




Aprotic lithium air batteries with oxygen-selective membranes

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Abstract

Rechargeable batteries have gained a lot of interests due to rising trend of electric vehicles to control greenhouse gases emissions. Among all type of rechargeable batteries, lithium air battery (LAB) provides an optimal solution, owing to its high specific energy of 11,140 Wh/kg comparable to that of gasoline 12,700 Wh/kg. However, LABs are not widely commercialized yet due to the reactivity of the lithium anode with the components of ambient air such as moisture and carbon dioxide. To address this challenge, it is important to understand the effects of moisture on the electrochemical performance of LAB. In this review, the effects of ambient air on the electrochemical performance of LAB have been discussed. The literature on the deterioration in the battery capacity and cyclability due to operation in ambient environment and degradation of lithium anode due to exothermic reaction between lithium and water is reviewed and explained. The effects of using oxygen-selective membrane (OSM) to block moisture and CO₂ contamination has also been discussed, along with suitable materials that can act as OSM. It is concluded that the utilization of OSM can not only make the safer operation of LAB in ambient air but could also enhance the electrochemical performance of LAB. Future direction of the research work required to address the associated challenges is also provided.

Keywords Lithium air battery · Energy storage · Oxygen selective membrane · Hydrophobic membrane

Introduction

Global warming is one of the major problems in the world due to which earth temperature is increasing continuously [1]. The main reason of the global warming is carbon emissions [2]. The amount of carbon dioxide in the beginning of 2019 was around 407 ppm which was 277 ppm in 1750 in a preindustrial era [3]. The contribution of transport sector in

global carbon dioxide emissions is around 24% [4] and [5] because of dependence on fossil fuel. On average, around 150 g per km of CO₂ is produced by conventional fossil fuel-based vehicles [6] which are capable to produce the tremendous amount of carbon dioxide. Therefore, it is important to look for an alternate of the fossil fuel-based transportation. The reliability and cost effectiveness are the main aspects of the alternative. Electric vehicles are considered as an alternate of fossil fuel-based transportation [7]. Electric vehicles normally utilize fuel cell or rechargeable batteries [8–10]. The use of fuel cell is an expensive option as it uses pure hydrogen, which requires costly production processes [11]. So, the use of batteries in electric vehicle is the most economic and effective option.

Batteries are commonly used for storage of electrical energy in the form of chemical energy. During discharging of battery, chemical energy is transformed into electrical energy thus providing an electric current. While, during charging, electrical energy is supplied to battery which ultimately stores as chemical energy. There are numerous commercial battery technologies available including lead acid battery, nickel cadmium battery and lithium-ion battery. Among all available battery technologies, lithium-ion

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batteries have achieved a lot of consideration as energy storage device in hybrid and electric vehicles [12] and mostly all the manufacturers of such types of vehicles are using lithium-ion batteries [13] due to their higher energy density as compared to the other available and commercial battery technologies. But still, energy density of lithium-ion battery is very much low as compared to gasoline. This means that it is not a suitable candidate for replacement of gasoline. So, it is desired to look for an alternate energy storage device [14]. Metal-air batteries are studied as the alternate of lithium-ion batteries and a lot of research has been conducted on metal-air batteries [15–25]. Among all types of metal-air batteries, LAB is the suitable candidate to replace the fossil fuel-based transportation in future due to its high theoretical energy density of 11,140 Wh/kg among the other types of batteries and is also comparable to the energy density of the gasoline which is 12,700 Wh/kg [26]. The energy density of different types of batteries is summarized in Table 1. The practical energy density of lithium air battery is ten times as that of lithium-ion battery [27]. Therefore, for complete shifting from fossil fuel-based transportation to electrical vehicles, a lot of research in lithium air batteries is required to make the operation of electric vehicles cheap and reliable.

There is a growing interest among researchers to address the challenges in operation of LAB; however, very few review articles have been reported recently explaining the technical problems in LAB function in ambient environment and solutions to avoid these. In this review paper, the fundamental operating principle of LABs has been explained and associated factors limiting the battery performance have been presented. Ambient air, moisture and CO₂ interact with the lithium anode and discharge products forming LiOH and Li₂CO₃. These compounds are found to be difficult to decompose thus results in low battery life and efficiency. The solution of such problem is the use of membrane which blocks the moisture and CO₂ to enter into the battery and allows only oxygen to enter. Recent studies on avoidance of moisture and CO₂ contamination on lithium electrodes

have been reviewed to indicate the future directions of LABs technology.

