Analysis of Electrolyte Level Change in a Lithium Air Battery

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Abstract

A two-dimensional physical model that employs the deformed mesh method to track the electrolyte level in a Li-air coin cell battery is presented and used to investigate the effects of electrolyte level drop during cell discharge. The electrolyte level drop is caused by solid phase volume decrease and electrolyte solvent evaporation. Simulation results show that by neglecting the drop in electrolyte level, a Li-air battery model would under-estimate cell discharge capacity by as much as 22.5% in the parameter range studied. This counter-intuitive result is explained by an in-depth analysis of simulation results. A more realistic prediction of Li_2O_2 deposit distribution is obtained, with the peak value of Li_2O_2 volume fraction in the middle of the cathode instead of on the top surface, as predicted by previous studies. The interaction between the battery and its surroundings is considered by incorporating the air chamber into the computation domain. The diffusion of solvent vapor and oxygen in this chamber is included. For batteries using volatile solvents such as DMF, increasing the air chamber radius from 5 cm to 15 cm would result in a 72% increase of discharge capacity at the cost of losing a large amount of electrolyte.

Keywords: Lithium air battery; Deformed mesh; Modeling; Electrolyte level

1. Introduction

Because of their high theoretical energy density, lithium air (Li-air) batteries, including lithium oxygen (Li-O₂) batteries, are considered to be promising candidates as the next generation secondary power supplies for portable devices and electric vehicles. A number of continuum-scale models have been developed to study the detailed charge and mass transport processes inside a Li-air battery. The first reported simulation model for Li-air batteries was by Sandhu et al. in 2007 [1]. Since then, various research groups have incorporated additional details to build more comprehensive models. Albertus et al. [2] was the first to consider solid product precipitation. Wang and Cho [3] developed a model to consider the coverage of reaction surface for different electrode pore shapes. The model by Sahapatsombut et al. [4,5] was the first reported to include the charging process and side reactions. Li and Faghri [6] developed a 2-D model and found that the micro pores closer to the separator/cathode interface were not fully utilized. They proposed a gradient cathode structure to increase specific capacity. Several models [7–9] considered the size distribution function of the pores or carbon particles in the cathode.

All previous studies neglected two important physical phenomena in a Li-air cell. The first is the electrolyte level drop during discharge caused by a decrease in solid phase volume. During discharge, the metallic lithium of the anode is converted to lithium ions, enters the electrolyte and moves to the cathode. In the micro-pores of the cathode, oxygen reduction reaction (ORR) occurs and consumes the lithium ions and electrons. Experimental studies [10] prove that

insoluble and partially insulating Li_2O_2 is the major product of this reaction in non-aqueous electrolyte; therefore the overall reaction can be expressed as:

According to the above equation, for each mole of lithium consumed 0.5 moles of Li_2O_2 are generated, which translates to 13.0 cm^3 of solid consumed and 9.93 cm^3 of solid generated. This means a 23.6% decrease of solid phase volume for each unit volume of lithium anode consumed during discharge. This vacated space must be replaced by the liquid electrolyte and therefore electrolyte level drops during discharge.

Figure 1 shows the structure of a typical Li–air coin cell used in previous experimental studies [11,12]. The cell is normally placed on a solid surface with breathing holes facing upward, exposed to an air chamber. To compensate for the volume change, a spring is placed under the anode current collector in the cell. This ensures a tight contact between anode, separator, cathode, and current collectors in the cell. Solid volume decreases during discharge and electrolyte level drops. This effect is noted as an unsolved issue by Yuan et al. [13]. Yoo et al. [14] attempted to address this problem through a 1D model. However, the proposed model assumed a fixed anode and the battery is placed vertically.

The solid phase volume change is not the only factor to cause electrolyte level change. The evaporation of solvent is another phenomenon that is often neglected in modeling works. Most experimental studies on non-aqueous Li–air batteries used volatile solvents such as 1,2–dimethoxyethane (DME) and acetonitril (ACN), as indicated by Balaish et al. [15], to achieve a

high oxygen solubility and diffusivity. Evaporated solvent escapes the battery through the breathing openings and is lost in ambient air. To our best knowledge, no previous modeling studies of the effect of solvent evaporation on cell performance have been reported.

Another often neglected physical phenomenon in Li–air battery models is the interaction of the cell with its surroundings. Lithium air batteries normally interact with their surroundings by consuming or releasing oxygen during the discharge and charge cycles, respectively. However, the computation domain of most existing Li-air battery models is generally bound by the interface of the cathode and ambient air, and assumes a constant dissolved oxygen concentration as the boundary condition. The diffusion of oxygen from the environment into the cell and solvent diffusion into the environment have not been considered in prior studies.

In this paper, the previously neglected physical phenomena are included in our proposed two dimensional transient Li–air coin cell model. These effects on cell performance are examined and discussed based on simulated results. The Arbitrary Lagrangian–Eulerian (ALE) method is employed to describe the deformed computation domain and to track the moving electrolyte level. The air chamber that provides oxygen to the cell is included in the computation domain. The simulation results, both with and without consideration of these effects, are compared and discussed.

