

# Lithium/air cell: Preliminary mathematical formulation and analysis

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## Abstract

Fundamentals of classical thermodynamics and chemical species mole balances have been applied to formulate the mathematical equations to compute lithium/air cell reversible reaction voltages, heat transfer rate between the cell and its surroundings, theoretical discharge capacity, and thermal efficiency. The developed formulation also provides a set of mathematical equations to compute the total cathode volume for a desired maximum discharge capacity of a lithium/air cell or battery.

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## 1. Introduction

Metal/oxygen or air batteries or cells are unique because the cell cathode active material, oxygen, is not stored in the battery. The cell environmental air can supply oxygen to the porous carbon cathode for the half-cell oxygen reduction process. A general diagram of a lithium/air cell is shown in Fig. 1.

Iron, zinc, aluminum, magnesium, calcium, and lithium have been used to develop metal/oxygen batteries. Most of the developed metal/oxygen systems employed alkaline electrolytes (e.g., KOH in H<sub>2</sub>O<sub>(l)</sub>). Only the zinc/oxygen battery has become a commercial product. Its main use is powering hearing aids. The lithium/oxygen aqueous electrolyte battery suffers from corrosion of the lithium electrode because of its chemical reaction with water [1]. A rechargeable lithium/oxygen battery, using a lithium ion conducting organic polymer electrolyte, was reported by Abraham and Jiang [2]. They concluded that the overall cell reaction during discharge is,  $2\text{Li}_{(s)} + \text{O}_{2(g)} \leftrightarrow \text{Li}_2\text{O}_{2(s)}$ . In addition to this reaction, Read [3] suggested, based on oxygen consumption measurements, that  $2\text{Li}_{(s)} + 1/2\text{O}_{2(g)} \leftrightarrow \text{Li}_2\text{O}_{(s)}$  is another cell reaction that can occur during discharge. Table 1 shows the characteristics of some metal/oxygen battery couples.

From the calculated data given in Table 1, it is apparent that the lithium/oxygen battery, with O<sub>2</sub> supplied from the cell's environmental air, has the highest theoretical specific energy of 11,140 Wh kg<sup>-1</sup> of Li. This energy density is higher than that of a methanol/air fuel cell, which is 6098 Wh kg<sup>-1</sup> of methanol.

The lithium/oxygen organic electrolyte battery differs from the aqueous metal/air batteries in that the oxygen reduction product is insoluble in the organic polymer electrolytes [2–4]. The peroxide O<sub>2</sub><sup>2-</sup> and oxide O<sup>2-</sup> ions are insoluble in an organic electrolyte. Therefore, Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O are formed at or near the sites where the peroxide ion O<sub>2</sub><sup>2-</sup> or oxide ion O<sup>2-</sup> are generated. A summary of the experimental work reported in Ref. [3] is as follows. The organic electrolyte formulation was found to have the largest effect on the battery discharge capacity and rate capability. The composition of the discharge product, percent of Li<sub>2</sub>O<sub>2(s)</sub> or Li<sub>2</sub>O<sub>(s)</sub> in the solid product mixture of Li<sub>2</sub>O<sub>2(s)</sub> and Li<sub>2</sub>O<sub>(s)</sub>, was dependent on both the discharge rate and the organic electrolyte formulation. The oxygen concentration in an electrolyte was dependent on the electrolyte formulation. During the lithium/air cell discharge, the lower oxygen concentration in the organic electrolyte resulted in the preferential formation of Li<sub>2</sub>O<sub>(s)</sub>. Measured oxygen solubility and electrolyte

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Table 1  
Characteristics of some metal/oxygen battery couples [2]

Metal/O <sub>2</sub> couple	Ideal cell reaction	Calculated open circuit voltage at 25 °C [V]	Theoretical specific energy <sup>a</sup> [Wh kg <sup>-1</sup> ]	
			O <sub>2</sub> mass included	O <sub>2</sub> mass excluded
Li/O <sub>2</sub>	4Li <sub>(s)</sub> + O <sub>2(g)</sub> ↔ 2Li <sub>2</sub> O <sub>(s)</sub> <sup>b</sup>	2.91	5200	11,140
Al/O <sub>2</sub>	4Al <sub>(s)</sub> + 3O <sub>2(g)</sub> ↔ 2Al <sub>2</sub> O <sub>3(s)</sub>	2.73	4300	8,130
Ca/O <sub>2</sub>	2Ca <sub>(s)</sub> + O <sub>2(g)</sub> ↔ 2CaO <sub>(s)</sub>	3.12	2990	4,180
Zn/O <sub>2</sub>	2Zn <sub>(s)</sub> + O <sub>2(g)</sub> ↔ 2ZnO <sub>(s)</sub>	1.65	1090	1,350

<sup>a</sup> Only the masses of the active reactant materials are included. The specific energy values are given for the cases of inclusion and exclusion of O<sub>2</sub>. The cell or battery mass starts to increase once discharge begins.

<sup>b</sup> The reduction of O<sub>2</sub> to O<sup>2-</sup> usually occurs in the presence of a catalyst such as cobalt. In the absence of a catalyst the product is the peroxide ion, O<sub>2</sub><sup>2-</sup>.

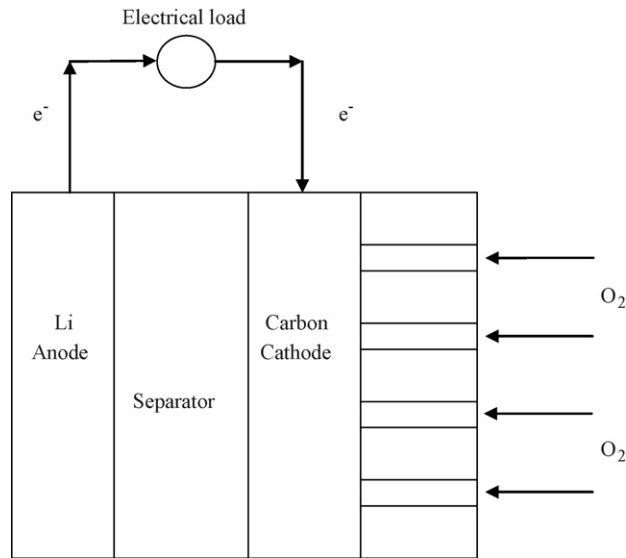


Fig. 1. Simple sketch of lithium/air system.

viscosity data were used to determine the oxygen diffusivity in several organic electrolytes [4]. Read et al. [4] concluded that the oxygen transport property, diffusivity, is of critical importance to the performance of a lithium/air or oxygen cell. Dolbey et al. [5] reported the results of their effort to increase the practical energy density of the lithium/air battery using carbon-air cathodes catalyzed by metals. The manganese (Mn) catalyzed cathodes showed the best performance followed by the cobalt catalyzed carbon cathodes. The specific discharge capacity of the Mn catalyzed carbon cathodes was determined to be 3137 mAh g<sup>-1</sup> of carbon at a discharge rate of 0.1 mA cm<sub>geom</sub><sup>-2</sup> at a cutoff voltage of 1.5 V. Kuboki et al. [6] investigated lithium/air batteries utilizing a hydrophobic ionic liquid consisting of 1-alkyl-3-methyl imidazolium cation and perfluoroalkylsulfonamide anion. 1-Ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl imide) has a higher lithium ion conductivity and prevents hydrolysis of the lithium anode, and showed the best electrolyte performance. The lithium/air cell using this electrolyte performed for 56 days in air and showed a discharge capacity of 5360 mAh g<sup>-1</sup> of cathode carbon.

