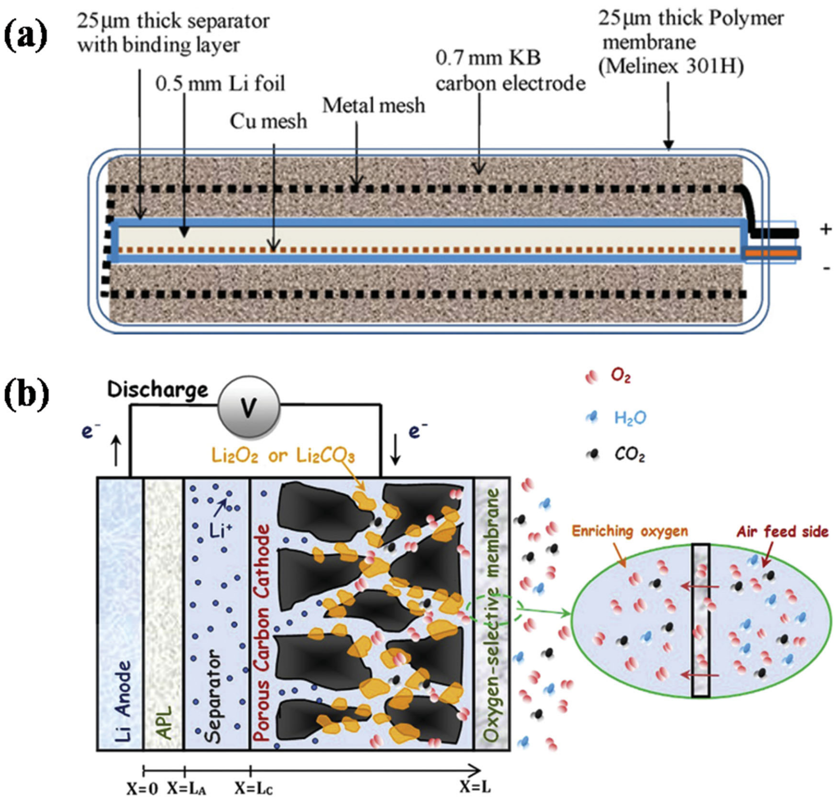

Figure 9. a) Schematic of a typical double-sided pouch Li/air cell with low-permeability polymer window. Reproduced with permission.[114] Copyright 2010, Elsevier, B.V. b) The possible design of a future Li-air battery, which is protected by an oxygen-selective membrane at the cathode. Reproduced with permission.[118] Copyright 2014, Elsevier, B.V.

Given the enormous progress in other aspects of Li-O_2 battery research, e.g., bifunctional air cathodes development,[18,27] it is time to look into Li-O_2 batteries that can operate in ambient air. In this case, one has to understand how contaminants in ambient air, above all, H_2O and/or CO_2, would impact the performance of a Li-O_2 battery. Encouragingly, some attempt as the transition from Li-O_2 to Li-air has been made very recently by investigating the cell using H_2O or CO_2 "contaminated" oxygen as a simplified model and scenario.[59,63,113–119] Among these efforts, Zhang et al. reported the first-ever real Li-air primary battery using non-aqueous electrolytes that was able to operate in ambient conditions for more than a month at a specific energy of 362 Wh kg^{-1}, with the cell design shown in **Figure 9**a.[114] More recently, some groups showed that Li-air batteries could be made into a rechargeable system operating in ambient air.[59,116,118,119] However, their cycle life is far from satisfactory. There is a long way to go to make these cells practically useful and economically viable.

Based on the constituents of air, the major reaction in the discharge of a Li-air battery should still be the electrochemistry of Li_2O_2 formation. Despite the remote likelihood of an electrochemical reaction between Li and H_2O, a chemical reaction of H_2O with Li_2O_2 is possible that leads to the formation of a side product, LiOH. Another major side product is Li_2CO_3, forming via the reaction of Li with "impurities" of various sources, including the decomposition of electrolytes, the oxidative reaction of carbon cathodes, the electrochemical reactions (CO_2, superoxide anion radical species, and lithium ion), and the chemical reactions (CO_2 with Li_2O_2 or LiOH). All these will complicate the recharging process, involving the decomposition of Li_2O_2, LiOH and Li_2CO_3. As discussed above, LiOH and Li_2CO_3 exhibited much higher overpotential when compared to pure Li_2O_2. Such a high overpotential will greatly and adversely impact the cycle life and energy efficiency of Li-air batteries. The question to ask here is how to further improve the performance of Li-air batteries. A seemingly straightforward answer would be to employ a highly selective membrane[120–124] that allows for fast O_2 transportation but fully blocks the diffusion of CO_2 and H_2O, and meanwhile prevents the electrolyte from evaporation (see Figure 9b, the possible design of future Li-air batteries). Unfortunately, most membranes today present better permeability for CO_2 and H_2O than O_2; a 100% O_2-selective membrane system remains unavailable.[32,121,125] An alternate way is to get all possible discharge products (Li_2O_2, LiOH, and Li_2CO_3) fully oxidized upon charge to mitigate the capacity fade in the cycling of cells.[126] From a comprehensive understanding of how H_2O and CO_2 impact the performance of Li-air batteries and the cathode reaction mechanism, we believe that the most feasible solution would be a combination of a highly effective catalytic air cathode and a system that least disturbs the electrolyte during both discharge and charge processes. In addition, dry air may contain small amounts of other gases such as sulfur oxides, nitrogen oxides, and carbon monoxide etc., which are common pollutants in ambient air. The contents might be comparably high where the air pollution is notorious. These gas molecules may enter the cell system and affect the cell chemistry, which should not be ignored in future investigations. Some recent studies showed that, although SO_2 results in the high overpotential, it may be used to control and limit the growth of Li_2O_2 in specific directions and increase the electronic conduction through the formation of interface between Li_2O_2 and $Li_2(SO_2)$-type inclusion, which may ultimately increase the capacity of the cell.[86]