2. Physical Model

The battery to be modeled has a typical coin cell structure, as shown in Figure 1, and has been widely used in previous experimental studies. Structural parameters of the cell are listed in

Table 1. The thickness of the cathode is 800 μm . This value is chosen based on two reasons. First, using a thin cathode means higher percentage of the battery volume is occupied by separator and gas channel, consequently leads to a lower overall capacity. To achieve a competitive capacity, a thicker cathode must be used. Secondly, in most experimental and simulation studies, the cathode thickness is in the range between 500 μm to 1mm [4–6,16,17]. It is assumed that the gas diffusion layer (GDL), cathode, separator and anode lithium metal have the same radius. To reduce the model to two dimensions, a single breathing hole is located at the center of the cathode casing. An axisymmetric assumption is adopted and the total computation domain is shown by the grey area in Figure 2, which contains five sub-domains: the air chamber, GDL, cathode, separator, and anode. The governing equations developed below are used on one or several sub-domains depending on the physical phenomena.

The following assumptions are included to make the computation feasible:

1. Li_2O_2 is considered completely insoluble in electrolyte and precipitates on the cathode pore surface immediately upon generation.
2. The reaction shown in eq. (1) is considered. Side reactions are neglected.
3. The charging process is not considered due to the lack of an established understanding of the mechanisms of these reactions.
4. Bulk velocity of the electrolyte is negligible and convection is not considered in mass transport, since the length scale in the cell is in the order of 10^{-3} m and the time scale of discharge is in the order of 1~10 hours.

5. Thermal effect is assumed to be negligible, including the temperature drop caused by solvent evaporation and consequent change of saturation vapor pressure. This is justifiable due to the small size of the cell and a long time scale of discharge (10^2 - 10^3 minutes).

2.1 Mass and charge transfer

The governing equations to describe the mass and charge transport inside the cell follow the common framework used in most previous Li–air continuum-scale models based on concentrated solution and porous electrode theory [18].

Conservation of all species in the electrolyte can be expressed as:

$$\frac{\partial(\varepsilon c_i)}{\partial t} = -\nabla \cdot \mathbf{N}_i + r_i \quad (2)$$

where c_i is molarity of species i , ε is local porosity, $\mathbf{N}_i$ is the molar flux of species i , and r_i is the species generation rate. According to concentrated solution theory [18], the molar flux of Li^+ ions in electrolyte can be expressed as:

$$\mathbf{N}_{\text{Li}} = -D_e^{\text{eff}} \nabla c_{\text{Li}} + \frac{i_2 t_+^0}{F} \quad (3)$$

where D_e^{eff} is the effective diffusion coefficient of the salt, t_+^0 is the transference number of lithium ion with respect to the solvent velocity, and F is the Faraday constant. The current density in electrolyte, i_2 , can be expressed as:

$$i_2 = -k_e^{\text{eff}} \nabla \phi_2 - \frac{2RTk_e^{\text{eff}}}{F} (t_+^0 - 1) \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_{\text{Li}}} \right) \nabla \ln c_{\text{Li}} \quad (4)$$

where k_e^{eff} is the effective ionic conductivity of the electrolyte, $f_{\pm}$ is the salt activity coefficient, and $\left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_{Li}}\right)$ is the thermodynamic factor [19]. In this model, the electrolyte conductivity is assumed to be a constant because of lack of data. This needs to be addressed in future studies because with the evaporation of solvent, electrolyte concentration change might be high enough to have a significant effect on conductivity and salt diffusivity.

To simplify the equations, the diffusion conductivity, k_D , is defined [20]:

$$k_D = \frac{2RTk_e^{eff}}{F} (t_+^0 - 1) \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_{Li}}\right) \quad (5)$$

Combining eqs. (2) – (5) yields the following equation for lithium ion transport:

$$\varepsilon \frac{\partial c_{Li}}{\partial t} + \nabla \cdot (-D_e^{eff} \nabla c_{Li}) = r_{Li} - \nabla \cdot \left(\frac{\mathbf{i}_2 t_+}{F} \right) \quad (6)$$

Dissolved oxygen is transported in the electrolyte by diffusion and therefore its molar flux can be expressed as [21]:

$$\mathbf{N}_{O_2} = -D_{O_2}^{eff} \nabla c_{O_2} \quad (7)$$

Combining eqs. (2) and (7) leads to the following equation for dissolved oxygen transport:

$$\varepsilon \frac{\partial c_{O_2}}{\partial t} + \nabla \cdot (-D_{O_2}^{eff} \nabla c_{O_2}) = r_{O_2} \quad (8)$$

The generation rates of the lithium ion, r_{Li} , in eq. (6), and oxygen, r_{O_2} , in eq. (8), can be related to the local transfer current density between electrolyte and electrode, j_R , as:

$$r_{Li} = \frac{A_{ED} j_R}{F}, \quad (9)$$

and

$$r_{O_2} = \frac{A_{ED} j_R}{2F} \quad (10)$$

where A_{ED} is the specific reaction surface. The product $A_{ED} j_R$ is the cathode volumetric current density which is the direct indicator of local electrochemical reaction rate.