For the theoretical formulation work presented in the next section, the electrochemical cell is comprised of a lithium foil pressed onto a nickel or copper sheet or grid as the cell anode; LiPF<sub>6</sub> in an organic solvent (e.g., PC or a mixture of PC and DME) as the electrolyte held in a polymer such as PAN (polyacrylonitrile); and a mixture of carbon grains, binder (PVDF, polyvinylidene fluoride), and polymer electrolyte laminated onto an aluminum or nickel grid as the cathode. The organic polymer electrolyte membrane separator electronically insulates the cell cathode from the anode.

## 2. Cell mathematical formulation

### 2.1. Thermodynamic formulation

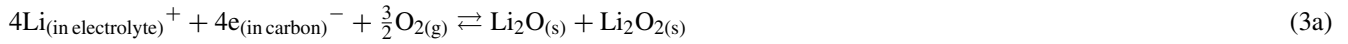
The half-cell reactions are given as follows. At the anode during cell discharge:



At the cathode during the cell discharge two reactions are possible:



Under the situation of reactions (2a) and (2b) occurring simultaneously in the cathode reaction layer, addition of reactions (2a) and (2b) leads to the following overall reaction stoichiometric equation:



If reaction (2a) is the only one occurring then the overall cell reaction is:



and if reaction (2b) is the only one occurring then the overall cell reaction is:



and if both reactions (2a) and (2b) occur then the overall cell reaction is:



The thermodynamic fundamental criterion of reaction equilibrium is applied to reactions (1) and (2a) to obtain the mathematical equations for the prediction of the reversible half-cell reactions that occur at the cell anode and cathode during the cell discharge. The condition of equilibrium for reaction (1) is:

$$\mu_{\text{Li}_{(\text{s})}}^{\text{chem}} = \mu_{\text{Li}^+(\text{in electrolyte})}^{\text{echem}} + \mu_{\text{e}^-(\text{in Li})}^{\text{echem,A}} \quad (4)$$

The condition of equilibrium for reaction (2a) is:

$$2\mu_{\text{Li}^+(\text{in electrolyte})}^{\text{echem}} + 2\mu_{\text{e}^-(\text{in carbon})}^{\text{echem,C}} + \mu_{\text{O}_{2(\text{g})}}^{\text{chem}} = \mu_{\text{Li}_2\text{O}_{2(\text{s})}}^{\text{chem}} \quad (5\text{a})$$

where  $\mu_{\text{Li}_{(\text{s})}}^{\text{chem}}$ ,  $\mu_{\text{O}_{2(\text{g})}}^{\text{chem}}$ , and  $\mu_{\text{Li}_2\text{O}_{2(\text{s})}}^{\text{chem}}$  are the chemical potentials of  $\text{Li}_{(\text{s})}$ ,  $\text{O}_{2(\text{g})}$ , and  $\text{Li}_2\text{O}_{2(\text{s})}$ , respectively.  $\mu_{\text{Li}^+(\text{in electrolyte})}^{\text{echem}}$  is the electrochemical potential of  $\text{Li}^+$  ion in the electrolyte, and  $\mu_{\text{e}^-(\text{in Li})}^{\text{echem,A}}$  and  $\mu_{\text{e}^-(\text{in carbon})}^{\text{echem,C}}$  are the electrochemical potentials of an electron in the anode and cathode reaction layer, respectively. For a charge neutral species ( $i$ ),  $\mu_i^{\text{chem}}$  is expressed as:

$$\mu_i^{\text{chem}} = \mu_i^0 + RT \ln(a_i) \quad (5\text{b})$$

where  $\mu_i^0$  is the standard-state chemical potential of a species ( $i$ ) at the cell temperature and  $a_i$  is the activity of species ( $i$ ). The electrochemical potential of  $\text{Li}^+$  in the electrolyte solution is expressed as:

$$\mu_{\text{Li}^+(\text{in electrolyte})}^{\text{echem}} = \mu_{\text{Li}^+(\text{in electrolyte})}^{\text{chem}} + z_{\text{Li}^+} F\phi^{\text{S}} = \mu_{\text{Li}^+(\text{in electrolyte})}^0 + RT \ln(a_{\text{Li}^+(\text{in electrolyte})}) + z_{\text{Li}^+} F\phi^{\text{S}} \quad (5\text{c})$$

where  $\mu_{\text{Li}^+(\text{in electrolyte})}^0$  is the standard-state chemical potential of  $\text{Li}^+$  ion in the cell electrolyte solution,  $a_{\text{Li}^+(\text{in electrolyte})}$  the activity of  $\text{Li}^+$  in the electrolyte solution at the cell electrolyte solution pressure and composition conditions,  $z_{\text{Li}^+}$  the number of positive charges on the lithium ion and has a value of +1 and  $\phi^{\text{S}}$  is the electric potential in the electrolyte solution just outside of the outer Helmholtz plane (OHP) of the double charge layer between the bulk electrolyte solution and an electrode. The electrochemical potentials,  $\mu_{\text{e}^-(\text{in Li})}^{\text{echem,A}}$  and  $\mu_{\text{e}^-(\text{in carbon})}^{\text{echem,C}}$  are expressed as:

$$\mu_{\text{e}^-(\text{in Li})}^{\text{echem,A}} = \mu_{\text{e}^-(\text{in Li})}^{\text{chem}} + z_{\text{e}^-} F\phi^{\text{A}} = \mu_{\text{e}^-(\text{in Li})}^0 + RT \ln(a_{\text{e}^-(\text{in Li})}) + z_{\text{e}^-} F\phi^{\text{A}} \quad (6\text{a})$$

and

$$\mu_{\text{e}^-(\text{in carbon})}^{\text{echem,C}} = \mu_{\text{e}^-(\text{in carbon})}^{\text{chem}} + z_{\text{e}^-} F\phi^{\text{C}} = \mu_{\text{e}^-(\text{in carbon})}^0 + RT \ln(a_{\text{e}^-(\text{in carbon})}) + z_{\text{e}^-} F\phi^{\text{C}} \quad (6\text{b})$$

where  $\mu_{\text{e}^-(\text{in Li})}^0$  and  $\mu_{\text{e}^-(\text{in carbon})}^0$  are the standard-state chemical potentials of an electron in the lithium and carbon electrodes, respectively, at the cell temperature;  $a_{\text{e}^-(\text{in Li})}$  and  $a_{\text{e}^-(\text{in carbon})}$  are the electron activities in the lithium and carbon electrodes, respectively;  $z_{\text{e}^-}$  is the number of charges on an electron and has a value of  $-1$ ; and  $\phi^{\text{A}}$  and  $\phi^{\text{C}}$  are the electric potentials in the bulk regions of the lithium anode and carbon cathode, respectively. The electron activities,  $a_{\text{e}^-(\text{in Li})}$  and  $a_{\text{e}^-(\text{in carbon})}$ , are usually set equal

to 1. The information provided in Eqs. (5b), (5c), (6a), and (6b) is used in Eqs. (4) and (5a) to obtain, after algebraic simplification, the expressions for reversible reaction electrode electric potentials as follows:

$$(\phi^A - \phi^S) = E^A = \left( \frac{\mu_{\text{Li}^+(\text{in electrolyte})}^0 + \mu_{\text{e}^-}^0 - \mu_{\text{Li(s)}}^0}{F} \right) + \left( \frac{RT}{F} \right) \ln \left( \frac{a_{\text{Li}^+(\text{in electrolyte})}}{a_{\text{Li(s)}}} \right) \quad (7a)$$

$$E^A = E^{A,0} + \left( \frac{RT}{F} \right) \ln \left( \frac{a_{\text{Li}^+(\text{in electrolyte})}}{a_{\text{Li(s)}}} \right) \quad (7b)$$

where  $E^{A,0}$  is the standard-state electric potential of the anode reaction (1).

