

# Prediction of the theoretical capacity of non-aqueous lithium-air batteries



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## HIGHLIGHTS

- The theoretical capacity of non-aqueous lithium-air batteries is predicted.
- Key battery design parameters are defined and considered.
- The theoretical battery capacity is about 10% of the lithium capacity.
- The battery mass and volume changes after discharge are also studied.

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## ABSTRACT

In attempt to realistically assess the high-capacity feature of emerging lithium-air batteries, a model is developed for predicting the theoretical capacity of non-aqueous lithium-air batteries. Unlike previous models that were formulated by assuming that the active materials and electrolyte are perfectly balanced according to the electrochemical reaction, the present model takes account of the fraction of the reaction products ( $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$ ), the utilization of the onboard lithium metal, the utilization of the void volume of the porous cathode, and the onboard excess electrolyte. Results show that the gravimetric capacity increases from 1033 to 1334 mA h/g when the reaction product varies from pure  $\text{Li}_2\text{O}_2$  to pure  $\text{Li}_2\text{O}$ . It is further demonstrated that the capacity declines drastically from 1080 to 307 mA h/g when the case of full utilization of the onboard lithium is altered to that only 10% of the metal is utilized. Similarly, the capacity declines from 1080 to 144 mA h/g when the case of full occupation of the cathode void volume by the reaction products is varied to that only 10% of the void volume is occupied. In general, the theoretical gravimetric capacity of typical non-aqueous lithium-air batteries falls in the range of 380–450 mA h/g, which is about 10–12% of the gravimetric capacity calculated based on the energy density of the lithium metal. The present model also facilitates the study of the effects of different parameters on the mass and volume change of non-aqueous lithium-air batteries.

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## 1. Introduction

The rapid growth of portable devices and vehicles has driven the need for high-capacity storage devices. Lithium-air batteries have recently attracted much attention mainly because of their extremely high energy density resulting from two factors. First, as the lightest metal, lithium has the highest specific capacity ( $3.86 \times 10^3$  mA h/g), corresponding to a specific energy of  $1.14 \times 10^4$  W h/kg for a theoretical potential of 3.0 V, which is much higher than any other metal-air batteries [1] or Li-ion batteries ( $4.2 \times 10^2$  W h/kg) [2]. The second factor that renders lithium-air batteries a high specific energy is that the cathode active material, oxygen, can be taken from ambient air without occupying the battery volume.

In general, lithium-air batteries can be divided into four types [3] in terms of electrolytes, including aqueous, non-aqueous, mixed aqueous/non-aqueous (hybrid), and solid-state. In aqueous [4–10], hybrid [11–16], and solid-state [17–24] lithium-air batteries, a solid-state layer is generally used to transport  $\text{Li}^+$  ions. The internal resistance associated with this solid plate can be a main factor that limits the performance of these types of battery. In non-aqueous lithium-air batteries, the internal resistance is typically low as only a thin glass-fiber paper is used to separate the Li anode and the cathode. This creates a potential for high performance. For this reason, non-aqueous lithium-air batteries have received more attention. During the discharge process of non-aqueous lithium-air batteries, as the oxygen reduction reaction takes place at the porous cathode, the solid products will deposit in pores, which will resist the oxygen transport. For this reason, tremendous efforts have been made to the development of air cathodes. For example, Xiao et al. [25] developed a novel air

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## Nomenclature

$m$	mass, g
$x$	fraction of $\text{Li}_2\text{O}_2$ in the products
$C_p$	gravimetric capacity, mA h/g
$C_v$	volumetric capacity, mA h/cm <sup>3</sup>
$C_{\text{Li}}$	actual capacity of the Li anode, mA h
$F$	Faraday constant, 96,485 C/mol
$V$	volume, cm <sup>3</sup>
$M$	mass of the battery, g

## Greek letters

$\alpha$	utilization ratio of lithium in the anode
$\beta$	utilization ratio of the cathode void volume
$\gamma$	excess electrolyte coefficient
$\rho$	mass density, g/cm <sup>3</sup>
$\varepsilon$	porosity
$\omega$	molecular weight, g/mol

electrode consisting of an unusual hierarchical arrangement of functionalized graphene sheets without catalysts, and achieved a very high capacity of 15,000 mA h/g. The cathode made of a special porous graphene oxide-derived carbon enabled an increase in the capacity to 10,600 mA h/g [26]. Jung et al. [27] designed an appropriate air electrode and demonstrated a lithium-air battery capable of operating over many cycles with the capacity as high as 5000 mA h/(g-carbon). Peng et al. [28] used a nanoporous gold electrode and obtained a capacity of about 300 mA h/(g-gold) while retaining 95% of its capacity after 100 cycles. In addition to the effects of cathode materials, the catalyst [29,30], the electrolyte solvent and the lithium salt [31,32], the current collector [33], and the current density [34] were also found to significantly influence the battery capacity.