To maintain charge balance, the divergence of electrolyte current density should be equal to the volumetric current density:

$$\nabla \cdot \mathbf{i}_2 = A_{ED} j_R \quad (11)$$

Combining eqs. (4) and (11) results in the following equation for electrolyte potential:

$$\nabla \cdot (-k^{eff} \nabla \phi_2) = \nabla \cdot \left(\frac{k_D}{c_{Li}} \nabla c_{Li} \right) + A_{ED} j_R \quad (12)$$

The governing equations for c_{Li} , c_{O_2} , and ϕ_2 (eqs. (6), (8), and (12)) are computed over a set of deforming meshes covering the subdomains of the cathode and separator shown in Figure 2. The moving boundary of the deforming mesh reflects the drop in electrolyte level during discharge.

The current balance between the electrolyte and cathode solid phase indicates that:

$$\nabla \cdot \mathbf{i}_1 + \nabla \cdot \mathbf{i}_2 = 0 \quad (13)$$

where $\mathbf{i}_1$ is the current density in the cathode solid phase, which can be expressed simply by Ohm's law:

$$\mathbf{i}_{1c} = -k_c^{eff} \nabla \phi_{1c} \quad (14)$$

where k_c^{eff} is the electronic conductivity of the cathode solid phase. Therefore, cathode electric potential can be obtained from eqs. (11), (13), and (14) as:

$$\nabla \cdot (-k_c^{eff} \nabla \phi_c) = -A_{ED} j_R \quad (15)$$

which is computed on a set of fixed meshes covering the GDL and cathode subdomains, shown in Figure 2.

Oxygen and solvent vapor transport in the GDL and air chamber are controlled by diffusion according to Fick's law:

$$\varepsilon \frac{\partial c_{oa}}{\partial t} + \nabla \cdot (-D_{oa}^{eff} \nabla c_{oa}) = 0 \quad (16)$$

$$\varepsilon \frac{\partial c_{sa}}{\partial t} + \nabla \cdot (-D_{sa}^{eff} \nabla c_{sa}) = 0 \quad (17)$$

where c_{oa} and c_{sa} are the concentrations of oxygen and solvent vapor in air, respectively; D_{oa}^{eff} and D_{sa}^{eff} are the effective diffusion coefficients of oxygen and solvent vapor in air, respectively.

Equations (16) and (17) are solved on the subdomains of the GDL and air chamber shown in Figure 2.

The effective parameters used in the above equations, including D_{Li}^{eff} , k_c^{eff} , D_{O_2} , D_{oa}^{eff} , and D_{sa}^{eff} , can be calculated through the Bruggeman correlation [22]:

$$\Phi^{eff} = \Phi \varepsilon^\beta \quad (18)$$

where Φ can be D_{Li} , k_c , D_{O_2} , D_{oa} , and D_{sa} . Similarly, k_c^{eff} can be expressed as:

$$k_c^{eff} = k_c (1 - \varepsilon_0 - \varepsilon_b)^\beta \quad (19)$$

where k_c is the electron conductivity in the carbon phase of the cathode and ε_b is the volume fraction of electrode binder. The Bruggeman coefficient, β , is assumed to be a constant 1.5 [23].

Due to the deposition of the insoluble reaction product Li_2O_2 , porosity in the cathode is a function of both location and time during the discharge process. It can be related to the volume fraction of precipitated product ε_s , and original porosity ε_0 , through:

$$\varepsilon = \varepsilon_0 - \varepsilon_s \quad (20)$$

The mass conservation of discharge product, Li_2O_2 , is used to obtain ε_s :

$$\frac{\partial \varepsilon_s}{\partial t} = -\frac{M_{\text{Li}_2\text{O}_2}}{2\rho_{\text{Li}_2\text{O}_2}F} A_{ED} j_R \quad (21)$$

where $M_{\text{Li}_2\text{O}_2}$ is the molecular weight of Li_2O_2 , and $\rho_{\text{Li}_2\text{O}_2}$ is the density of Li_2O_2 . The transfer current density j_R , is to be determined by reaction kinetics. Equation (21) is computed on a set of fixed meshes covering the subdomain of the cathode shown in Figure 2.

The driving force for the cathode reaction is the local activation overpotential η_c , which can be defined as:

$$\eta_c = \phi_{1c} - \phi_2 - \Delta\phi_{\text{Li}_2\text{O}_2} - E_c^0 \quad (22)$$

where $\Delta\phi_{\text{Li}_2\text{O}_2}$ is the voltage drop over the Li_2O_2 film and E_c^0 is the cathode theoretical potential. The voltage drop across the Li_2O_2 film is calculated by Ohm's law [4]:

$$\Delta\phi_{\text{Li}_2\text{O}_2} = j_R R_{\text{Li}_2\text{O}_2} \varepsilon_s \quad (23)$$

where $R_{\text{Li}_2\text{O}_2}$ is the electrical resistivity across the Li_2O_2 film.

