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Challenges and potential advantages of membranes in lithium air batteries: A review

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ABSTRACT

Many studies recognize that membrane lithium air batteries (LABs) are preferable to non-membrane lithium air batteries for future applications as an energy source. An intensive collection of work was published several years ago regarding air cathodes, lithium metal anodes, and electrolytes, among others. Typically, the membrane is sandwiched between an air cathode and a lithium metal anode and protects the anode from any impurities such as oxygen and water that diffuse from cathode to anode in LABs. Membranes have been used as electrolytes and separators and have been used at the outer side of the cathode and the inner side of the cathode and anode in LABs. Therefore, there is an urgent need to discuss the potential advantages of different membranes to understand the possible mitigations of challenges related to LABs. This review examines the effectiveness of various membranes in the primary components of LABs, including air cathodes, lithium metal anodes, electrolytes and electrodes. Several membranes were effective in limiting the gas permeation and water permeability in LABs. The prospects of these membranes in LABs are determined by their efficacy in overcoming the related problems that work against the energy storage in LABs for future studies.

1. Introduction

The global energy demand from fossil fuels is unsustainable due to their increasing cost and fast depletion, as well as the greenhouse effect caused by the continuous consumption and application of these fuels. The search for cleaner energy sources is required to shift focus to the generation of energy from electrochemical systems, batteries and fuel cells, solar cells, and super capacitors, among others. Lithium is readily available in the market and has no serious issues regarding its availability, even under the increasing demands up to 2050 [1]. The lithium batteries exhibit promising capabilities for energy storage compared to most energy storage cell devices used in hybrid or electric vehicles and smart grids [2–5]. A lithium-ion battery's energy storage capability is limited by the positive electrode to a value of approximately 150 $mA\,h\,g^{-1}$ of charge compared to a graphite anode, which can easily store up to 300 $mA\,h\,g^{-1}$ of charge. An improved electrode can alleviate this problem to increase the energy storage capability of the lithium batteries to fulfill the obligations of storing a large amount of energy [6–8]. The lithium oxygen battery, often referred to as a lithium-air battery, becomes the innovative system that provides an elevated energy storage potential compared to that of lithium ion batteries [9,10]. The cell design of a typical lithium-air battery (LAB) consists of a carbon cathode, electrolyte and a lithium metal anode. The LAB energy values compare favorably to those of the air engine/gasoline (11,860 W h/kg) and air fuel cell/methanol (5524 W h/kg) batteries [11], justifying its energy storage potential for automotive applications. The wide range of energy storage of the LABs renders it superior to other innovative batteries due to its upgraded energy storage ability that drives EVs to more than 300 miles/charge, which is identical to that achieved with gasoline vehicles [9,12]. Subsequently, there has been great enthusiasm for Li-air battery research globally [3]. Abraham et. al [13], presented the first true LAB system with a non-aqueous electrolyte in 1996 [13]. The electrochemical energy generated from the battery is governed by the following reactions:

$$Li^{(s)} + ½\,O_2 \rightarrow ½\,Li_2O_2 \quad (1)$$

$$Li^{(s)} + ¼\,O_2 \rightarrow ½\,Li_2O, \quad (2)$$

$E^1 = 2.959$ V is the reversible cell voltage for reaction (1), and $E^2 = 2.913$ V is the reversible cell voltage for reaction (2) [14,15]. However, the reactions break down in a real lithium-air cell into the anode and cathode as described below:

$$Li(s) \leftrightarrow Li+ + e^- \text{ (reaction at anode)} \quad (3)$$

$$Li+ + ½\,O_2 + e^- \leftrightarrow ½\,Li_2O_2 \text{ (reaction at cathode)} \quad (4)$$

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$$Li+e^{-}+1/4\ O_2 \leftrightarrow 1/2\ Li_2O \text{ (reaction at cathode)} \quad (5)$$

The rising trend for renewables has some serious concerns such as energy security and climate change, decreasing wind prices and solar PV, rising prices of electricity etc. Renewable energies such as sun and wind energies are not constant and can be fluctuated by change in weather, time and location; that draws attention towards alternatives. Currently, various batteries are being used to store output from renewables and release the power when it is needed. As stated by the International Renewable Energy Agency, the storage capacities of the batteries are expected to increase from 360 MW to 14 GW by 2023. The electric vehicles can get more response with advances in battery technology, which will reduce the greenhouse-gas emissions; also, the reduction of CO_2 from vehicles will lead to a better environment and be advantageous for some serious issues such as global warming, health and renewable energies. The lead acid batteries have a short life of only 3–4 years but still used in many applications to support renewable energy. In contrast, the cycle life of Nickel cadmium batteries is better than lead acid batteries; however, their materials costs are high. At present, the lithium ion batteries are used because of their higher energy density compared to many other rechargeable batteries [16]. However, the current lithium ion battery has limited energy density due to the intercalation chemistry of its electrode materials; thus, it does not easily meet the required criteria for practical applications in electric vehicles [17,18]. Therefore, metal air batteries are considered a promising alternative due to their extremely high energy density compared with other batteries, as shown in Fig. 1. Lithium sulfur battery is closer for its practical availability for EVs than lithium oxygen battery [19]; however, challenges associated with lithium sulfur battery are too complicated and have not yet been solved completely. Also, the lithium oxygen battery has not found much attention compared to lithium sulfur battery until now and expected to produce further improved performance in future [20]. Several reports on lithium-air batteries have confirmed their variant energy storage characteristics [3,12,17,21–25]. Fig. 2 shows the atmospheric O_2 that is electrochemically coupled with the lithium anode by the porous oxygen-breathing positive electrode. The electrons and lithium ions can move between the positive (+ve) and negative (–ve) electrodes during charge and discharge. The LAB system can be viewed as the best for future energy storage because it can produce a considerably higher energy than a lithium-ion battery [12,15]. However, many technical and scientific challenges must be overcome to achieve the desired oxygen-breathing electrode of LABs. Researchers have focused on filling the gaps to achieve the goals of attaining a viable lithium-air battery [26].