Working principle of lithium air batteries

Lithium air batteries are composed of pure lithium anode, carbon-based oxygen cathode and an organic electrolyte. Upon discharging lithium and oxygen combines electrochemically and form discharge product Li_2O or Li_2O_2 depending on the type of oxidation–reduction reaction (ORR) [35]. Upon charging, discharge product decomposes and gives back lithium and oxygen back to the atmosphere. The schematic of lithium air battery working principle is presented in Fig. 1. Abraham and Jiang [36] first reported the non-aqueous lithium oxygen battery in 1996. Afterwards, many research groups conducted the research on lithium air batteries [37–44]. Awan, Christy, Hwang and Nahm [45], reported following four types of lithium air batteries on the basis of electrolyte:

- i. Non-aqueous/aprotic electrolyte LAB
- ii. Aqueous electrolyte LAB
- iii. Solid-state electrolyte LAB
- iv. Hybrid electrolyte LAB (combination of all three).

All of the four abovementioned batteries have their separate challenges. In the non-aqueous/aprotic electrolyte LAB, the reaction of moisture and CO₂ with the lithium anode results in the decrement of battery capacity, cyclability and efficiency [46–49]. Also, for non-aqueous electrolyte LAB, the discharge product is insoluble in aprotic electrolyte thus causing the clogging of cathode [49–52].

In aqueous electrolyte LAB, discharge product is soluble in electrolyte but their specific energy is around 30% lower than that of aprotic one [35, 53–55]. The production of Solid

Table 1 Theoretical energy density of different batteries and gasoline

Battery type	Energy density	Reference
Lead acid	123 Wh/kg	[28]
Lithium ion	250 Wh/kg	[29]
Zinc–oxygen	1084 Wh/kg	[15]
Sodium–oxygen	1605 Wh/kg	[30]
Magnesium–oxygen	6800 Wh/kg	[31]
Aluminum–oxygen	8100 Wh/kg	[32]
Lithium–sulfur	2600 Wh/kg	[33]
Lithium–air	11,140 Wh/kg	[34]
Gasoline	12,700 Wh/kg	[26]

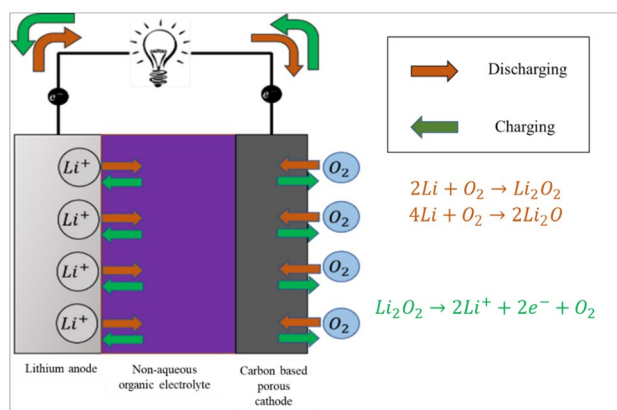


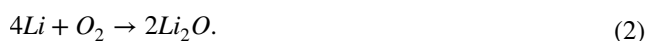
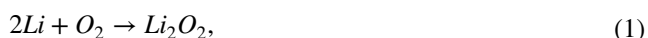
Fig. 1 Aprotic LAB working principle

electrolyte for LAB normally occurs at high temperature of around 800 °C [56, 57] which ultimately decreases the net energy density of the battery. Also, the conductivity of solid electrolyte LAB is around 1.92×10^{-4} S/cm at room temperature and is increased by increasing the temperature [58].

The above-mentioned issues need to overcome in order to commercialize lithium air batteries. The operation of lithium air battery is similar to that of a fuel cell. During the discharge operation, lithium anode gives lithium ions which are dissolved in the electrolyte and then travel towards the carbon cathode where joining of lithium ions with oxygen from atmosphere occurs while the electrons travel from the lithium anode towards the cathode via an outer electrical network giving us an electrical power [59]. The discharge operation is governed by oxidation–reduction reaction. The formation of discharge product entirely depends on the nature of catalyst. During the charging operation, the discharged products are decomposed by electrochemical reaction, providing Li ions which travels back to the lithium anode and oxygen is released into the atmosphere. The charging of the battery is governed by oxygen evolution reaction (OER) and then electrical energy is stored as chemical energy [26].

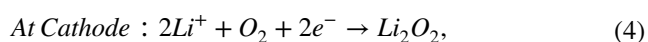
The charging and discharging cycles in LABs can be presented using the following set of chemical reactions:

Upon discharging



The reversible voltage for reactions given by Eq. 1 and Eq. 2 are $E^\circ = 2.96\text{V}$ and $E^\circ = 2.91\text{V}$ [60], respectively, with an open circuit voltage of around 3.7 V [61]. The reversible voltage can be calculated using Gibbs free energy, $E^\circ = -\Delta G/nF$ where n is the representation of total number of electrons transfer in 1 molar reaction and F is known as Faraday's constant. Upon charging, the discharge products are decomposed giving back lithium metal at anode and oxygen back to the atmosphere.

The half-cell reactions at the anode and cathode are given by Eqs. 3, 4 and 5.



