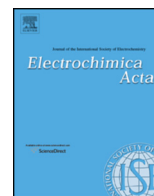




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# Three-dimensional transient modeling of a non-aqueous electrolyte lithium-air battery

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## ABSTRACT

A three-dimensional transient model is developed for a non-aqueous-electrolyte lithium-air battery to investigate numerically key phenomena during discharging. The proposed model rigorously assesses lithium peroxide ( $\text{Li}_2\text{O}_2$ ) formation and growth in an air electrode, and its complex interactions with electrochemical reactions and species/charge transport. We assume that the porous air electrode mainly consists of sphere-like carbon particles, and hence a spherical film growth model is adopted to simulate the precipitation of  $\text{Li}_2\text{O}_2$  on the spherical carbon surfaces. The model is first validated against voltage evolution data measured at different discharging current densities. Good agreement between the simulation results and experimental data is achieved, demonstrating that the model accurately captures voltage decline behaviors due to accumulated  $\text{Li}_2\text{O}_2$  in the air electrode. Additional simulations are carried out with different air electrode designs in order to establish the optimization strategy for the air electrode. Detailed simulation results, including multidimensional contours, clearly indicate that the electrode thickness and degree of electrolyte filling are key factors for improving the discharging performance of lithium-air batteries.

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## 1. INTRODUCTION

The specific energy density of most lithium-ion batteries is  $\sim 150 \text{ Wh kg}^{-1}$  or  $650 \text{ Wh L}^{-1}$ , which is not sufficient for electric vehicles (EVs) to attain a driving range comparable to that of internal combustion engine vehicles, i.e.  $\sim 700 \text{ Wh kg}^{-1}$  [1,2]. However, metal-air batteries have received much attention in recent years for EV applications, since much higher specific energy densities than lithium-ion batteries can be achieved owing to the unlimited supply of oxygen from the surrounding air. Among them, lithium-air batteries exhibit the highest theoretical specific energy density of  $11,140 \text{ Wh kg}^{-1}$  that is close to that of gasoline fuel ( $13,000 \text{ Wh kg}^{-1}$ ).

Various lithium-air batteries with different electrolytes, electrodes, and cell designs have been developed and presented in the literature [3]. These can be classified into two types: an aqueous electrolyte type and a non-aqueous electrolyte type. Using aqueous electrolytes can mitigate the issue of air electrodes clogging with discharged products (i.e., Li oxides), because these are generally

soluble in the aqueous electrolyte. However, lithium metal is highly reactive with water and thus, in the aqueous electrolyte types, lithium ion conducting and a water impermeable membrane must be present to prevent undesired reactions between water and the lithium electrode. Hasegawa et al. [4] examined the water stability of the NASICON-type lithium ion-conducting LAMP ( $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ) in various types of aqueous solutions. They fabricated a Li-air cell with LAMP and aqueous 1 M LiCl, and showed that a stable open circuit voltage of 3.6 V at 25 °C could be successfully maintained for one week. Stevens et al. [5] designed a composite air electrode with an anionic polymer electrolyte membrane and applied it to an aqueous lithium hydroxide electrolyte-based lithium-air cell. They showed that using an anionic polymer electrolyte membrane successfully mitigated the precipitation of lithium carbonate and lithium hydroxide inside the air electrode using untreated air and 5 M or saturated lithium hydroxide electrolyte. Puech et al. [6] fabricated a ceramic LAMP-AP for aqueous electrolyte-based lithium-air batteries. Although the membranes were thin (40–55  $\mu\text{m}$ ) and exhibited good mechanical and watertight properties, the overall ionic resistance of the membrane (55  $\mu\text{m}$ ) and coated layer (LiPON thin film of 12  $\mu\text{m}$ ) were still high, around 105  $\Omega$  over the area of 1  $\text{cm}^2$ .

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**Nomenclature**

<i>a</i>	Ratio of active surface area per unit electrode volume, $\text{m}^2 \text{m}^{-3}$
<i>C</i>	Molar concentration of species, $\text{mol m}^{-3}$
<i>D</i>	Species diffusivity, $\text{m}^2 \text{s}^{-1}$
<i>E</i>	Roughness factor
$E^\circ$	Equilibrium potential, V
<i>f</i>	Activity coefficient of $\text{LiPF}_6$ salt
<i>F</i>	Faraday's constant, $96,487 \text{C mol}^{-1}$
<i>H</i>	Henry's constant
<i>i</i>	Superficial current density, $\text{A m}^{-2}$
<i>I</i>	Current density, $\text{A m}^{-2}$
<i>j</i>	Transfer current density, $\text{A m}^{-3}$
<i>k</i>	Reaction rate constant, $\text{m s}^{-1}$
<i>K</i>	Effective permeability
<i>n</i>	Number of electrons transferred in the electrode reaction
<i>N</i>	Molar flux of species, $\text{mol s}^{-1} \text{m}^{-2}$
<i>MW</i>	Molecular weight, $\text{kg mol}^{-1}$
<i>P</i>	Pressure, Pa
<i>r</i>	Particle radius, m
<i>R</i>	Universal gas constant, $8.314 \text{J mol}^{-1} \text{K}^{-1}$
$R_{\text{Li}_2\text{O}_2}$	Film resistance, $\Omega \text{m}^2$
$R_{\text{O}_2}^e$	Oxygen transport resistance in electrolyte, $\text{s m}^{-1}$
<i>S</i>	Source term in transport equation
<i>t</i>	Time, s
$t_+$	Transfer number
<i>T</i>	Temperature, K
<i>u</i>	Superficial velocity, $\text{m s}^{-1}$
$v_e$	Velocity of the electrolyte, $\text{m s}^{-1}$