The Tafel equation [24] is used to express the cathode reaction kinetics:

$$j_R = -k_R \left(\frac{c_{\text{Li}}}{c_{\text{Li}}^{\text{ref}}} \right)^2 \left(\frac{c_{\text{O}_2}}{c_{\text{O}_2}^{\text{ref}}} \right) \exp \left(-\frac{\alpha_c F}{RT} \eta_c \right) \quad (24)$$

where k_R is the rate constant for the cathode reaction, and α_c is the transfer coefficient, equal to 0.5. Reference concentrations c_{Li}^{ref} and $c_{O_2}^{ref}$ are set to be 1 M and the saturated oxygen concentration, $c_{O_2,sat}$, respectively.

Anode reaction kinetics is described by the Butler–Volmer equation [24]:

$$j_a = i_0 \left[\exp\left(\frac{(1-\alpha_a)F}{RT} \eta_a\right) - \exp\left(-\frac{\alpha_a F}{RT} \eta_a\right) \right] \quad (25)$$

where j_a is the transfer current density at the anode/separator interface (denoted as ④ in Figure 2), and i_0 is the exchange current density for the anode. The anode activation overpotential, η_a , is defined as:

$$\eta_a = \phi_{la} - \phi_2 - E_a^0 \quad (26)$$

where ϕ_{la} is the anode electrode potential and E_a^0 is the anode theoretical potential, 0 V. The anode electrode potential is governed by Ohm's law:

$$\nabla \cdot (-k_{Li} \nabla \phi_{la}) = 0 \quad (27)$$

where k_{Li} is the conductivity of lithium metal. This governing equation is computed on the moving mesh set covering the subdomain of the anode shown in Figure 2. The moving mesh reflects the shrinking of the anode lithium foil during discharge.

The effect of reaction area loss due to Li_2O_2 deposition is described by the following empirical relation [5]:

$$A_{ED} = A_{ED,0} \left[1 - \left(\frac{\varepsilon_s}{\varepsilon_0} \right)^z \right] \quad (28)$$

where $A_{ED,0}$ is the original specific area and the value for z is set to 0.5. In summary, there are eight unknowns in the model described above: electrolyte concentration c_{Li} , dissolved oxygen concentration c_{O_2} , electrolyte potential ϕ_2 , cathode electrode potential, ϕ_c , oxygen gas concentration c_{O_2} , solvent vapor concentration c_{sv} , anode electrode potential ϕ_a and deposit layer volume fraction ε_s . They are described by seven partial differential equations (6), (8), (12), (15), (16), (17), (27), and one ordinary differential equation (21).

2.2 Moving boundaries

As discussed in section 1, the velocity of the moving electrolyte level (① in Figure 2) consists of two parts:

$$V_1 = -(V_{lv} + V_{le}) \quad (29)$$

where V_{lv} is the velocity due to the liquid replacing the vanishing solid phase, and V_{le} is caused by solvent evaporation. The negative sign is due to the surface moving in the negative direction of z . V_{lv} is related to discharge current density I :

$$V_{lv} = \frac{I}{\varepsilon_1 F} \left(\frac{M_{Li}}{\rho_{Li}} - \frac{M_{Li_2O_2}}{2\rho_{Li_2O_2}} \right) \quad (30)$$

where ε_1 is the average porosity of the cathode at the electrolyte level, and M and ρ are the molecular weight and density, respectively. The subscripts Li and Li_2O_2 denote lithium and deposited lithium peroxide, respectively. V_{le} is related to the molar flux of solvent vapor N_{sv} on the electrolyte surface:

$$V_{1e} = \frac{\int_{A_{es}} N_{sv} dA}{A_{es}} \frac{M_{sv}}{\varepsilon_1 \rho_s} \quad (31)$$

where A_{es} denotes the area of the electrolyte surface and the subscript sv denotes solvent. The molar flux of evaporated solvent N_{sv} is calculated by:

$$N_{sv} = -D_{sv} \left. \frac{\partial c_{sv}}{\partial z} \right|_{A_{es}} \quad (32)$$

where D_{sv} is the diffusion coefficient of solvent vapor in air and c_{sv} is the concentration of solvent vapor in air.

The bottom of the anode lithium foil (② in Figure 2), moves upward during discharge and its velocity is:

$$V_2 = \frac{M_{Li}}{F \rho_{Li}} I \quad (33)$$

This velocity is expected to be constant since the discharge is under constant current.

2.3 Boundary conditions

At the anode/separator interface (③ in Figure 2), the electrolyte current density is equal to the discharge current density and the molar flux of dissolved oxygen is zero. At the separator/cathode interface (④ in Figure 2), the cathode electrode current is zero. At the cathode/GDL interface (① in Figure 2), the electrolyte current and Li^+ molar flux are both equal to zero, and the concentration of the dissolved oxygen is determined based on Henry's law:

$$c_{\text{O}_2} = \frac{c_{oa}}{c_0} c_{\text{O}_2, sat} \quad (34)$$

where c_0 is the total molar concentration of ideal gas at 1 bar and 25 °C and $c_{O_2,sat}$ is the solubility of oxygen in the electrolyte. Concentration of solvent vapor at this boundary is determined by the ideal gas law and its vapor saturation pressure p_{sa} :