$$(\phi^C - \phi^S) = E^C = \left( \frac{\mu_{\text{O}_{2(\text{g})}}^0 + 2\mu_{\text{Li}^+(\text{in electrolyte})}^0 + 2\mu_{\text{e}^-}^0 - \mu_{\text{Li}_2\text{O}_{2(\text{s})}}^0}{2F} \right) - \left( \frac{RT}{2F} \right) \ln \left( \frac{a_{\text{Li}_2\text{O}_{2(\text{s})}}}{a_{\text{O}_{2(\text{g})}} a_{\text{Li}^+(\text{in electrolyte})}^2} \right) \quad (8a)$$

$$E^C = E^{C,0} - \left( \frac{RT}{2F} \right) \ln \left( \frac{a_{\text{Li}_2\text{O}_{2(\text{s})}}}{a_{\text{O}_{2(\text{g})}} a_{\text{Li}^+(\text{in electrolyte})}^2} \right) \quad (8b)$$

where  $E^{C,0}$  is the standard-state electric potential of the cathode reaction in (2a) with  $\text{Li}_2\text{O}_{2(\text{s})}$  considered to be the only discharge product formed.

If a pure solid phase film of  $\text{Li}_2\text{O}_2$  is assumed to be formed on the carbon cathode  $a_{\text{Li}_2\text{O}_{2(\text{s})}}$  is set equal to 1. Furthermore,  $\mu_{\text{e}^-}^0$ , the standard-state chemical potential of an electron is also set equal to 0. Also,  $a_{\text{Li(s)}}$  is set equal to 1 since  $\text{Li(s)}$  is assumed to be a pure solid phase. The resultant equations to compute reversible anode and cathode reaction electric potentials are:

$$E^A = (\phi^A - \phi^S) = E^{A,0} + \left( \frac{RT}{F} \right) \ln(a_{\text{Li}^+(\text{in electrolyte})}) \quad (9)$$

and

$$E^C = (\phi^C - \phi^S) = E^{C,0} - \left( \frac{RT}{2F} \right) \ln \left( \frac{1}{a_{\text{O}_{2(\text{g})}} a_{\text{Li}^+(\text{in electrolyte})}^2} \right) \quad (10)$$

By subtracting Eq. (9) from (10) the reversible electric potential for the overall cell reaction given in Eq. (3b), where  $\text{Li}_2\text{O}_{2(\text{s})}$  is the discharge product, is obtained.

$$E = E^C - E^A = (\phi^C - \phi^S) - (\phi^A - \phi^S) = (E^{C,0} - E^{A,0}) - \left( \frac{RT}{2F} \right) \ln(a_{\text{O}_{2(\text{g})}}^{-1}) \quad (11a)$$

$$= (E^{C,0} - E^{A,0}) + \left( \frac{RT}{2F} \right) \ln(a_{\text{O}_{2(\text{g})}}) \quad (11b)$$

$$= E^0 + \left( \frac{RT}{2F} \right) \ln(a_{\text{O}_{2(\text{g})}}) \quad (11c)$$

where

$$E^0 = E^{C,0} - E^{A,0} = \left( \frac{1}{2F} \right) (\mu_{\text{O}_{2(\text{g})}}^0 + 2\mu_{\text{Li(s)}}^0 - \mu_{\text{Li}_2\text{O}_{2(\text{s})}}^0) \quad (11d)$$

is the standard-state electric potential of the overall cell reaction (3b). The activity of a gaseous species ( $i$ ) in a gas phase mixture is given by:

$$a_i = \hat{\phi}_i \frac{y_i P}{P^0} \quad (11e)$$

where  $\hat{\phi}_i$  is the fugacity coefficient of a species  $i$  in the gaseous mixture to take account of the energetic interactions between the molecules resulting in nonideal gas behavior. For gas phase mixtures at pressures less than 10 atm, it is quite reasonable to assume that  $\hat{\phi}_i = 1$ . Finally, the reversible electric potential for the overall cell reaction (3b) is:

$$E = E^0 + \frac{RT}{2F} \ln(a_{\text{O}_{2(\text{g})}}) \quad (12a)$$

$$E = E^0 + \frac{RT}{2F} \ln \left( \frac{y_{O_2} P}{P^0} \right) \quad (12b)$$

which gives the reversible electric potential for the lithium/O<sub>2</sub> cell assuming reaction (3b).

Using the above procedure, one can obtain the following equations to predict the reversible electrical potential of the overall cathodic reaction (3a) and that of the overall cell reaction (3d) for the case of formation of Li<sub>2</sub>O<sub>2(s)</sub> and Li<sub>2</sub>O<sub>(s)</sub> simultaneously at the carbon cathode during cell discharge:

$$E^C = \phi^C - \phi_{\text{electrolyte}} = E_{\text{simul}}^{C,0} - \left( \frac{RT}{4F} \right) \ln \left( \frac{a_{\text{Li}_2\text{O}_{(s)}} a_{\text{Li}_2\text{O}_{2(s)}}}{a_{\text{Li}^+}^4 (\text{in electrolyte}) a_{\text{O}_2(g)}^{1.5}} \right) \quad (13a)$$

$$= E_{\text{simul}}^{C,0} + \left( \frac{RT}{4F} \right) \ln (a_{\text{Li}^+}^4 (\text{in electrolyte}) a_{\text{O}_2(g)}^{1.5}) \quad (13b)$$

since  $a_{\text{Li}_2\text{O}_{(s)}} = a_{\text{Li}_2\text{O}_{2(s)}} = 1$  for the assumption of the formation of pure solid phases Li<sub>2</sub>O<sub>(s)</sub> and Li<sub>2</sub>O<sub>2(s)</sub> and where the standard-state electric potential of the overall cathodic reaction (3a),  $E_{\text{simul}}^{C,0}$ , is given by:

$$E_{\text{simul}}^{C,0} = \frac{4\mu_{\text{Li}^+}^0 (\text{in electrolyte}) + 1.5\mu_{\text{O}_2(g)}^0 - \mu_{\text{Li}_2\text{O}_{(s)}}^0 - \mu_{\text{Li}_2\text{O}_{2(s)}}^0}{4F} \quad (13c)$$

