# Modelling of operation of a lithium-air battery with ambient air and oxygen-selective membrane

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## HIGHLIGHTS

- A macro-homogeneous model is developed to operate Li-air battery in ambient air.
- The Li-air model is combined with an oxygen-selective membrane.
- The model shows the battery deterioration when using air.
- The Li-air performance increases with integration of oxygen-selective membrane.
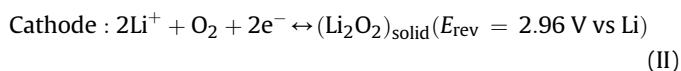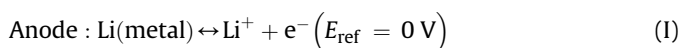
## ARTICLE INFO

## ABSTRACT

A macro-homogeneous model has been developed to evaluate the impact of replacing pure oxygen with ambient air on the performance of a rechargeable non-aqueous Li-air battery. The model exhibits a significant reduction in discharge capacity, e.g. from 1240 to 226 mAh $g_{carbon}^{-1}$ at 0.05 mA cm$^{-2}$ when using ambient air rather than pure oxygen. The model correlates the relationship between the performance and electrolyte decomposition and formation of discharge products (such as $Li_2O_2$ and $Li_2CO_3$) under ambient air conditions. The model predicts a great benefit of using an oxygen-selective membrane on increasing capacity. The results indicate a good agreement between the experimental data and the model.

## 1. Introduction

Several times higher specific energy than Li-ion batteries makes the rechargeable Li-air a candidate of new generation of energy storage devices [1–4]. Since the first report of a non-aqueous electrolyte Li-air battery in 1996 [5], especially after a breakthrough in cycle life by Bruce's group [6], the rechargeable Li-air battery has been investigated intensively [6–11]. However, many science and technical challenges have to be overcome to realise the potential of this cutting-edge technology. A key area is to gain insights into chemical/electrochemical processes that take place inside the Li-air battery via an effective modelling.

An aprotic Li-air battery contains a metal lithium anode, a solid separator and a porous air electrode filled with a non-aqueous Li$^+$ electrolyte. The fundamental electrochemical reactions are shown below:

$$\text{Anode}: \text{Li(metal)} \leftrightarrow \text{Li}^+ + \text{e}^- \left( E_{ref} = 0\,\text{V} \right) \tag{I}$$

$$\text{Cathode}: 2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \leftrightarrow (\text{Li}_2\text{O}_2)_{solid} (E_{rev} = 2.96\,\text{V vs Li}) \tag{II}$$

Here, Eq. (II) is an ideal electrochemical reaction, desired to make a truly rechargeable Li-air battery [6,12,13]. In practice, there are other side reactions, forming detrimental products, such as Li$_2$CO$_3$ [6,12,13].

However, almost all the current studies of Li-air batteries are run in pure oxygen and controlled a dried atmosphere in a glove box to minimise the contaminated substances from ambient air, thus this

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battery can perform in high rate capability, owing to high oxygen concentration, and maintain the long-term operation. Our recent model studies also simulated the Li-air battery including the electrolyte degradation and operating in pure oxygen [14,15]. To success in making a Li-air battery for use in practical applications, one critical problem to be solved is operating Li-air batteries in ambient air environment [16,17]. There are several challenges when Li-air batteries are applied with air condition comparing to those of pure oxygen feeding. The first is unavoidable moisture (about 1% in volume) in surrounding air, which may penetrate into the cell system together with oxygen. The present of moisture can corrode the metallic lithium anode due to the hydrolysis reaction with highly reactive lithium as shown in reaction III [17]. This results in the fast battery failure and causes a serious safety issues.

$$2Li + 2H_2O \leftrightarrow 2LiOH + H_2 \tag{III}$$

The second is the insufficient concentration of oxygen due to its low partial pressure in atmosphere, leading to limit Li-air batteries from high discharge rates because of small oxygen solubility in the electrolyte. The third problem is that the small amount of carbon dioxide ($CO_2$) from air feeding may react with superoxide anions, which is formed during the initial oxygen reduction on discharge process, to generate carbonate species, leading to the deposition of these by-products on the cathode surface [12,18,19]. It is worth noting that $CO_2$ could be considered as the active material to form the $Li_2CO_3$ and lithium alkyl carbonates instead of desired produce $Li_2O_2$ [12,19,20]. Furthermore, these side reactions lead to continuous and irreversible consumption of electrolytes and thus the Li-air batteries cannot maintain their sustainable ability during charge/discharge cycles.