For operation in ambient air, the electrolyte of choice for Li-air battery ought to possess the features of excellent non-volatility, high thermal stability, a broad electrochemical window, and high hydrophobicity. The prevailing DMSO-, glyme-, and ionic liquids-based electrolytes[127–129] are under intense scrutiny. Some emerging binary and ternary electrolyte systems composed of a polymer-organic solvent and selected ionic liquid might also be interesting candidates.[63,130–132] The key development of cathode materials has been summarized in Table 1 at the beginning of this review. Good catalysts may be able to reduce the overpotential and raise the stability of the system;[15,21] and a promising example is the soluble redox mediators.[40,44,133–135] Very recently Grey et al. demonstrated a highly efficient, rechargeable Li-O_2 battery with extremely large capacities and excellent energy efficiency (93.2%) by using reduced graphene oxide electrode, and redox media LiI with additive H_2O in a DME-based electrolyte.[136] This is an excellent example for the use of H_2O, which was previously held to be detrimental, and meanwhile, gives us more confidence on the practical adoption of real Li-air batteries in the near future.

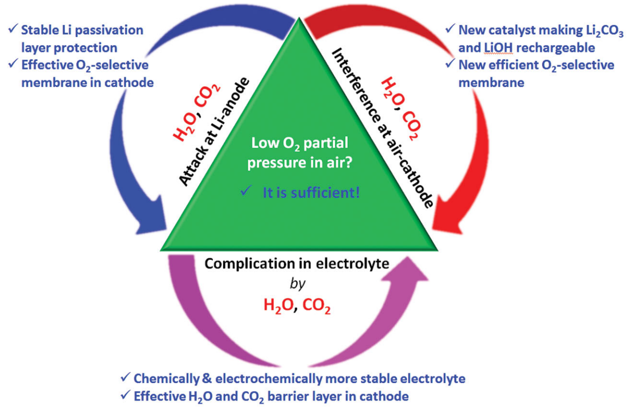

Figure 10. Summary of the challenges and the solutions from Li-O_2 to Li-air batteries.

Although the irreversible side reactions could be detrimental to cell performance, their impact on the cycling stability is only chronic.[34,80,137] As demonstrated by Gowda et al., Li_2CO_3 formed by the spontaneous reaction between CO_2 and Li_2O_2 was not decomposable in the charge process, while their counterparts formed due to the decomposition of electrolytes (DME) could still deliver capacity at high voltages. A more stable electrolyte is beneficial for the cycling stability of Li-air batteries; however, such an electrolyte is by no means easily available. For instance, DMSO, a suggested good solvent to replace ethers in electrolyte, was soon proven problematic by Shao-Horn et al., as it was found to react with Li_2O_2 which led to the formation of LiOH.[138] DMSO may also undergo anodic oxidation to form $DMSO_2$ in the presence of a trace of water under higher overpotentials.[139,140] As seen from Reactions 10–14 and Figure 6, the synergy of CO_2 and O_2 with the higher dielectric electrolyte results in the formation of Li_2CO_3. In addition, the side products of LiOH and Li_2CO_3 may also orginate from CH_3OLi, CH_3Li, and polymeric layers through reactions with lithium metal, depending on the cell configuration.[95] In light of these complications, on one hand the co-effects between gas environments and electrolytes should be considered, just as we must consider the catalyst and electrolyte synergy in Li-O_2 batteries.[141] On the other hand the detection of unwanted chemical products during both the charge and the discharge processes should be carefully conducted prior to any meaningful assessment on the cycling stability of a Li-O_2 cell. Combination of S/TEM, online mass spectrometry, XPS, FT-IR or Raman spectroscopy, operando X-ray diffraction, and other in situ synchrotron techniques will play a paramount role in identifying the intermediate or final products in the operation of a Li-O_2 battery, which in turn helps elucidate the mechanism of oxygen reduction/evolution.[142–155] Based on the above discussion, a summary of the prominent issues presented, and the feasible solutions from Li-O_2 to Li-air batteries is given in **Figure 10**.

Some unusual but useful discoveries in Li-air battery research include the H_2O addition-triggered formation of crystalline Li_2O_2 with varied size and morphologies, which boosts the cell capacity and improves the cycling stability, and the dependence of the Li-air battery performance on the concentration of H_2O and CO_2 in electrolytes. According to some recent reports,[61–63] crystalline Li_2O_2 could form under lower discharge current densities in CO_2 free Li-O_2 batteries, which was likely enabled by the trace amount of water contaminant in electrolyte. In order to eliminate such uncertain factors and enhance the reproducibility and repeatability of the Li-air cells, it is essential to improve the sealing of cell hardware and quantify the water and carbon dioxide content in electrolytes, so that the reaction mechanism can be more accurately analyzed prior to any electrochemical tests. Our discussions presented in this review provide necessary clues to facilitate good understanding of the electrochemical mechanisms, guide the design of research on future battery materials (e.g., the electrolytes and electrocatalysts) and feedback the needs in the architecture of the next generation cell systems, which altogether will expedite research development in the area and thus bring the Li-air battery technology one big step forward.

Acknowledgements

This research was supported by the Advanced Energy Storage Research Programme (IMRE/12-2P0503 and IMRE/12-2P0504), Institute of Materials Research and Engineering (IMRE) of the Agency for Science, Technology and Research (A*STAR), Singapore, and Nature Sciences and Engineering Research Council of Canada (NSERC) and Canada Research Chair (CRC) Program.

Received: November 2, 2015
Revised: January 19, 2016

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