In addition to the above-mentioned experimental investigations, theoretical efforts have also been made for the prediction of the capacities of lithium-air batteries. Zheng et al. [35] developed a model for predication of the gravimetric and volumetric energy densities of aqueous and non-aqueous lithium-air batteries; the model was formulated based on the minimum mass and volume of the electrolyte and air electrode needed for complete oxidation of the Li metal at the anode; and the influences of porosity on the battery capacities, energy density, and mass/volume change were discussed. A similar method was also used to estimate the theoretical energy densities of hybrid lithium-air batteries [36].

An issue with previous models for estimating the capacities of non-aqueous lithium-air batteries is that they were formulated by assuming that the active materials and electrolyte are perfectly balanced according to the electrochemical reactions, which means the lithium metal is 100% used up and the pore volume in the cathode is designed for just being able to be filled by solid discharge product, and the amount of electrolyte could just fill the pore volume before discharge. For this reason, the models are limited to the calculation of the upper limits of the gravimetric and volumetric capacities as well as the mass and volume change ratios of batteries for given amounts of the Li metal and electrolyte and the porosity of the cathode electrode. A model that can be used to calculate the key quantities of non-aqueous lithium-air batteries for the real-world cases, including that the Li metal is partially oxidized, the cathode void volume is partially occupied by reaction products after discharge, and excess electrolyte is required, is missing. The objective of this work, therefore, is to address the issues associated with previous models and to develop a more robust model for predicting the theoretical capacities of non-aqueous lithium-air batteries. The aspects that make the present model different from previous model are as follows: (i) a utilization ratio of lithium is thus introduced and considered in the present model; (ii) a utilization ratio of the cathode void volume is incorporated in the present model; and (iii) excess electrolyte is considered by a defined excess electrolyte coefficient in the present model. With incorporation of the above mentioned factors, the present model not only enables a more

realistic estimation of the capacity of non-aqueous lithium-air batteries, but also facilitates the analysis of the effects of different design parameters on the capacities of the batteries.

## 2. Theoretical

Fig. 1 illustrates a typical non-aqueous lithium-air battery consisting of a Li anode, a porous cathode and the non-aqueous electrolyte. In the discharge process, at the anode electrochemical potential forces the lithium metal to donate electrons and Li ions, while at the porous cathode, oxygen is reduced by receiving electrons transported through an external circuit and Li ions transported via the electrolyte. In order to prevent the internal short-circuit between the anode and cathode, a glass-fiber paper is used to separate both electrodes.

With regard to the discharge products at the cathode of a typical non-aqueous lithium-air battery as a result of the oxygen reduction, the formation of both  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  were reported in many early studies [37–43]. For instance, with the oxygen volume measurements, Read [37] found the proportion of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  varied with the current density. Zhang et al. [38] found that at low discharge currents the battery exhibited two discharge voltage plateaus, and the second one was attributed to the formation of  $\text{Li}_2\text{O}_2$  into  $\text{Li}_2\text{O}$ . Thapa et al. [41] used Pd mixed with  $\text{MnO}_2$  as the catalyst and confirmed the formation of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  through Raman analyses. A recent study [44] showed that the amount of  $\text{Li}_2\text{O}_2$  formed during discharge strongly depended on the electrolyte used in the system. More recent studies demonstrated that  $\text{Li}_2\text{O}_2$  is the main discharge product with a stable electrolyte. For instance, Peng et al. [28] found the proportion of  $\text{Li}_2\text{O}_2$  at the end of discharge exceeded 99% with dimethyl sulfoxide (DMSO) as the electrolyte. In another recent work by McCloskey et al. [45], it was shown that with dimethoxyethane (DME) as the electrolyte, about  $2e^-/\text{O}_2$  consumed/produced during discharge/charge, implying that  $\text{Li}_2\text{O}_2$  predominates in the discharge products.

The above discussion indicates that recent studies showed that  $\text{Li}_2\text{O}_2$  is the main discharge product. However, in an attempt to formulate a general theoretical framework, in this work we treat  $\text{Li}_2\text{O}$  as a hypothetical product while taking  $\text{Li}_2\text{O}_2$  as the main discharge product, with  $x$  representing its fraction. As such, the both scenarios with  $\text{Li}_2\text{O}_2$  as the pure discharge product ( $x = 1.0$ ) and as the

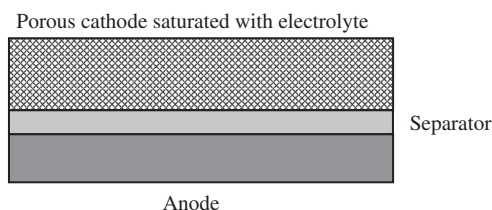


Fig. 1. Schematic of a non-aqueous lithium-air battery.

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