Now the reversible electric potential,  $E_{\text{simul}}$ , for the overall cell reaction (3d) is given by (assuming Li<sub>2</sub>O<sub>(s)</sub> and Li<sub>2</sub>O<sub>2(s)</sub> form solid crystal grains):

$$E_{\text{simul}} = (\phi^C - \phi_S) - (\phi^A - \phi_S) = E_{\text{simul}}^0 - \left( \frac{RT}{4F} \right) \ln \left( \frac{a_{\text{Li}_2\text{O}_{(s)}} a_{\text{Li}_2\text{O}_{2(s)}}}{a_{\text{O}_2(g)}^{1.5}} \right) \quad (14a)$$

$$= E_{\text{simul}}^0 + \left( \frac{RT}{4F} \right) \ln (a_{\text{O}_2(g)}^{1.5}) \quad (\text{with } a_{\text{Li}_2\text{O}_{(s)}} = a_{\text{Li}_2\text{O}_{2(s)}} = 1) \quad (14b)$$

where  $E_{\text{simul}}^0$  is the standard-state electric potential of reaction (3d) and is given by:

$$E_{\text{simul}}^0 = \frac{4\mu_{\text{Li}_{(s)}}^0 + 1.5\mu_{\text{O}_2(g)}^0 - \mu_{\text{Li}_2\text{O}_{(s)}}^0 - \mu_{\text{Li}_2\text{O}_{2(s)}}^0}{4F} \quad (14c)$$

For the situation of a homogeneous mixture of the Li<sub>2</sub>O<sub>2(s)</sub> and Li<sub>2</sub>O<sub>(s)</sub> in the solid phase in the cathode reaction layer, the activities  $a_{\text{Li}_2\text{O}_{(s)}}$  and  $a_{\text{Li}_2\text{O}_{2(s)}}$  should be computed from:

$$a_{\text{Li}_2\text{O}_{(s)}} = \gamma_{\text{Li}_2\text{O}_{(s)}} x_{\text{Li}_2\text{O}_{(s)}} \quad (15a)$$

$$a_{\text{Li}_2\text{O}_{2(s)}} = \gamma_{\text{Li}_2\text{O}_{2(s)}} x_{\text{Li}_2\text{O}_{2(s)}} \quad (15b)$$

where  $\gamma_{\text{Li}_2\text{O}_{(s)}}$  and  $\gamma_{\text{Li}_2\text{O}_{2(s)}}$  are the energetic interaction coefficients to account for the nonideal behavior of the solid phase mixture of Li<sub>2</sub>O<sub>(s)</sub> and Li<sub>2</sub>O<sub>2(s)</sub> and where  $x_{\text{Li}_2\text{O}_2}$  is the mole fraction of Li<sub>2</sub>O<sub>2(s)</sub> and  $x_{\text{Li}_2\text{O}}$  is the mole fraction of Li<sub>2</sub>O<sub>(s)</sub>. Eq. (14a) coupled with Eqs. (15a) and (15b) provides the cell method to determine the solid phase energetic coefficients experimentally. The activity of the Li<sup>+</sup> ion in an electrolyte solution,  $a_{\text{Li}^+} (\text{in electrolyte})$ , is expressed as follows:

$$a_{\text{Li}^+} = \gamma_{\text{Li}^+,m} m_{\text{Li}^+} \quad (16a)$$

where  $m_{\text{Li}^+}$  is the molality of the Li<sup>+</sup> ions (g mol of Li<sup>+</sup> ion kg<sup>-1</sup> of solvent), and  $\gamma_{\text{Li}^+,m}$  is the activity coefficient of the Li<sup>+</sup> ion to account for the electrolyte nonideal behavior due to its interaction with the surrounding charged and uncharged particles. If  $\gamma_{\text{Li}^+,m}$  is considered to be a dimensionless quantity; then,  $m_{\text{Li}^+}$  must be divided by  $m_0 = 1 \text{ g-mol kg}^{-1}$  solvent. Then,  $a_{\text{Li}^+}$  may be expressed as:

$$a_{\text{Li}^+} = \gamma_{\text{Li}^+,m} \frac{m_{\text{Li}^+}}{m_0} \quad (16b)$$

If the Li<sup>+</sup> ion concentration is given in molar units, it can be expressed in molality units using the following expression:

$$m_{\text{Li}^+} = \frac{C_{\text{Li}^+}}{\rho_0} \quad (17)$$

where  $C_{\text{Li}^+}$  is the lithium ion molar concentration, g mol of Li<sup>+</sup> ion per liter of solution, and  $\rho_0$  is the density of the pure solvent at the solution temperature and pressure conditions. The volume of the liquid phase solution is usually assumed to be equal to the pure

solvent volume. Analytical expressions to compute activity coefficients of individual ionic species such as  $\text{Li}^+$  ion and mean molal activity coefficients of electrolytic solutions can be found in Refs. [7,8].

The variation of the reversible voltage of the overall cell reaction (3b) or (3d) is given by [7]:

$$\left(\frac{\partial E}{\partial T}\right)_P = \frac{\Delta S}{nF} \quad (18a)$$

where  $\Delta S$  and  $n$  are the entropy change and g mol of electrons involved per g mol occurrence of the overall cell reaction (3b) or (3d). Over a small temperature range, the assumption of constant entropy change of a reaction is usually justified, and integration of Eq. (18a) with respect to temperature leads to:

$$E - E_1 = \frac{\Delta S}{nF}(T - T_1) \quad (18b)$$

where  $E_1$  is the cell reversible reaction voltage at temperature  $T_1$  and  $E$  is the reversible voltage at temperature  $T$ . If the entropy change varies significantly with temperature, then an integration of the temperature dependent entropy function in Eq. (18a) should be carried out. The reversible voltage change for the overall cell reaction (3b) or (3d) with pressure is given by:

$$E_2 - E_1 = -\frac{2.303 \Delta NRT}{nF} \log_{10} \left(\frac{P_2}{P_1}\right) \quad (18c)$$

where  $\Delta N$  is the change in g mol of the gaseous species [7] due to the 1 g mol occurrence of an overall cell reaction in the forward direction where  $n$  g mol of electrons are involved in each half-cell reaction at each electrode. Note that  $\Delta N$  is  $-1$  and  $n=2$  for reaction (3b) and  $\Delta N$  is  $-1.5$  and  $n=4$  for reaction (3d).

The thermodynamic equilibrium constant,  $K$ , for an overall cell reaction (3b) or (3d) is given by:

$$K = \exp\left(\frac{nFE^0}{RT}\right) \quad (19a)$$

where  $E^0$  is the standard-state potential of the cell reaction at the cell temperature,  $T$  [K].  $K$  corresponds to the point at which the driving force for the further electrochemical reaction is zero. The equilibrium constant,  $K$ , is related to the activities of chemical species taking part in the overall cell reaction at the cell equilibrium state. That is:

$$K = \left(\prod_i a_i^{\nu_i}\right) \quad (19b)$$

where  $\nu_i$  is the stoichiometric coefficient and  $a_i$  is the activity of a chemical species taking part in the overall cell reaction. For reaction (3b)  $\nu_{\text{Li(s)}} = -2$ ,  $\nu_{\text{O}_2(\text{g})} = -1$ ,  $\nu_{\text{Li}_2\text{O}_2(\text{s})} = 1$ ,  $a_{\text{Li(s)}} = a_{\text{Li}_2\text{O}_2(\text{s})} = 1$ , and  $a_{\text{O}_2(\text{g})} = y_{\text{O}_2} P/P^0$  (for  $P < 10$  atm) and for reaction (3d),  $\nu_{\text{Li(s)}} = -4$ ,  $\nu_{\text{O}_2(\text{g})} = -3/2$ ,  $\nu_{\text{Li}_2\text{O}_2(\text{s})} = 1$ ,  $\nu_{\text{Li}_2\text{O(s)}} = 1$ ,  $a_{\text{Li(s)}} = a_{\text{Li}_2\text{O(s)}} = a_{\text{Li}_2\text{O}_2(\text{s})} = 1$ , and  $a_{\text{O}_2(\text{g})} = y_{\text{O}_2} P/P^0$  (for  $P < 10$  atm). Using Eq. (19a), one can calculate the reaction extent to which a reaction can proceed theoretically for a given temperature, pressure, and internal reactant composition conditions.