Membrane technology is one of the most preferred techniques to overcome the mentioned challenges. The use of an appropriate membrane can provide better solutions to many problems associated with LABs. For example, the hydrolysis reaction occurs at the lithium anode due to H_2O when the cathode is exposed to air. Additionally, the presence of CO_2 in the air results in the formation of Li_2CO_3. Therefore, preventing the penetration of undesirable gases into LABs is a priority. An oxygen diffusion membrane can be used as the outer surface of the porous cathode to avoid the penetration of air moisture and CO_2 into the LAB and to attain better O_2 solubility [14,27]. Previously, most of the porous and non-porous oxygen selective membranes were developed and used in O_2/N_2 separation only [28,29]. Only a few articles have been published with regard to oxygen selective water barrier membranes. The value of O_2 permeance was noted as approximately 1.7×10^{-10} mol m^{-2} s^{-1} Pa^{-1}, whereas this value was 3.9 for O_2/H_2O selectivity at 50 °C when polyperfluoropropylene oxide co-perfluoromaldehyde (PFPO) was soaked into a polymer celgard 2500 porous substrate [30]. An oxygen sensor-based electrochemical device is often used to measure the effective diffusivity in cathodes of LABs [31]. Another problem such as electrolyte evaporation from the lithium-air battery can be minimized by using a protective membrane [26]. In addition, polymer selection is an important factor to fabricate an effective membrane and is primarily important for avoiding unwanted discharge products and compatibility issues of polymers and electrolytes. Polymers such as PAN, PVCF, PVC, PVP and PVDP-HFP are unstable, as they react with lithium and form unwanted discharge products. However, PTFE, Nafion, PEO and PMMA are stable with Li_2O_2[32].

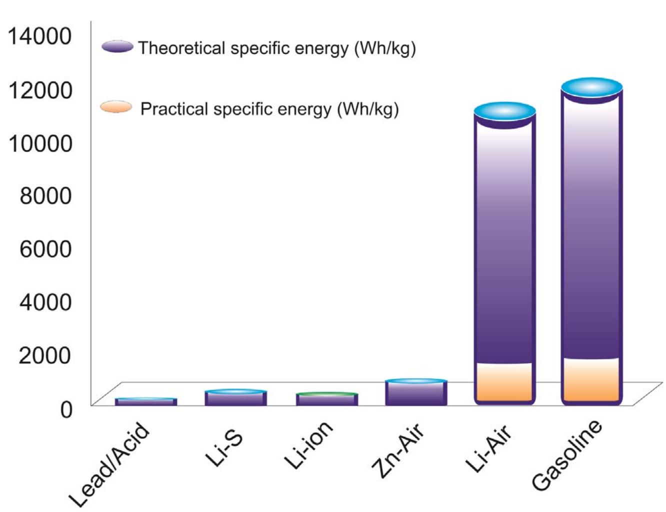

Fig. 1. Theoretical and practical energy densities of various types of rechargeable battery.

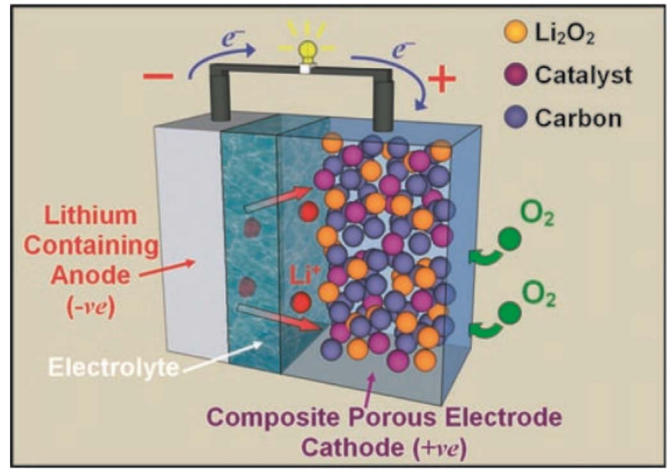

Fig. 2. Schematic representation of Lithium-Oxygen Battery. (Ref. [141] reproduced with permission).

LABs are faced with intrinsic challenges, and each of the challenges requires a specific and effective method to overcome it. Many possible methods have been attempted to mitigate these challenges; however, considering all of the mitigation methods is beyond the scope of this review. The effective use of a suitable membrane has a significant positive impact on the major compartments of LABs; therefore, this review specifically deals with the potential advantages of different membranes in mitigating some crucial challenges associated with air cathodes, lithium metal anodes, electrolytes and electrodes, gas permeation and water permeability. In addition, this review includes the importance of ambient air operations for LABs as well as future challenges and prospects to promote the current performance of LABs.

2. Optimization of air cathode

The air cathode is one of the most important and complicated areas to operate in LABs. The limitations hindering a substantial performance of a lithium-air cell are related to the air cathode. Several findings have suggested the importance of air cathode improvement to