In general, Li_2O_2 is the product formed during discharging of lithium air battery, the production of Li_2O has low evidences. Both Li_2O and Li_2O_2 are unsolvable in organic electrolyte and they get deposited in the pores of carbon

cathode which ultimately results in deterioration of cyclability and capacity of cell with respect to time. Upon charging, the discharged product decomposes into lithium ions which travel back towards lithium anode and oxygen which is sent back to atmosphere. The oxygen evolution reaction (OER) is governed by Eq. 6.

Upon charging



Different researchers have also worked on aqueous lithium air batteries [62–68]. Figure 2 describes the function of the aqueous lithium air batteries. They consist of lithium anode protected by lithium-ion conductive water stable solid electrolyte, aqueous electrolyte and carbon-based porous cathode. Water stable solid electrolyte is incorporated to protect the lithium metal from corrosion by water. In aqueous lithium air battery water molecules take part in the electrochemical reaction according to Eq. 7 and also their energy density is 30% lesser than that of aprotic one [54, 55]. One of the major advantages of aqueous lithium air batteries is that the discharge product is easily soluble in aqueous electrolyte [69] but due to their low energy density than that of aprotic one, the major portion of the research is oriented towards aprotic lithium air batteries.



Problems associated with operation of aprotic lithium air batteries in atmosphere

Mostly, the research on aprotic lithium air battery was conducted using pure oxygen [69–79]. The use of pure oxygen in practical application had some serious issues like

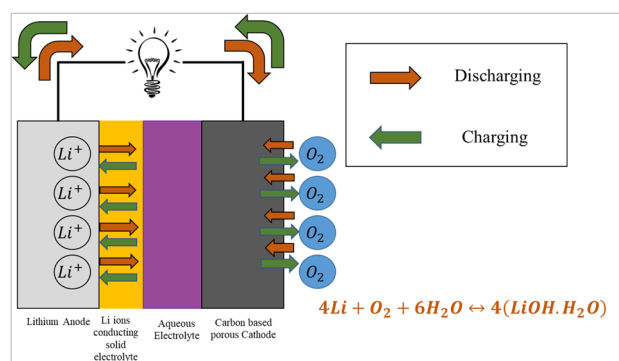
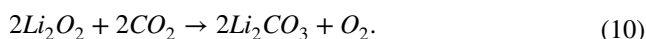


Fig. 2 Aqueous LAB working principle

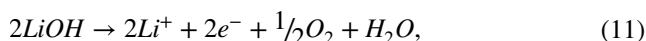
additional storage weight, refilling of cylinder and safety issues which are considered to be the hindrances in practical LAB. These hindrances can be overcome by replacing pure oxygen with air. Air is made up of nitrogen (78.1%), oxygen (20.9%), carbon dioxide (0.035%) and traces of moisture [80]. It was expected that carbon dioxide and moisture content can affect the battery performance.

Effects of moisture and CO₂ on the battery performance

Huang, Cui, Zhao, Sun, Guo [81] has discussed the effects of using air for oxygen supply on the performance of lithium air battery. The battery was composed of lithium anode, tetra ethylene glycol dimethyl ether (TEGDME) as electrolyte and cathode made up of carbon nanotube. It was noticed that during operation with air, the discharge product Li_2O_2 react with moisture and CO_2 to form $LiOH$ and Li_2CO_3 , respectively. Similar formation of $LiOH$ and Li_2CO_3 was also observed by Zhang and Zhou [82] and noted that the recharging is accomplished by decomposition of Li_2O_2 , $LiOH$ and Li_2CO_3 which ultimately results in high overpotential. The possible reaction upon discharging may be as followed:

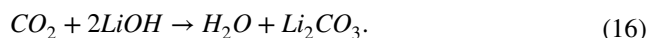
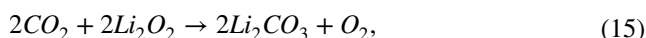
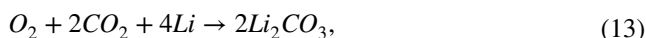


Upon charging, the possible decomposition of $LiOH$ and Li_2CO_3 is as follows:

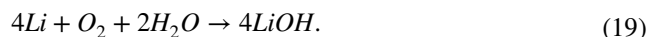
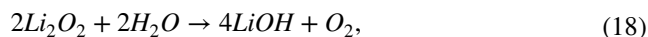
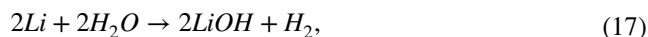


Liu, Wang, Cao, Shang, Wang, He, Yang, Cheng and Lu [83] has reviewed the side reactions in LAB due to the presence of carbon dioxide and moisture and reported that these side reactions can result in the corrosion of cathode and electrolyte degradation. The following side reactions were reported.