## 2.2. The species mole balances and heat transfer

A lithium/air cell is assumed to be operating under isothermal, i.e., constant temperature, and isobaric conditions to deliver total current  $I$  [A] at the cell voltage  $E^{\text{cell}}$  [V]. The oxygen supply for the lithium/air cell is assumed to come from the surrounding air at temperature,  $T_{\text{surr}}$  [K], and pressure,  $P_{\text{surr}}$  [atm]. In the thermodynamic language, the cell is labeled here as the system to be analyzed as shown in Fig. 2. It is assumed that there is no mass loss due to solvent evaporation and thermal degradation of components.

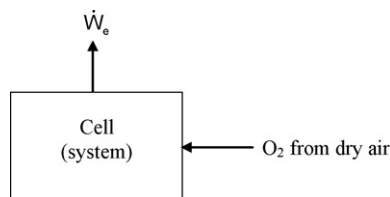


Fig. 2. Schematic representation of the overall lithium/air system.

### 2.2.1. The chemical species mole balances

During the cell discharge period, the rate of increase of the total cell mass is given by:

$$\frac{dm_{\text{sys}}^t}{dt} = (\text{rate of oxygen mass consumed per unit time in an overall chemical reaction}) \quad (20a)$$

$$\frac{dm_{\text{sys}}^t}{dt} = (\text{rate of oxygen mass supplied per unit time from the cell surrounding air}) \quad (20b)$$

Now if reaction (3b) is the overall cell reaction then:

$$\frac{dm_{\text{sys}}^t}{dt} = \left( \frac{I^t}{2F} M_{\text{O}_2} \right) \quad (21a)$$

and if reaction (3d) is the overall cell reaction then:

$$\frac{dm_{\text{sys}}^t}{dt} = \left( \frac{3}{8} \right) \frac{I^t}{F} M_{\text{O}_2} \quad (21b)$$

Masses of the electrolyte, carbon, binding material, and gases in the dissolved state in the electrolyte are assumed to be invariant with respect to time. Furthermore, change in the amount of oxygen, and nitrogen present in the electrolyte solution in pore volume of the porous carbon cathode is assumed negligible.

If the overall cell reaction is as given in reaction (3b), then the rate of change of g-mol of  $\text{Li}_{(s)}$  in the anode and  $\text{Li}_2\text{O}_{2(s)}$  in the cathode are given by:

$$\frac{dN_{\text{Li}_{(s)}}^t}{dt} = -2 \left( \frac{I^t}{2F} \right) = -\frac{I^t}{F} \quad (22a)$$

$$\frac{dN_{\text{Li}_2\text{O}_{2(s)}}^t}{dt} = \frac{I^t}{2F} \quad (22b)$$

On integration of Eqs. (22a) and (22b) with respect to time one obtains equations to determine the amount of lithium and lithium peroxide in the cell at any time,  $t$ , for cell reaction (3b):

$$N_{\text{Li}_{(s)}} = N_{\text{Li}_{(s),0}} - \frac{I^t}{F} t \quad (23a)$$

$$N_{\text{Li}_2\text{O}_{2(s)}} = N_{\text{Li}_2\text{O}_{2(s),0}} + \frac{I^t}{2F} t \quad (23b)$$

Similarly, for cell reaction (3d) the amounts of lithium in the cell anode and lithium peroxide and oxide in the cathode, for the situation of equimolar formation of  $\text{Li}_2\text{O}_{2(s)}$  and  $\text{Li}_2\text{O}_{(s)}$ , are given by:

$$N_{\text{Li}_{(s)}} = N_{\text{Li}_{(s),0}} - \frac{I^t}{F} t \quad (24a)$$

$$N_{\text{Li}_2\text{O}_{2(s)}} = N_{\text{Li}_2\text{O}_{2(s),0}} + \frac{I^t}{4F} t \quad (24b)$$

$$N_{\text{Li}_2\text{O}_{(s)}} = N_{\text{Li}_2\text{O}_{(s),0}} + \frac{I^t}{4F} t \quad (24c)$$

For the case of different molar formation rates of  $\text{Li}_2\text{O}_{2(s)}$  and  $\text{Li}_2\text{O}_{(s)}$ , the following approach can be used in the absence of experimentally obtained intrinsic kinetic rate laws for their formation rates. Here the total current,  $I^t$ , is the sum of the currents,  $I_{\text{Li}_2\text{O}_{2(s)}}^t$  and  $I_{\text{Li}_2\text{O}_{(s)}}^t$ , associated with the formation rates,  $R_{\text{Li}_2\text{O}_{2(s)}}^t$  and  $R_{\text{Li}_2\text{O}_{(s)}}^t$ , of  $\text{Li}_2\text{O}_{2(s)}$  and  $\text{Li}_2\text{O}_{(s)}$ , respectively. That is:

$$I^t = I_{\text{Li}_2\text{O}_{2(s)}}^t + I_{\text{Li}_2\text{O}_{(s)}}^t \quad (24d)$$

Also,

$$\frac{I_{\text{Li}_2\text{O}_{(s)}}^t}{I_{\text{Li}_2\text{O}_{2(s)}}^t} = \frac{(2F)R_{\text{Li}_2\text{O}_{(s)}}^t}{(2F)R_{\text{Li}_2\text{O}_{2(s)}}^t} = \frac{R_{\text{Li}_2\text{O}_{(s)}}^t}{R_{\text{Li}_2\text{O}_{2(s)}}^t} = r \quad (24e)$$

where  $r$  is the ratio of the solid product species molar formation rates that can be adjusted. Solution of Eqs. (24d) and (24e) for  $I_{\text{Li}_2\text{O}_2(\text{s})}^t$  and  $I_{\text{Li}_2\text{O}(\text{s})}^t$  leads to:

$$I_{\text{Li}_2\text{O}_2(\text{s})}^t = \frac{I^t}{1+r} \quad (24f)$$

$$I_{\text{Li}_2\text{O}(\text{s})}^t = \left(\frac{r}{1+r}\right) I^t \quad (24g)$$

The amounts of lithium peroxide and oxide in the cell cathode, for the case of their different molar formation rates, are given at any time,  $t$ , by:

$$N_{\text{Li}_2\text{O}_2(\text{s})} = N_{\text{Li}_2\text{O}_2(\text{s}),0} + \frac{1}{1+r} \left(\frac{I^t}{2F}\right) t \quad (24h)$$

$$N_{\text{Li}_2\text{O}(\text{s})} = N_{\text{Li}_2\text{O}(\text{s}),0} + \frac{r}{1+r} \left(\frac{I^t}{2F}\right) t \quad (24i)$$

Eq. (24a) is still valid for the amount of solid lithium in the cell anode. Eqs. (24h) and (24i) reduce to Eqs. (24b) and (24c) for  $r = 1$ ; the case of equimolar formation rates of the solid product species.