To minimise the battery problem when using air, Li-air batteries under current research are mainly operated in pure oxygen [5—7,9]. There is a small volume of published works demonstrating the behaviour of Li-air battery with air feeding [11,16,17,21]. These studies solved the contaminated gases problems by using an oxygen-selective water barrier membrane covering the outer surface of the cathode to prevent moisture and permeate oxygen into the porous cathode at the same time. Zhang et al. developed an oxygen-selective immobilised liquid membrane for a non-aqueous Li-air battery operated in ambient air with 20—30% relative humidity [17]. The membranes were easily prepared by soaking high viscosity silicone oil into porous metal or Teflon substrates. A Li-air integrated with these membranes can be operated in ambient air for 16.3 days with a specific capacity of 789 mAh g$^{-1}$ and specific energy of 2182 Wh kg$^{-1}$ based on the weight of carbon. The same group also studied the hydrophobic zeolite membrane and poly(-tetrafluoroethylene) (PTFE) membrane as oxygen-selective water barriers [16]. The latter protected a Li-air against moisture and supplied oxygen for 21 day with a specific capacity of 1022 mAh g$^{-1}$ and specific energy of 2792 Wh kg$^{-1}$ based on the weight of carbon.

Zhang et al. investigated the ambient operation of non-aqueous Li-air batteries integrating with a heat-sealable polymer membrane to serve as both an oxygen-diffusion membrane and moisture barrier [11]. The membrane could also reduce the evaporation of electrolytes during battery operation. The Li-air battery with this membrane demonstrated the discharge capability in ambient air for more than one month with a specific energy of 362 Wh kg$^{-1}$ based on the total weight of the battery including its packaging. However, all the previously mentioned ambient air works only studied the Li-air performances on discharge phase without showing those on charging or cycling process, which could provide more important data for battery stability than only single discharge.

In this paper our previous Li-air model with electrolyte degradation is modified to operate the Li-air battery in ambient air

environment [14,15], which severely damages Li-air performance and is still a critical problem to be solved before the Li-air battery can be used for practical application. The two species of oxygen and $CO_2$ are considered in the model as air feeding condition with the exception of moisture or using dried air in the model. Although this model does not include all the effects that could occur in the Li-air battery with ambient air operation, at least we carefully consider the key mechanisms covering the main impacts of using air that directly affect the porous cathode behaviour during cell operation, leading to detrimental cell performance. Therefore, mathematical model for Li-air battery with air feeding condition can be used to identify cell-limiting mechanisms and reduce the time-consuming work compared to experiment aspect. Moreover, it also avoids the serious safety problems that could happen when the ingress of moisture reacts with lithium metal anode. This model can be used to describe the behaviour of Li-air batteries in ambient air condition as well as to optimise the performance and structure of these battery electrodes.

## 2. Theoretical mechanism analysis

A typical Li-air battery, shown in Fig. 1a, contains a lithium metal anode, a separator containing electrolyte, and a porous carbon or catalyst-loaded carbon air electrode filled with an organic electrolyte comprising a dissolved lithium salt in an aprotic solvent. During discharge the lithium metal anode oxidises to Li$^+$ and electrons conduct through the external circuit, while Li$^+$ transports towards the porous cathode. Oxygen is reduced at the active surface with Li$^+$, thus leading to the desired discharge products of $Li_2O_2$ and the by-product of $Li_2CO_3$ or lithium alkyl carbonates resulting from the electrolyte decomposition [12,13,19]. These products influenced the Li-air performance and cannot completely remove during battery cycling. To simplify our simulation, the model assumed that $Li_2O_2$ was the main discharge product depositing inside the porous cathode (Eq. (II)) and the irreversible $Li_2CO_3$ by-product coexisting with $Li_2O_2$ when using non-aqueous electrolytes. This section describes the two main mechanisms that occur inside the Li-air battery and were applied to the model.

### 2.1. Effect of using ambient air condition

The critical problems when using air as a feeding reactant for the Li-air battery are the low oxygen solubility in the electrolyte and the $CO_2$ gas diffusing into the battery with oxygen. To investigate these effects, the Li-air model was changed the feeding condition from pure oxygen to ambient air at the porous cathode entrance. Considering the amount of oxygen and $CO_2$ content in the atmosphere [22] (78% $N_2$, 21% $O_2$, 0.035% $CO_2$), the concentration of oxygen and $CO_2$ in the electrolyte can be determined in term of Henry's law which states that

$$c_g = H_g \bar{p}_g \tag{1}$$

where $c_g$ is the concentration of gasses in the electrolyte, $H_g$ is the Henry's law constant which depends on the electrolyte and temperature used in the Li-air battery, and $\bar{p}_g$ is the partial pressure of the gas which depends on mole fraction of each specie in the atmosphere. Henry's law is correct to describe the solubility of gas for low concentrations and low partial pressures. The concentrations of oxygen and $CO_2$ calculated from Henry's law can be compared in Table 1. These concentrations are applied in the Li-air model to represent the air feeding condition, unless specified otherwise. It can be seen that although the $CO_2$ composition is not much in the atmosphere, its Henry's law constant is almost two times higher than that of oxygen, i.e. the solubility of $CO_2$ in non-aqueous