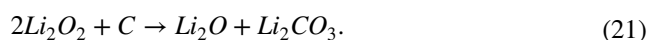
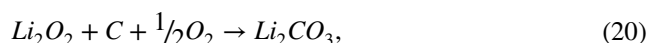
For CO_2



For H_2O

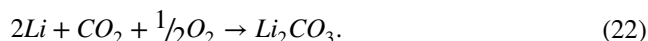


McCloskey, Speidel, Scheffler, Miller, Viswanathan, Hummelshøj, Nørskov and Luntz [84] have discussed that discharge product Li_2O_2 can react with carbon cathode and can form Li_2CO_3 by the following reactions:



The reaction of lithium with water is exothermic in nature and is governed by Eq. 17 [85]. Tan, Shyy, Zhao, Zhang and Zhu [86] has conducted experiments to find the effects of moisture on the performance of battery. They have found that the energy efficiency of the battery when operated in dry air is 66.2% and when operated in air with relative humidity of 84%, the energy efficiency is 73.8%. Although the energy efficiency of the battery is high when operated in moist air but moisture content can seriously deteriorate the cell life [87]. The deterioration of battery life due to corrosion of lithium anode by moisture was also found by Wang, Huang, Liu, Xie, Zhang, Zhu, Cao, Zhao [88]. The excess moisture can pass through the electrolyte and react with lithium anode and can cause the deterioration of the lithium anode governed by Eq. 17. Zhu, Liu, Rong, Chen, Yang, Jia, Yu, Karton, Ren, Xu, Adams and Wang [89] has reported that the operation of LAB with pure air is safe as long as lithium anode is protected.

Lim, Lim, Park, Seo, Gwon, Hong, Goddard and Kim [90] demonstrated that Li_2CO_3 can be disintegrated electrochemically at high voltage of 4.5 V which ultimately decreases the charging efficiency of lithium air battery. The decomposition of Li_2CO_3 is governed by Eq. 11. Zhang and Zhou [91] have also stated the formation of Li_2CO_3 as a discharged product when operated in pure air. Gowda and Brunet [92] have mentioned that carbon dioxide in air can react with lithium anode and can form Li_2CO_3 . It was also reported that the practical rechargeable LAB requires the avoidance of carbon dioxide into the cell for better charging capability. The electrochemical reaction between Li and CO_2 was governed by Eq. 22.



Keeping in view the literature that has been discussed in this section, it can be stated that the presence of moisture is

riskier than the presence of carbon dioxide and can significantly reduce the battery life [84]. However, for high coulombic efficiency, it is desired to avoid the carbon dioxide as well [85].

Solutions to avoid moisture and CO₂ contamination on lithium electrodes

In order to operate non-aqueous lithium air battery in open air, it is required to block the moisture and carbon dioxide to go into the battery. From above discussion, it can be noted that blockage of moisture is more important than carbon dioxide to ensure the safe operation. This has been achieved by introducing a membrane known as oxygen-selective membrane (OSM) which permits only the oxygen to enter into the battery whereas blocks the moisture and carbon dioxide reach the active site [27]. The use of membrane for blocking of moisture was first suggested by Muthiah, Hsu, and Sigmund [93]. They suggested that polyvinylidene fluoride (PVDF)-Teflon amorphous fluoropolymer (AF) can be used as hydrophobic material in lithium air battery. However, they did not evaluate the electrochemical performance of the battery. Crowther and Salomon [94] were the first who came up with an idea of using Teflon coated fiberglass cloth as oxygen-selective membrane (OSM) for operation of lithium air batteries in air and reported 94% increment in the capacity. Using OSM, they have optimized quantity of LiBF₄ in the electrolyte for lithium air. They have used propylene carbonate, 1,2-dimethoxyethane, dimethyl carbonate and tetra ethylene glycol dimethyl ether as an electrolyte and tested the battery in 23 °C with 23% relative humidity.

Required properties of OSM

Different researchers have studied the required properties of OSM for LAB [27, 95–101]. All of them have mentioned the following four required properties of OSM for efficient working of LAB in ambient air.

- OSM should allow high oxygen diffusion because capacity of the battery is highly dependent on the oxygen partial pressure [102].
- It should be highly hydrophobic and should block the moisture to go into the battery as moisture degrades the battery capacity and cyclability.
- It should avoid penetration of carbon dioxide into the battery because CO₂ reacts with the discharge product to form the Li₂CO₃ which ultimately decreases the battery efficiency.
- It should decrease the evaporation of electrolyte because during battery operation the temperature of

the battery increases which ultimately results in the evaporation of electrolyte.

Crowther and Salomon [95] have also mention that two major groups can be served as potential OSMs which are perfluorocarbons and silicone-based oils.

LAB operation with OSM

Sahapatombut, Cheng and Scott [103] modeled the LAB with silicone oil as oxygen-selective membrane with operation in air. It was demonstrated that while operating in ambient air without OSM, the capacity of the battery was much low than that of when operated in pure oxygen as shown in Fig. 3. From the model, it was demonstrated that the discharge capacity is around 4 times high as that of without using membrane as shown in Fig. 4. The model also predicts that battery can provide 800 mAh/g when discharge at a rate of 0.05 mA/cm².