$$c_{sa} = \frac{p_{sa}}{p_0} c_0 \quad (35)$$

where p_0 is 1 bar. The effect of lithium salt on solvent vapor pressure is neglected. The molar flux of oxygen and solvent vapor are zero at the air chamber wall (⑧ in Figure 2). The current density is equal to the discharge current density divided by the open ratio at the cathode casing (⑥ in Figure 2). The thickness of the cathode casing is neglected in the model. It should be noted that eqs. (34) and (35) are derived based on the assumption that pressure in the air chamber is constant. This is considered to be a reasonable assumption because the influx of evaporated DMF in the air chamber would cause an increase in pressure of less than 0.52% (516 Pa vapor pressure vs. 1 bar initial air chamber pressure) even if oxygen consumption is not considered, which conversely decreases pressure. The governing equations, boundary conditions and initial conditions are summarized in Table 2.

At the start of discharge, the air chamber and GDL are filled with air at 1 bar and with 0 pa solvent vapor. The electrolyte and dissolved oxygen concentrations are all uniform, at the values of 1 M and the saturated value $c_{O_2,sat}$, respectively. The cathode, separator, anode and spring are all immersed in electrolyte.

2.4 Computational methodology

The above governing equations are discretized and solved using the finite element method in COMSOL Multiphysics 4.4. Two sets of meshes are used. The first mesh set has 3643 elements, and it covers all the subdomains shown in Figure 2. The air chamber domain is discretized using a free triangular mesh while the other domains are discretized using a mapped rectangular mesh. In this mesh set, boundaries ① and ② can translate along the z direction, therefore the GDL, cathode, and anode sub-domains deform during the time-dependent calculation. The velocities of the moving boundaries are defined in eqs. (29) – (31) and (33). The ALE method [25] is used to enable geometry deformation. The second mesh set (4000 elements) is fixed and includes the cathode and GDL. Governing equations for ε_s and ϕ_{lc} are solved on this mesh set. Cathode specific surface area A_{ED} and transfer current density j_R are mapped from the deformed mesh onto this fixed mesh. The resulting values of ε_s and ϕ_{lc} are then mapped back to the deformed mesh through linear projection on a spatial frame. A time-dependent solver is employed to solve all the governing equations. A constant discharge current density I is imposed and the cell voltage is obtained through the difference between the cathode electrode potential at boundary ⑥ and the anode electrode potential at boundary ② for each time step. The maximum time step ranges between 10 and 100 seconds depending on the discharge current density; higher discharge current densities require a smaller time step. All results are proven to be mesh independent and time step independent.

Two different electrolytes are used in the calculations, including dimethyl formamide (DMF) and tetraethylene glycol dimethyl ether (TEGDME). These are chosen as solvents because of their opposing high and low vapor pressures, respectively. TEGDME is a widely used low vapor pressure organic solvent (~ 1 Pa) in experimental studies, while DMF has a fairly high vapor pressure (516 Pa at standard condition). The associated properties of both solvents are listed in Table 3. The diffusion coefficients of the solvent vapor in air are calculated using the FSG/LaBas method [26]. Oxygen diffusivities in the electrolyte are estimated through the Stokes–Einstein relation based on solvent viscosity [27]. Other parameters used in the calculation are provided in Table 4.

3. Results and discussion

3.1 Model calibration

The model is calibrated by comparing the simulated discharge curves with the experimental results of Read [16], in which PC:DME was used as electrolyte solvent. The evaporation of solvent is not considered in this comparison because of the lack of vapor pressure data for a PC:DME mixture. The open ratio of the cathode casing was assumed to be 100% and the air chamber was assumed to be filled with pure oxygen initially. There are two purposes of this comparison. Firstly, the cathode rate constant, k_R , is obtained by matching the discharge curves to experimental results [16]. Secondly, it shows that the model is able to predict the key discharge characteristics of a Li-air battery: sudden death at the end and lower capacity at higher discharge current.

3.2 Tracking the electrolyte level

Figure 4 indicates the position (z value) of the electrolyte level and anode/spring interface for two different electrolytes. Figure 4(a) shows the case with the DMF based electrolyte while Figure 4(b) shows the case with TEGDME based electrolyte. Discharge current densities for both cases are 0.5 A m^{-2} and the cathode opening radius is 0.5 mm. The upper solid line represents the drop in electrolyte level while the lower solid line depicts the rise of the bottom of the anode lithium foil. The anode bottom surface rises linearly over time due to a constant discharge current, and therefore V_2 remains constant according to eq. (33). The dashed line separates the displacement of electrolyte surface into two parts for both solvents: The upper region is caused by solvent evaporation while the lower area is attributed to solid phase volume decrease. Solvent evaporation occurs quickly and fills the air chamber in several hundred minutes. Solvent evaporation then gradually slows when the partial pressure of solvent vapor in the chamber approaches its saturated value. The electrolyte level displacement caused by the solvent evaporation correspondingly stops. The distance between the dashed line and the lower solid line represents the electrolyte level drop caused by the solid phase volume decrease. The electrolyte level drops faster towards the end of discharge because of a higher V_{1v} . The only non-constant parameter that influences V_{1v} is the average porosity ε_1 , as noted in eq. (30), which changes due to the increased Li_2O_2 deposition. There are two features of significance when comparing Figure 4(a) and (b). The first is that DMF evaporation causes a much larger electrolyte level drop due to its higher vapor pressure. V_{1e} is several times larger for the DMF based cell than for the

TEGDME based cell. Secondly, the discharge time of the DMF based cell is much greater than that of TEGDME, due to a much higher oxygen diffusivity in DMF (see Table 3).