### 2.2.2. Cell heat transfer

The following general enthalpy balance equation for constant temperature and pressure conditions is applied over the lithium/air cell as the system:

$$\begin{aligned} &[\text{rate of change in the system thermal energy content due to change in the amounts of the solid phase reactant and product species} \\ &\text{at constant temperature and pressure}] = [\text{rate of thermal energy production because of occurrence of the overall cell reaction}] \\ &+ [\text{rate at which enthalpy enters with the gaseous reactant oxygen}] \\ &+ [\text{rate of heat exchange between the system and its surroundings}] \\ &+ [\text{rate of work exchange between the system and its surroundings in the form of electrical energy}] \\ &+ [\text{rate of work exchange between the system and its surroundings due to the system volume change at constant pressure}] \end{aligned} \quad (25)$$

and this results in the following equation for the reaction (3b):

$$\frac{d}{dt} \left( \sum_i N_i C_{P,i} (T - T_0) \right) = \left( \frac{I^t}{2F} (-\Delta H_{r \times n}) \right) + \left[ H_{\text{O}_2(\text{g}),T_{in}} \frac{I^t}{2F} \right] + \dot{Q} + \dot{W}_e + \dot{W}_{\text{sys}}. \quad (26)$$

Under constant temperature condition, Eq. (26) becomes:

$$\left( \frac{I^t}{2F} \right) (C_{P,\text{Li}_2\text{O}_2(\text{s})} - 2C_{P,\text{Li}(\text{s})}) (T - T_0) = \left( \frac{I^t}{2F} (-\Delta H_{r \times n}) \right) + \left[ H_{\text{O}_2(\text{g}),T_{in}} \frac{I^t}{2F} \right] + \dot{Q} + \dot{W}_e + \dot{W}_{\text{sys}}. \quad (27a)$$

where  $C_{P,\text{Li}_2\text{O}_2(\text{s})}$  and  $C_{P,\text{Li}(\text{s})}$  are the solid phase heat capacities of  $\text{Li}_2\text{O}_2(\text{s})$  and lithium, respectively, on a per g mol basis;  $T$  and  $T_0$  are the system and reference temperatures, respectively;  $\dot{Q}$  the heat exchange rate;  $\dot{W}_e$  the electric work exchange rate; and  $\dot{W}_{\text{sys}}$  is the rate of exchange of work between the system and surroundings due to the net change in the system volume at the constant pressure. Derivation of the left-hand side of Eq. (27a) from the left-hand side of Eq. (26) is as follows. Under constant temperature condition:

$$\begin{aligned} \frac{d}{dt} \left[ \sum_i N_i C_{P,i} (T - T_0) \right] &= \frac{d}{dt} [N_{\text{Li}(\text{s})} C_{P,\text{Li}(\text{s})} + N_{\text{Li}_2\text{O}_2(\text{s})} C_{P,\text{Li}_2\text{O}_2(\text{s})}] (T - T_0) = \left[ \frac{dN_{\text{Li}(\text{s})}}{dt} C_{P,\text{Li}(\text{s})} + \frac{dN_{\text{Li}_2\text{O}_2(\text{s})}}{dt} C_{P,\text{Li}_2\text{O}_2(\text{s})} \right] \\ &\times (T - T_0) = \left[ \left( -\frac{I^t}{F} \right) C_{P,\text{Li}(\text{s})} + \left( \frac{I^t}{2F} \right) C_{P,\text{Li}_2\text{O}_2(\text{s})} \right] (T - T_0) \\ &= \left( \frac{I^t}{2F} \right) (C_{P,\text{Li}_2\text{O}_2(\text{s})} - 2C_{P,\text{Li}(\text{s})}) (T - T_0) \end{aligned} \quad (27b)$$



For reaction (3b) the enthalpy of reaction is:

$$\Delta H_{r \times n} = (H_{\text{Li}_2\text{O}_{2(s)}} - 2H_{\text{Li}_{(s)}} - H_{\text{O}_{2(g)}}) \quad (28)$$

It should be noted that the quantities  $\dot{Q}$ ,  $\dot{W}_e$ , and  $\dot{W}_{\text{sys}}$  have positive number values if heat and work enter the system and negative values if heat and work leave the system.

During the period of cell discharge delivering total current at the level  $I^t$  [A] at the cell voltage  $E_{\text{actual}}^{\text{cell}}$  [V] the electrical work is given by:

$$\dot{W}_e = -I^t E_{\text{actual}}^{\text{cell}} \quad (29a)$$

It is assumed here that the discharge product,  $\text{Li}_2\text{O}_{2(s)}$ , due to the overall cell reaction in Eq. (3b), is formed in the pores of the carbon cathode layer. The cell stops delivering electric power once the cathode pores are filled with the discharge product or even before the filling of pores with the solid product if oxygen is unable to reach the carbon-electrolyte interface active sites for the net cathodic electrochemical reaction to occur due to pore mouth plugging with the discharge product. The system volume change is due only to the lithium metal consumption and  $\text{Li}_2\text{O}_{2(s)}$  formation. Therefore:

$$\begin{aligned} \dot{W}_{\text{sys}} &= (\text{system volume change per g mol of reaction (2b) occurring})(\text{g mol of reaction (2b) occurring per unit time})P_{\text{sys}} \\ &= - \left( \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(s)}}} - \frac{2M_{\text{Li}}}{\rho_{\text{Li}_{(s)}}} \right) \left( \frac{I^t}{2F} \right) P_{\text{sys}} \end{aligned} \quad (29b)$$

Substituting for  $\dot{W}_e$  and  $\dot{W}_{\text{sys}}$  from Eqs. (29a) and (29b), respectively, into Eq. (27a) and further simplifying the algebraic expression leads to:

$$\dot{Q} = \left( \frac{I^t}{2F} \right) \left( \Delta H_{r \times n} - H_{\text{O}_{2(g),T_{in}}} + 2FE_{\text{actual}}^{\text{cell}} + \left( \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(s)}}} - \frac{2M_{\text{Li}}}{\rho_{\text{Li}_{(s)}}} \right) P_{\text{sys}} + (C_{P,\text{Li}_2\text{O}_{2(s)}} - 2C_{P,\text{Li}_{(s)}})(T - T_0) \right) \quad (30)$$

Eq. (30) is the expression to calculate the amount of heat required to be removed for the isothermal operation of the cell at a temperature,  $T$ , during its discharge.