Zhang, Xu, and Liu [104] experimentally evaluated the influence of using OSM comprised of silicone oil loaded on Teflon films and porous metal sheets and reported that battery performed well in ambient air with 20–30% relative humidity with OSM. They have also reported that the battery is able to operate for 16.3 days at a relative humidity of 20% with a capacity of 789 mAh/g and is able to provide the specific energy of 2182 Wh/kg. While the reference battery which is composed of only PTFE as moisture barrier was able to run only for around 5.5 days with a specific capacity of 267 mAh/g and specific energy of 704 Wh/kg. Zhang, Wang, Xu, Xiao and Williford [105] tested the battery by utilizing heat sealed polymer as OSM. The membrane not only served as the moisture resistant but also the packaging material. It was found that the battery was able to run

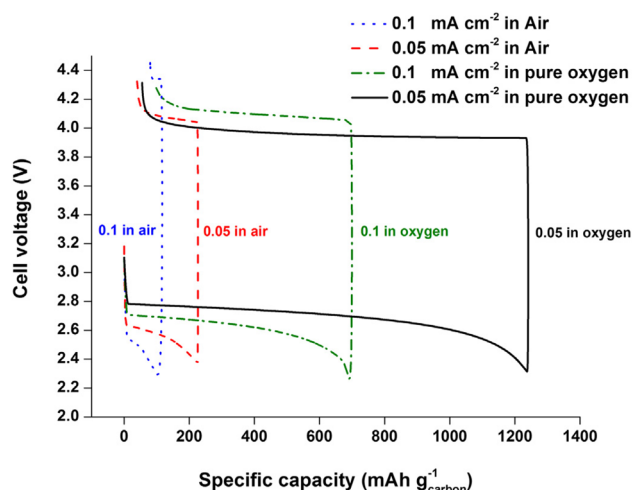


Fig. 3 Specific capacity of battery in pure oxygen and ambient air without membrane [103]

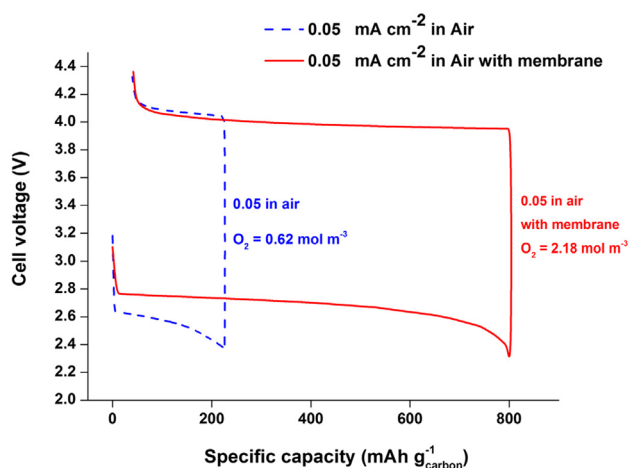


Fig. 4 Specific capacity of battery with and without OSM [103]

for a month when operated in ambient conditions and is also able to provide the capacity of 362 Wh/kg. Zou, Liao, Wang, Lu, Zhou, He, Ran, Zhou, Jin and Shao [106] used silica-aerogel-based oxygen-selective membrane to check the battery cyclability in dry and humid environment. It was found that the battery with membrane in dry environment was able to run for 165 cycles when discharge at a capacity of 500 mA/g while the battery without membrane was only able to run for 55 cycles when discharged at the same rate. While when the battery was operated in 45% relative humidity with OSM, the battery was able to run for 130 cycles at rate of 500 mA/g; however, without OSM the battery was

able to operate only for 12 cycles under similar conditions as shown in Fig. 5. The discharge product when operated without membrane is LiOH while using membrane it was mainly Li₂O₂.

Wang, Pan, Zhang, Cheng, Liu, and Peng [107] utilized low-density polyethylene as OSM. They have reported that polyethylene is very good for the ambient operation of lithium air battery. They tested the battery in 50% relative humidity and found that battery could last till 610 cycles when discharged at a fixed capacity of 1000 mAh/g. Ruan, Sun, Song, Yu, Chen, Li and Qin [108] investigated the performance of LAB using perfluorocarbon-silicone oil as oxygen-selective membrane and found that battery has a discharge capacity of 4991 mAh/g. They have also found that the performance of battery with the membrane in ambient operations is comparable to the performance of battery with pure oxygen. Amici, Francia, Zeng, Bodoardo and Penazzi [109], investigated the battery using polyvinylidene fluoride co-hexafluoropropylene as OSM and tested the battery in ambient air with 17% relative humidity. It was found that battery could provide 640 mAh/g when operated with OSM which is far higher than that of without OSM. It was also found that lithium anode is also safe with the utilization of OSM. Xie, Huang, Lin, Li, Huang, Yuan, Shen, and Huang [110] have used perfluoropolyether as oxygen-selective membrane and found good hydrophobic behavior of the membrane. It was also found that battery can run up to 144 cycles and is able to provide the capacity of 500 mAh/g when discharged at 100 mA/g while without membrane it was able to run only for 6 cycles as shown in Fig. 6.