3.3 Effect of electrolyte level change

It seems intuitive that a model accounting for electrolyte level change would predict a lower discharge capacity because of the loss of electrolyte. However, the predicted result indicates the opposite trend. Figure 5 compares the discharge curves of models with and without consideration of electrolyte level drop during discharge. The present model predicts a 22.5% higher discharge capacity for a DMF based cell at 5 A m^{-2} and a 14.9% higher discharge capacity for a TEGDME based cell at 0.5 A m^{-2} . Therefore, neglect of electrolyte level drop during discharge would result in an underestimation of cell discharge capacity. To better explain this conclusion, the effects of electrolyte level drop need to be examined.

There are three primary effects of electrolyte level drop on Li-air battery operation. The first is less cathode soaked in electrolyte and consequently less reaction surface. A higher overpotential must then be maintained for the required current output, which yields a smaller discharge time and capacity. However, an inspection of the distribution of reaction rate reveals that the electrochemical reaction takes place only in a small section of the cathode adjacent to the electrolyte surface, which means only a small percentage of the cathode reaction surface is used. Therefore, the loss of reaction surface only has a small influence on discharge capacity.

The second effect caused by electrolyte level drop is a decrease in electrolyte thickness, and consequent lower ion migration resistance and higher discharge capacity. The overpotential caused by the finite electrolyte conductivity can be approximated as:

$$\eta_2 = \frac{I(h_{cath}/2 + h_{sep})}{k_e}$$

where h_{cath} is the thickness of the electrolyte in the cathode (which decreases) and h_{sep} is the thickness of the separator. The electrolyte level drops 0.17 mm for a DMF based cell and 0.013 mm for a TEGDME based cell at the end of discharge, when the discharge current density is 0.5 A m⁻². This corresponds to a 0.03 mV and 0.05 mV decrease of η_2 , for DMF and TEGDME based cells, respectively. These value are negligible compared to other overpotentials, such as that for reaction activation. The decreased ion migration resistance caused by electrolyte level drop is also relatively insignificant.

Compared to the above two phenomena, the third effect caused by electrolyte level drop is significant based on the model prediction. Figure 6(a) illustrates the Li₂O₂ deposition on the cathode solid phase surface with a constant electrolyte level during discharge. The electrolyte level remains unchanged during discharge. The reaction rate and Li₂O₂ generation rate are at their highest because the oxygen concentration at this surface is also at its highest at any location in the cathode. This leads to the thickest deposition layer of Li₂O₂ at the cathode/GDL interface. Most existing modeling studies showed a similar Li₂O₂ distribution profile [5,8,17]. However, if electrolyte level drop is considered, this distribution profile is no longer valid. Figure 6(b) shows

the electrolyte level at various times during discharge. As the electrolyte level drops, the position with maximum reaction rate and Li_2O_2 deposition drops accordingly. This leads to a final Li_2O_2 volume fraction (ε_s) distribution curve that peaks where the electrolyte surface is located at the end of the discharge. At each time interval, the maximum reaction rate area is lowered slightly. This alleviates electrode blocking and predicts a better electrode utilization than for a constant electrolyte level. Figure 7 shows the predicted final ε_s distribution with and without consideration of electrolyte level change. The results match with the qualitative analysis of Figure 6. An integration of ε_s over the entire cathode volume shows that without considering electrolyte drop, 22.0% of the cathode pore volume is used at the end of discharge while inclusion of the electrolyte level drop increases this value to 24.3%. This agrees with the prediction of increased cathode specific capacity.

3.4 Effect of air chamber size

Solvent evaporation causes a large part of electrolyte level drop for a DMF based cell, as evidenced by Figure 4(a). The size of the air chamber directly affects the amount of solvent evaporation. The larger the chamber, the more solvent vapor can be accommodated before saturation, which affects cell discharge capacity. The chamber size was chosen to ensure that less than 5% of the oxygen original stored in the chamber was used during discharge, and therefore during discharge the pressure in the chamber keeps at a constant pressure. Figure 8 shows the discharge curves of a cell using DMF based electrolyte undergoing a 0.5 A m^{-2} discharge. It reveals that cathode specific capacity increases 72% from 530 mAh g^{-1} to 910 mAh g^{-1} when the

air chamber radius is increased from 5 cm to 15 cm. However, with a 15 cm radius, 33.8% of the cathode is exposed to air instead of immersed in electrolyte at the end of discharge, about half of which is caused by solvent evaporation. In comparison, for a cell with a 5 cm air chamber radius, only 8.2% of the cathode is exposed to air at the end of discharge. The same calculation was done for a TEGDME based cell, with the result showing that air chamber size has negligible effect on cell performance because of a very low vapor pressure. The current model only considers the first discharge of the battery. The charging process needs to be included in future models to study the effect of chamber size on cycling performance of the battery. It should also be noted that if it is assumed that the air chamber is already saturated with solvent vapor at the start of the discharge, the effect of chamber size on electrolyte level change would be negligible.