## Greek symbols

$\beta$	Transfer coefficient
$\delta$	Thickness, m
$\varepsilon$	Volume fraction
$\eta$	Surface overpotential, V
$\kappa$	Proton conductivity, $\text{S m}^{-1}$
$\phi$	Phase potential, V
$\rho$	Density, $\text{kg m}^{-3}$
$\sigma$	Electronic conductivity, $\text{S m}^{-1}$
$\tau$	Surface effect factor
$\mu$	Viscosity, $\text{kg m}^{-1} \text{s}^{-1}$

## Superscripts

<i>e</i>	Electrolyte
<i>eff</i>	Effective
<i>g</i>	Gas
<i>0</i>	Initial conditions or standard conditions, i.e., 298.15 K and 101.3 kPa (1 atm)

## Subscripts

<i>avg</i>	Average
<i>carbon</i>	Carbon particle in air electrode
<i>e</i>	Electrolyte
<i>electrode</i>	Air electrode
<i>g</i>	Gas
<i>i</i>	Species
$\text{Li}^+$	Lithium ion
KC	Kozeny–Carman constant
$\text{Li}_2\text{O}_2$	Lithium peroxide
$\text{O}_2$	Oxygen

<i>ref</i>	Reference
<i>s</i>	Solid, surface
<i>void</i>	Void
<i>0</i>	Initial conditions

It may be difficult to meet all the requirements of a membrane (sufficient lithium conductivity, mechanical strength, and water impermeability) for the aqueous-electrolyte-based lithium-air batteries. Therefore, considerable efforts have been directed toward non-aqueous electrolytes, or mixed electrolytes comprising both aqueous and non-aqueous electrolytes. In 1996, Abraham and Jiang [7] presented the first rechargeable lithium-air battery in which a non-aqueous organic membrane was sandwiched between a thin lithium electrode and a carbon composite air electrode. They successfully showed an open circuit voltage of  $\sim 3.0 \text{V}$  and a specific energy density range of  $250\text{--}350 \text{Wh kg}^{-1}$  with good rechargeability over three cycles. Since then, lithium-air batteries with various non-aqueous electrolytes have been studied intensively [8–19]. The major issue with a non-aqueous electrolyte is that the discharged products are not soluble in the electrolyte, and hence continuously accumulate in the air electrode during the discharging process. This product discharge substantially raises resistance to both oxygen and electron transport in the air electrode. Generally, there are two types of discharged products formed during the oxygen reduction reaction (ORR) in non-aqueous electrolytes: lithium peroxide ( $\text{Li}_2\text{O}_2$ ) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ). While  $\text{Li}_2\text{O}_2$  electrochemically decomposes into Li and  $\text{O}_2$  by an oxygen evolution reaction (OER) during the charging process,  $\text{Li}_2\text{CO}_3$  resulting from the decomposition of non-aqueous electrolytes (carbonates, ethers, etc.) or  $\text{CO}_2$  in the atmospheric air is an irreversible byproduct. Many researchers have conducted experimental and theoretical studies to resolve the issues related to the precipitation of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{CO}_3$  in non-aqueous lithium-air batteries [8,9]. Xu et al. [8] analyzed the discharge products in non-aqueous organic carbonate electrolytes for lithium-oxygen batteries using X-ray diffraction and in situ gas chromatography/mass spectroscopy. Their data indicated that  $\text{Li}_2\text{CO}_3$  was the main product at the air electrode and was hardly oxidized below 4.6 V versus  $\text{Li}/\text{Li}^+$ . In lithium-oxygen batteries with alkyl-carbonate electrolytes and Ketjenblack (KB)-carbon-based air electrodes, the primary discharge product was irreversible  $\text{Li}_2\text{CO}_3$ . Freunberger et al. [9] applied ether-based electrolytes to a lithium-oxygen battery and showed that the majority of the discharged products were  $\text{Li}_2\text{O}_2$  during the first discharge/charge cycle, indicating that the ether-based electrolyte was more stable than the organic carbonate electrolytes. Thereafter, however, the decomposition of the ether-based electrolytes occurred by continuous cycling, and the fraction of  $\text{Li}_2\text{O}_2$  produced considerably decreased with increasing cycle number. Hence, identifying appropriate non-aqueous electrolytes to make lithium-oxygen batteries fully rechargeable remains a major challenge.

Searching for an optimum air-electrode material and structure is another key factor for improving the capacity and performance of lithium-air batteries. Xiao et al. [10] tested various commercial carbon materials for air electrodes in lithium-air batteries. Among them, KB carbon exhibited higher absorption capability for the electrolyte, and larger volume expansion that facilitated the  $\text{Li}/\text{O}_2$  reaction, and extra volume to hold the discharged products. Consequently, the highest capacity of  $1756 \text{mAh g}^{-1}$  was achieved with a KB-based air electrode under a dry air environment. Mirzaeian et al. [11] fabricated an air electrode using activated carbon that were synthesized through polycondensation of resorcinol with formaldehyde. They showed that the cell voltage

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