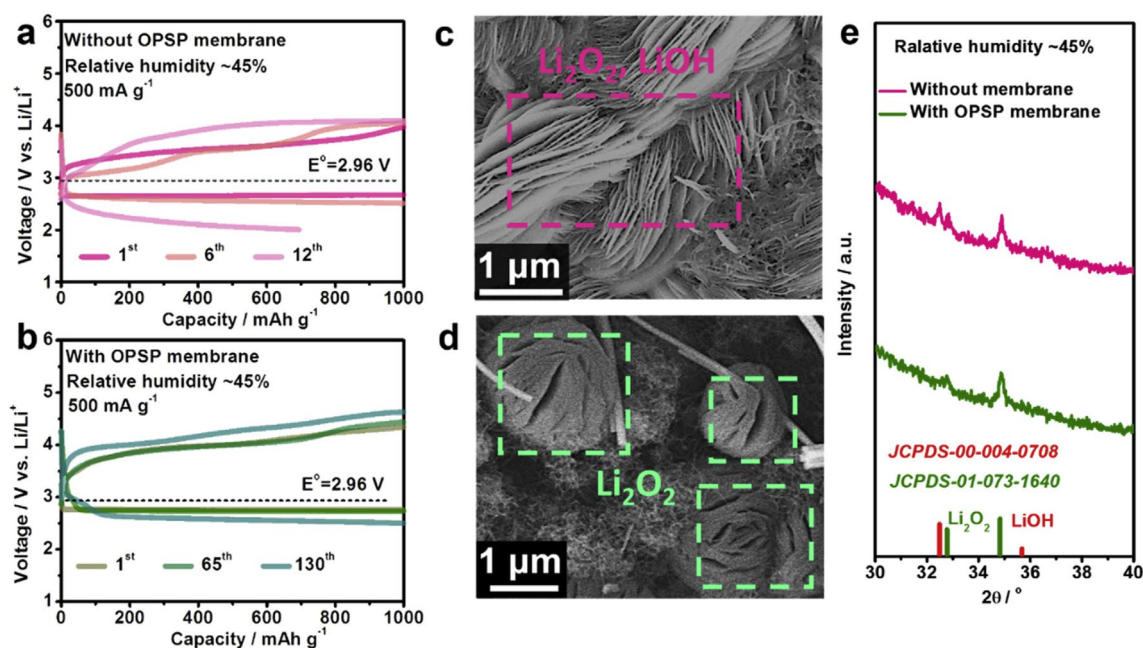


Fig. 5 Cycling comparison and discharge product of batteries without and with OPSP membrane. [106]

Amici, Alidoost, Francia, Bodoardo, Martinez, Aman-tia, Biasizzo, Caldera, and Trotta [111] has added dextrin nano sponge into a poly vinylidene fluoride co-hexafluoro-propylene matrix and utilized as OSM. It was found during experimentation that without OSM battery was able run just for 38 cycles at a current density of 20 mA/g when operated in 17% RH while the battery was able to run for 144 cycles with OSM when operated in same conditions. Fu, Wei, Lin, Huang and Yu [112] has tested polyaniline (PANI) membranes for blocking of moisture and found that battery could deliver 3240mAh/g when discharge at a slower rate of 0.1 mA/g in 20% relative humidity. Zhang, Xu, Li and Liu [113] have used silicate zeolite and polytetrafluoroethylene for the preparation of OSM and utilized in lithium air battery. They have operated the battery for 21 days at 20% relative humidity and found that the battery is able to provide the specific capacity of 1022 mAh/g and specific energy of 2792 Wh/kg. Zhu, Zhao, Wei, Tan, and An [114] silicone oil-based OSM and reported the improved results. Lujie Cao, Fucong, Ying, Wenxi, Yifeng, Xianzhu, and Lu [115] have used mixed matrix-based membrane using polydopamine and then utilized the membrane for lithium air battery operation. They have found that the prepared membrane is very good for the blockage of moisture and carbon dioxide. The

battery along with membrane is able to run for 66 cycles and is able to provide the capacity of 450 mAh/g when discharge at a fixed rate of 450 mA/g at 30% relative humidity. Zhong, Papandrea, Xu, Lin, Zhang, Liu, Huang, and Duan [116] have utilized three-dimensional (3D) hydrophobic graphene membrane and found that operation in air with membrane is similar to that of in pure oxygen. They have reported that the battery is able to run for 100 cycles and is also able to provide the capacity of 1425 mAh/g when discharged at a rate of 2.8 A/g. Chen, Jiang, Yang, and Shen [117] has conducted the waterproofing of Carbon Black cathode with polytetrafluoroethylene and found the membrane formed over the surface of cathode which ultimately enhances the electrochemical performance of the battery. Dong, Wang, Tang, Wang, Li, Yin, and Yang [118], have used the composite membrane consist of polyethylene oxide (PEO) and polytetrafluoroethylene (PTFE) for the blockage of moisture in LAB. Several membranes by varying the proportion of PEO and PTFE were prepared. The studied proportion includes 10:30, 10:35, 10:40 and 10:50 of PEO and PTFE. It was reported that the use of such membrane is effective for moisture blocking with 10:35 is the best among all the proportions. The battery with 10:35 PEO/PTFE membrane was able to run for 230 cycles when operated in pure oxygen