Enthalpy of a species at any temperature can be computed as follows:

$$H_{i(s)} = H_{i(s),T_0} + \int_{T_0}^T C_{P(s),i} dT \quad (31a)$$

$$= \Delta H_{i(s),f,T_0}^\circ + \int_{T_0}^T C_{P(s),i} dT \quad (31b)$$

$$H_{i(g)} = H_{i(g),T_0} + \int_{T_0}^T C_{P(g),i} dT \quad (31c)$$

$$= \Delta H_{i(g),f,T_0}^\circ + \int_{T_0}^T C_{P(g),i} dT \quad (31d)$$

where  $\Delta H_{i(s),f,T_0}^\circ$  and  $\Delta H_{i(g),f,T_0}^\circ$  are the standard-state enthalpies of formation of the solid state and gas phase species from their respective elements at the reference temperature of  $T_0 = 298.15$  K and  $C_{P,i}$ 's are the chemical species heat capacities. Following the above procedure one can obtain the following expression to calculate heat transfer between the cell system and its surroundings when the overall cell reaction is that given in Eq. (3d), where  $\text{Li}_2\text{O}_{(s)}$  and  $\text{Li}_2\text{O}_{2(s)}$  are both formed during the period of cell discharge.

$$\dot{Q} = \left( \frac{I^t}{4F} \right) \left( \Delta H_{r \times n} - 1.5H_{\text{O}_{2(g),T_{in}}} + 4FE_{\text{actual}}^{\text{cell}} + \left( \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(s)}}} + \frac{M_{\text{Li}_2\text{O}}}{\rho_{\text{Li}_2\text{O}_{(s)}}} - \frac{4M_{\text{Li}}}{\rho_{\text{Li}_{(s)}}} \right) P_{\text{sys}} + (C_{P,\text{Li}_2\text{O}_{2(s)}} + C_{P,\text{Li}_2\text{O}_{(s)}} - 4C_{P,\text{Li}_{(s)}})(T - T_0) \right) \quad (32a)$$

where the enthalpy of reaction (3d) is given by:

$$\Delta H_{r \times n} = (H_{\text{Li}_2\text{O}_{2(s)}} + H_{\text{Li}_2\text{O}_{(s)}} - 4H_{\text{Li}_{(s)}} - 1.5H_{\text{O}_{2(g)}}) \quad (32b)$$

In the derivation of Eq. (32a), it has been assumed that the discharge products  $\text{Li}_2\text{O}_{(s)}$  and  $\text{Li}_2\text{O}_{2(s)}$  are formed in the pores of the carbon cathode. When the pore mouths in the carbon cathode are plugged and the reactant oxygen is prevented from reaching the active carbon-electrolyte interface sites or when the pores are completely filled with the solid discharge product species, the cell stops delivering electrical power.

Actual cell voltage,  $E_{\text{actual}}^{\text{cell}}$ , when the cell is delivering total current  $I$  [A] to an external load, is given by [9]:

$$E_{\text{actual}}^{\text{cell}} = E_{\text{rev}} - (|\eta^{\text{A}}| + |\eta^{\text{C}}| + |\Delta\phi_{\text{ionic}}| + |\Delta\phi_{\text{electronic}}|) \quad (33)$$

where  $E_{\text{rev}}$  is the reversible cell voltage either for cell reaction (3b) or for (3d). Eq. (33) is strictly valid for the low current density condition where resistance to mass transfer of a reactant, for example, oxygen, to the active sites at the cathode-electrolyte interface is negligible. At high current densities, resistance to mass transfer of a reactant species to the reaction active sites would also influence the cell performance. Then, the cell voltage loss associated with the reactant mass transfer should also be accounted for as explained in the reference [9]. Eqs. (12b) and (14b) can be used to compute  $E_{\text{rev}}$  for reaction (3b) or (3d), respectively. The overvoltages at the anode and cathode,  $|\eta^{\text{A}}|$  and  $|\eta^{\text{C}}|$ , respectively, should either be determined experimentally or from the Butler-Volmer kinetic equation [8] written as:

$$i = i_0^{\text{A}} \left( \exp\left(\frac{(1-\beta)F|\eta^{\text{A}}|}{RT}\right) - \exp\left(\frac{-\beta F|\eta^{\text{A}}|}{RT}\right) \right) \quad (34a)$$

which is for the lithium oxidation process at the anode, and:

$$|i| = |i_0^{\text{C}}| \left( \exp\left(\frac{\beta n F |\eta^{\text{C}}|}{RT}\right) - \exp\left(\frac{-(1-\beta)n F |\eta^{\text{C}}|}{RT}\right) \right) \quad (34b)$$

which is for the oxygen reduction process at the cathode. Here, the symbols  $i$  and  $|i|$  on the left-hand sides of Eqs. (34a) and (34b) represent the net currents per unit electrode-electrolyte interfacial area at the cell anode and cathode electrode, respectively;  $|\eta^{\text{A}}|$ ,  $|\eta^{\text{C}}|$ ,  $|i_0^{\text{C}}|$  represent their respective absolute or positive number values;  $\beta = 0.5$ ,  $n$  = the number of electrons involved in an elementary reaction step that controls the overall oxygen reduction process at the cathode. Assuming the oxygen reduction process follows the reduction mechanism scheme in the presence of  $\text{Li}^+$  ions similar to that in the presence of  $\text{H}^+$  ions, one may assume  $n = 1$  in Eq. (34b).  $i_0^{\text{A}}$  and  $i_0^{\text{C}}$  are the exchange current densities at the lithium anode and carbon cathode, respectively. The voltage loss due to the ohmic resistance to  $\text{Li}^+$  ion movement under electric field effect in the electrolyte solution is given by:

$$|\Delta\phi_{\text{ionic}}| \simeq \frac{i_{\text{geom}} l_{\text{electrolyte}}}{k_{\text{electrolyte}}} \quad (35)$$

where  $i_{\text{geom}} = I/A_{\text{geom}}$  [ $\text{A cm}_{\text{geom}}^{-2}$ ],  $A_{\text{geom}}$  is the geometric area of the electrolyte separator,  $l_{\text{electrolyte}}$  the electrolyte path length [cm], and  $k_{\text{electrolyte}}$  the electrolyte conductivity [ $\text{S cm}^{-1}$ ].  $|\Delta\phi_{\text{electronic}}|$  the voltage drop due to electronic migration in the lithium metal and carbon cathode, would be small relative to  $|\Delta\phi_{\text{ionic}}|$  and  $|\eta^{\text{C}}|$  and may be neglected.

### 2.3. Theoretical discharge capacity and thermal efficiency

Theoretical discharge per unit mass of the active material, lithium, is:

$$q_{\text{theoretical}} = \frac{F}{M_{\text{Li}}} \quad (36)$$

where  $M_{\text{Li}}$  is the atomic weight of lithium,  $6.939 \text{ g g mol}^{-1}$ . Note: Eq. (36) applies to both reactions (3b) and (3d).

The theoretical or maximum thermal efficiency under cell reversible operating conditions is given by:

$$\eta_{\text{thermal,max}} = \frac{\Delta G}{\Delta H} \quad (37)$$

where  $\Delta G = \sum_i \nu_i G_i$  and  $\Delta H = \sum_i \nu_i H_i$  are the reaction Gibbs free energy change and the enthalpy change, respectively, per g mol of reaction (3b) or (3d) occurring at the cell temperature.

### 2.4. Cathode volume estimation

In this section, the mathematical expressions to compute volumes of the various components and the total volume of the composite carbon cathode are provided. It is assumed that the porous cathode is composed of carbon grains; a binder, such as PVDF; and a polymer electrolyte, such as  $\text{LiPF}_6$  in a mixture of propylene carbonate and 1,2-dimethoxyethane held in PAN (polyacrylonitrile). Maximum cell discharge is allowed to the extent that the discharge product, solid lithium peroxide or a mixture of solid lithium peroxide and lithium oxide, resides in the cathode pore volume. Also, it is assumed that a small pore volume would be available for air or oxygen access to the cathode reaction sites even by the end of a desired maximum discharge from the cell.