4. Conclusions

In a non-aqueous Li-air battery, the electrolyte level drops during discharge. This is caused by two phenomena, the decrease of the solid phase volume and electrolyte solvent evaporation. A 2-D Li-air coin cell physical model is developed with mesh deformation to track the electrolyte level during discharge. The position of electrolyte surface and its velocity are calculated. The diffusion of solvent vapor in the cell GDL and air chamber are also considered. The following conclusions are made based on the simulation results of a single cell with the cathode thickness of 800 μm :

1. The electrolyte surface velocity caused by solvent evaporation is at its highest at the beginning of discharge and then decreases to zero when the air chamber is saturated with solvent

vapor. The surface velocity imposed by solid volume decrease gradually rises because of increased Li_2O_2 deposition and decreased porosity.

2. A Li-air battery model would predict a higher cathode specific discharge capacity by including the effect of electrolyte level drop. In the cases studied in this paper, the increase can be up to 22.5% for a cell using DMF based electrolyte and 14.9% for a cell using TEGDME based electrolyte.

3. The proposed model describes a different Li_2O_2 distribution profile than those shown in previous studies. When electrolyte level drops during discharge, the position of the greatest Li_2O_2 deposition gradually moves with the surface. The final distribution of the Li_2O_2 volume fraction shows a peak in the middle of the cathode.

4. The air chamber has significant influence on discharge capacity for cells that use DMF based electrolyte. The discharge capacity increased by 72% when the radius of the chamber increased from 5 cm to 15 cm. This is accompanied by a large amount of solvent loss. At the end of discharge, 33.8% of the cathode volume is exposed in air instead of immersed in electrolyte.

Acknowledgement

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Nomenclature

A	specific area (m^{-1})
c	concentration (mol m^{-3})
D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
d	displacement (m)
E^0	thermodynamic equilibrium voltage (V)
F	Faraday constant ($96,485 \text{ C mol}^{-1}$)
$f_{\pm}$	Salt activity coefficient
I	discharge current density (A m^{-2})
i	current density (A m^{-2})
j	transfer current density between electrode and electrolyte (A m^{-2})
k_e	ionic conductivity (S m^{-1})
k_c	electron conductivity in carbon phase of electrode (S m^{-1})
k_D	diffusion conductivity (A m^{-1})
k_R	reaction rate constant (A m^{-2})
M	molecular weight (kg mol^{-1})
N	molar flux ($\text{mol m}^{-2} \text{s}^{-1}$)
O_r	cathode casing open ratio
p	pressure (Pa)

R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), electrical resistivity ($\Omega \text{ m}^2$), radius (m)
r	generation rate ($\text{mol m}^{-3} \text{ s}^{-1}$)
T	temperature (K)
t	time (s)
t_+	transference number
V	velocity (m s^{-1})
α	transfer coefficient
β	Bruggeman coefficient
ε	porosity
η	overpotential (V)
ρ	density (kg m^{-3})
ϕ	electric potential (V)

Superscripts and Subscripts

1	electrode solid phase
2	electrolyte phase
a	anode
c	cathode
eff	effective value
oa	oxygen in air

sa solvent vapor in air

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Table captions

Table 1 Structural parameters of the Li–air coin cell

Table 2 Effective domains of each dependent variable and corresponding boundary and
initial conditions

Table 3 Solvent/Electrolyte properties of the Li-air coin cell

Table 4 Parameters used in the simulation model of a Li-air coin cell

Table 1 Structural parameters of the Li–air coin cell

Radius [mm]		Original thickness [mm]				Original porosity		
Electrodes	Opening	GDL	Cathode	Separator	Anode	GDL	Cathode	Separator
2.5	0.1	0.1	0.8	0.025	0.2	0.75	0.73	0.5

Table 2 Effective domains of each dependent variable and corresponding boundary and