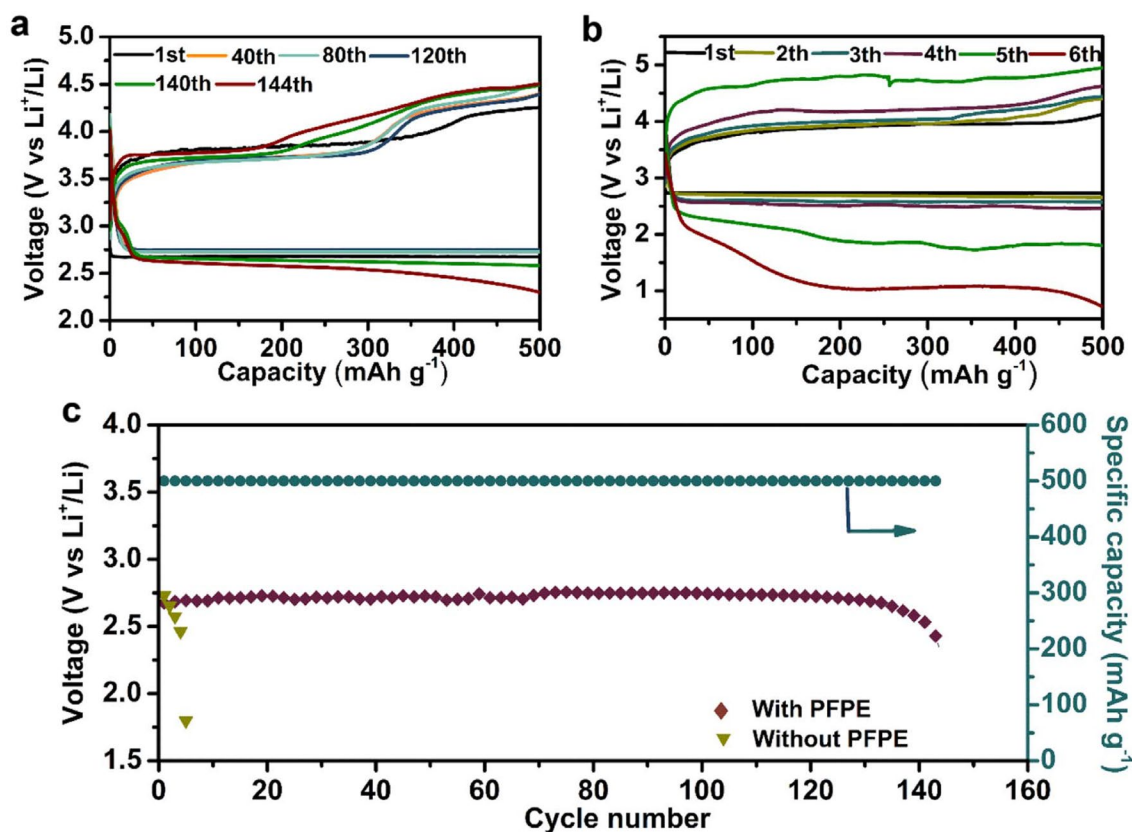


Fig. 6 Cyclic performance of LAB with and without PFPE membrane [110]

at a fixed capacity of 1000 mAh/gram at a fixed current density of 100 mA/gram. The battery was also able to run for 55 cycles when operated in ambient air with relative humidity of 50% under the same capacity and current density. Li, Hou, Luan, Zhang, and Sun [119] have simulated the mass transfer behavior of LAB equipped with PDMS–FTBA mixed OSM. By simulation, they have found that oxygen selectivity will be maximum using PDMS and FTBA with a mass ratio of 1:3. The comparison of different membranes utilized by the different researchers is presented in Table 2.

The schematic of battery with OSM is shown in Fig. 7. The OSM will act as the barrier for moisture and will allow only O_2 to go into the battery. O_2 will react electrochemically with the lithium anode and thus providing the electrical energy. Thus, the use of OSM will improve the battery cyclability as well as capacity.