initial conditions		
Variable	Effective Domain	Boundary Condition (BC) and Initial Condition (IC)
c_{Li} , eq. (6)	Sep*, Cath*	①**: $\frac{\partial c_{Li}}{\partial z} = 0$; ③: $-D_{Li}^{eff} \frac{\partial c_{Li}}{\partial z} = \frac{1-t_+}{F} I$; IC: $c_{Li} = 1 \text{ M}$
c_{O_2} , eq. (8)	Sep, Cath	①: $c_{O_2} = \frac{c_{oa}}{c_0} c_{O_2,sat}$; ③: $\frac{\partial c_{O_2}}{\partial z} = 0$; IC: $c_{O_2} = c_{O_2,sat}$
ϕ_2 , eq. (12)	Sep, Cath	①: $\frac{\partial \phi_2}{\partial z} = 0$; ③: $-k_c^{eff} \frac{\partial \phi_2}{\partial z} = I + \frac{k_D}{c_{Li}} \frac{\partial c_{Li}}{\partial z}$; IC: $\phi_2 = 0$
ϕ_{1c} , eq. (15)	Cath, GDL*	④: $\frac{\partial \phi_{1c}}{\partial z} = 0$; ⑤: $\frac{\partial \phi_{1c}}{\partial z} = 0$; ⑥: $-k_c^{eff} \frac{\partial \phi_{1c}}{\partial z} = \frac{I}{1-O_r}$; IC: $\phi_{1c} = E_0^c$
c_{oa} , eq. (16)	GDL, AC*	①: $N_{oa} = N_{O_2}$; ⑧: $N_{oa} = 0$; IC: $c_{oa} = 0.21c_0$
c_{sa} , eq. (17)	GDL, AC	①: $c_{sa} = \frac{p_{sa}}{p_0} c_0$; ⑧: $N_{oa} = 0$; IC: $c_{sa} = 0$
ϕ_{1a} , eq. (27)	Ano*	②: $\phi_{1a} = 0$; ③: $-k_{Li} \frac{\partial \phi_{1a}}{\partial z} = I$; IC: $\phi_{1a} = 0$
$\mathcal{E}_s$, eq. (21)	Sep, Cath	IC: $\mathcal{E}_s = 0$

* Sep: Separator; Cath: Cathode; GDL: Gas Diffusion Layer; AC: Air Chamber; Ano: Anode.

** ① – ⑧: Boundaries shown in Figure 2.

Table 3 Solvent/Electrolyte properties of the Li-air coin cell

		DMF	TEGDME
Diffusion coefficient in air [$\times 10^{-6} \text{ m}^2 \text{ s}^{-1}$]	D_{so}	9.49	5.13
Vapor pressure [Pa]	p_s	516 [28]	1.33
Molecular weight [g mol^{-1}]	M_s	73.09	78.13
Density [kg m^{-3}]	ρ_s	948	1100.4
O ₂ solubility [mol m^{-3}]	$C_{\text{O}_2, \text{sat}}$	4.8 [29]	4.84[27]
O ₂ diffusivity [$\times 10^{-9} \text{ m}^2 \text{ s}^{-1}$]	D_{O_2}	1.93	0.217[10]
Ionic conductivity [S/m]	k_e	1.0 [30]	0.06 [31]

Table 4 Parameters used in the simulation model of a Li-air coin cell

Parameter	Symbol	Value
Cathode specific area [$\text{m}^2 \text{m}^{-3}$]	$A_{\text{ED},0}$	3.75×10^6 [4]
Cathode rate constant [A m^{-2}]	k_R	2.5×10^{-9}
Transfer coefficient	α_c, α_a	0.5
Cathode theoretical potential [V]	E_c^0	3.1 [32]
Anode exchange current density [A m^{-2}]	i_0	1 [5]
Density of lithium [g cm^{-3}]	ρ_{Li}	0.534
Density of carbon [g cm^{-3}]	ρ_c	2.0
Density of lithium peroxide [g cm^{-3}]	$\rho_{\text{Li}_2\text{O}_2}$	2.14
Density of PTFE [g cm^{-3}]	ρ_{PTFE}	2.2
Electric resistivity of Li_2O_2 [Ωm^2]	$R_{\text{Li}_2\text{O}_2}$	50 [4]
Salt diffusivity in electrolyte [$\text{m}^2 \text{s}^{-1}$]	D_{Li}	1.5×10^{-10} [33]
Molecular weight of lithium [g mol^{-1}]	M_{Li}	6.94
Molecular weight of Li_2O_2 [g mol^{-1}]	$M_{\text{Li}_2\text{O}_2}$	45.88
Transference number	t_0^+	0.43 [34]
Thermodynamic factor	$1 + d \ln f_{\pm} / d \ln c$	$\frac{0.28687c_{\text{Li}}^2 - 0.74678c_{\text{Li}} + 0.44103}{0.1287c_{\text{Li}}^3 - 0.4106c_{\text{Li}}^2 + 0.4717c_{\text{Li}} + 0.5508}$ [19]

Figure captions

Figure 1 Structure of a Li-air coin cell.

Figure 2 Computational domain and boundaries of the Li-air coin cell.

Figure 3 Comparison of predicted battery discharge curves at various current densities with experimental results from Read [16].

Figure 4 Variation of electrolyte surface and anode/spring interface position with time for a Li-air coin cell using (a) DMF and (b) TEGDME as electrolyte solvent.

Figure 5 Discharge curves with and without consideration of electrolyte level change for a Li-air coin cell using (a) DMF and (b) TEGDME as electrolyte solvent.

Figure 6 Li_2O_2 deposition on the cathode solid phase surface (a) with constant electrolyte level and (b) with electrolyte level drop.

Figure 7 Distribution of Li_2O_2 deposition volume fraction, ε_s , with and without consideration of electrolyte level drop.

Figure 8 Discharge curves with various air chamber radii and DMF as electrolyte solvent.

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

(a)

(b)

Figure 6

Figure 7

Figure 8