Conclusion

From the above discussion and from the literature [120–122], it can be suggested that utilization of LAB in electric vehicles is the best possible alternate of the gasoline-based transportation due to its high specific capacity. But their operation is limited due to their side reactions with moisture and carbon dioxide present in the atmosphere [123–125]. The presence of moisture in the battery is more dangerous than CO_2 . When LAB operated in air, CO_2 reacts with the discharge product and forms Li_2CO_3 which decomposes at high

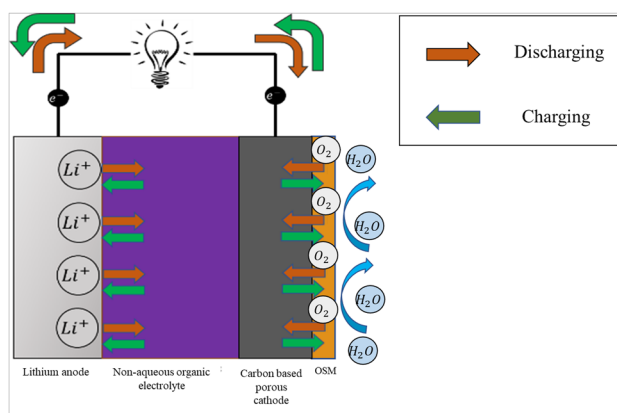


Fig. 7 Schematic of the lithium air battery with OSM

voltage and ultimately decreases the efficiency of the battery. But if moisture gets into the battery, even the traces of moisture in LAB abruptly reacts with the lithium anode and leads towards the battery failure due to exothermic reaction between Li anode and water. One option is the use of pure oxygen which ultimately increases the problems like additional weight of oxygen cylinder, refilling of the cylinder and some serious safety-related issues. Optimal solution for the ambient operation of lithium air battery is the use of oxygen-selective membrane, which allows only oxygen to enter into the battery while blocking the moisture and carbon dioxide. Polymeric membrane including PTFE, PDMS, PFPE and polypropylene seem to be good for blockage of moisture

Table 2 Comparison of membranes utilized by different researchers to avoid moisture and carbon dioxide

Membrane type	Relative humidity (%)	Current density	Capacity with membrane	Capacity without membrane	No. of cycles with membrane	No. of cycles without membrane	Reference
Silicon oil	–	0.05 mA/cm ²	800 mAh/gram	210 mAh/gram	–	–	[103]
Silicon oil loaded on PTFE	20	0.05 mA/cm ²	789 mAh/gram	267 mAh/gram	–	–	[104]
PDMS	40	500 mA/gram	1000 mAh/gram	1000 mAh/gram	165	55	[106]
Low-density polyethylene	50	2000 mA/gram	1000 mAh/gram	1000 mAh/gram	610	100	[107]
Silicon oil-loaded PVDF–HFP membrane	17	0.05 mA/cm ²	650 mAh/gram	200 mAh/gram	–	–	[108]
PFPE	30	100 mA/gram	500 mAh/gram	200 mAh/gram	144	6	[109]
Nanosponge in PVDF HFP membrane	17	20 mA/gram	100 mAh/gram	100 mAh/gram	140	38	[110]
Polyaniline	20	0.2 mA/cm ²	1700 mAh/gram	2453 mAh/gram	–	–	[111]
Polydopamine-coated metal organic framework	30	200 mA/gram	1480 mAh/gram	1100 mAh/gram	66	7	[112]
PEO and PTFE composite membrane	50	100 mA/gram	1000 mAh/gram	–	55	–	[118]

due to their hydrophobic nature. The batteries equipped with OSM have shown better performance than that of without membrane but showed very little cyclability and also failed to provide the high capacity and high specific energy.

Future direction

All of the above discussion shows that LAB will be the suitable candidate to replace the gasoline-based transportation, if the above-mentioned challenges have been addressed. The use of OSM can make the battery capable to operate in ambient air with high cyclability and capacity. Krichewski, Singh, Bormashenko, Multanen, and Schechter [126] have used bioinspired OSM for zinc air batteries. The membrane was made up of polycarbonate and iron (II) phthalocyanine in volatile chlorogenic solvent. The behavior of such type of membranes should be tested in LAB and their results should be tested. Such type of membrane can be used in lithium air batteries for moisture blockage. Similarly, different membranes which have been used in different metal–air batteries [127, 128] can be tested in LAB for blockage of moisture.

Future research should emphasize the following:

- Understanding the hydrophobic behaviors of different polymeric and inorganic membranes in lithium air batteries since there are number of hydrophobic membranes available [129–135]. However, their suitability for LABs needs to be investigated.
- Utilization of different nanoparticle in different polymeric membrane to enhance their hydrophobicity and then their utilization in lithium air batteries. The characteristics of the polymeric membranes are modified by incorporating the nanoparticles [136–142]. The use of nanoparticle-based membrane can affect the electrochemical performance of LAB.
- Optimization of electrolyte and cathode according to the type of membrane. The performance of LAB is varied with respect to the electrolyte and catalysts. Different electrolytes and catalysts should be tested with different membrane in order to select the optimized electrolyte and membrane for a particular membrane.
- Modeling of lithium air battery performance with different membrane. The membrane synthesis and testing in LAB is expensive and time consuming. So, it is better to develop the model for predicting the electrochemical performance of LAB equipped with membranes.

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