If the desired discharge maximum is  $q_d^{\max}$ , the amount of lithium consumed is:

$$-\Delta N_{\text{Li}} = \frac{q_d^{\max}}{F} \quad (38)$$

where  $q_d^{\max}$  [C], and is the maximum discharge desired from the battery. The decrease in the lithium metal volume in the anode is given by:

$$-\Delta V_{\text{Li(s)}}^A = \frac{(-\Delta N_{\text{Li}})M_{\text{Li}}}{\rho_{\text{Li}}} = \frac{q_d^{\max}M_{\text{Li}}}{F\rho_{\text{Li}}} \quad (39)$$

where  $\rho_{\text{Li}}$  is the density of solid lithium metal [ $\text{g cm}^{-3}$ ].

If  $\text{Li}_2\text{O}_{2(\text{s})}$  is the only solid discharge product, as described by Eq. (3b), being formed in the porous composite cathode, then the amount of  $\text{Li}_2\text{O}_{2(\text{s})}$  deposited is given by:

$$\Delta m_{\text{Li}_2\text{O}_{2(\text{s})}} = \frac{-\Delta N_{\text{Li}}M_{\text{Li}_2\text{O}_2}}{2} = \left(\frac{q_d^{\max}}{2F}\right)M_{\text{Li}_2\text{O}_2} \quad (40a)$$

If  $\text{Li}_2\text{O}_{2(\text{s})}$  and  $\text{Li}_2\text{O}_{(\text{s})}$  are simultaneously deposited as the solid discharge product, as described by Eq. (3d), being formed in the porous composite cathode; then, the amount of  $\text{Li}_2\text{O}_{2(\text{s})}$  and  $\text{Li}_2\text{O}_{(\text{s})}$  deposited for the equimolar formation situation is given, respectively, by:

$$\Delta m_{\text{Li}_2\text{O}_{2(\text{s})}} = \left(\frac{-\Delta N_{\text{Li}}}{4}\right)M_{\text{Li}_2\text{O}_2} = \left(\frac{q_d^{\max}}{4F}\right)M_{\text{Li}_2\text{O}_2} \quad (40b)$$

and

$$\Delta m_{\text{Li}_2\text{O}_{(\text{s})}} = \left(\frac{-\Delta N_{\text{Li}}}{4}\right)M_{\text{Li}_2\text{O}} = \left(\frac{q_d^{\max}}{4F}\right)M_{\text{Li}_2\text{O}} \quad (40c)$$

For the case of different molar formation rates of the solid product species simultaneously:

$$\Delta m_{\text{Li}_2\text{O}_{2(\text{s})}} = \frac{1}{1+r} \left(\frac{q_d^{\max}}{2F}\right)M_{\text{Li}_2\text{O}_2} \quad (40d)$$

$$\Delta m_{\text{Li}_2\text{O}_{(\text{s})}} = \frac{r}{1+r} \left(\frac{q_d^{\max}}{2F}\right)M_{\text{Li}_2\text{O}} \quad (40e)$$

In the above equations,  $M_{\text{Li}}$ ,  $M_{\text{Li}_2\text{O}}$  and  $M_{\text{Li}_2\text{O}_2}$  are the molecular weights of lithium, lithium oxide, and lithium peroxide, respectively [ $\text{g g mol}^{-1}$ ].

For  $\text{Li}_2\text{O}_{2(\text{s})}$  as the only discharge product, Eq. (3b), the increase in volume of the  $\text{Li}_2\text{O}_{2(\text{s})}$  discharge product in the cathode volume is given by:

$$\Delta V_{\text{Li}_2\text{O}_{2(\text{s})}} = \frac{\Delta m_{\text{Li}_2\text{O}_{2(\text{s})}}}{\rho_{\text{Li}_2\text{O}_{2(\text{s})}}} = \left(\frac{q_d^{\max}}{2F}\right) \left(\frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(\text{s})}}}\right) \quad (40f)$$

For  $\text{Li}_2\text{O}_{(\text{s})}$  and  $\text{Li}_2\text{O}_{2(\text{s})}$  as the discharge products, Eq. (3d), the volume increase of the discharge products in the cathode volume for the equimolar formation situation is given by:

$$\Delta V_{(\text{Li}_2\text{O}_{(\text{s})}+\text{Li}_2\text{O}_{2(\text{s})})} = \frac{\Delta m_{\text{Li}_2\text{O}_{(\text{s})}}}{\rho_{\text{Li}_2\text{O}_{(\text{s})}}} + \frac{\Delta m_{\text{Li}_2\text{O}_{2(\text{s})}}}{\rho_{\text{Li}_2\text{O}_{2(\text{s})}}} = \left(\frac{q_d^{\max}}{4F}\right) \left(\frac{M_{\text{Li}_2\text{O}}}{\rho_{\text{Li}_2\text{O}_{(\text{s})}}} + \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(\text{s})}}}\right) \quad (40g)$$

where  $\rho_{\text{Li}_2\text{O}_{(\text{s})}}$  and  $\rho_{\text{Li}_2\text{O}_{2(\text{s})}}$  are the respective densities of  $\text{Li}_2\text{O}_{(\text{s})}$  and  $\text{Li}_2\text{O}_{2(\text{s})}$  [ $\text{g cm}^{-3}$ ]. For the case of different molar formation rates of the solid product species simultaneously, the increase in volume of the discharge product species is given by:

$$\Delta V_{(\text{Li}_2\text{O}_{(\text{s})}+\text{Li}_2\text{O}_{2(\text{s})})} = \left(\frac{q_d^{\max}}{2F}\right) \left[\left(\frac{r}{1+r}\right) \frac{M_{\text{Li}_2\text{O}}}{\rho_{\text{Li}_2\text{O}_{(\text{s})}}} + \left(\frac{1}{1+r}\right) \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_{2(\text{s})}}}\right] \quad (40h)$$

If  $\delta_{\text{dischg}}^{\max}$  [cm], is the maximum thickness of the solid discharge product layer around every carbon grain present in the porous composite cathode reaction layer; then, the volume available for occupation by the solid discharge product around every carbon grain is given by:

$$V_{\text{dischg product on C-grain}} = \left(\frac{4\pi}{3}\right) \left[\left(\frac{d_{\text{ave,C-grain}}}{2} + \delta_{\text{dischg}}^{\max}\right)^3 - \left(\frac{d_{\text{ave,C-grain}}}{2}\right)^3\right] f_{\text{dischg product deposited}} \quad (41a)$$

$$= \left( \frac{4\pi}{3} \right) (\delta_{\text{dischg}}^{\text{max}}) [0.75d_{\text{ave,C-grain}}^2 + 1.5d_{\text{ave,C-grain}}\delta_{\text{dischg}}^{\text{max}} + (\delta_{\text{dischg}}^{\text{max}})^2] f_{\text{dischg product deposited}} \quad (41b)$$

$V_{\text{dischg product on C-grain}}$  has the units of  $[\text{cm}^3]$ ,  $f_{\text{dischg product deposited}}$  is the factor representing the fraction of a carbon grain surface available for the discharge product deposition, and  $d_{\text{ave,C-grain}}$  is the average diameter of the carbon grains present in the cathode. The number of carbon grains, each of diameter,  $d_{\text{ave,C-grain}}$ , needed in the cathode reaction layer is given by:

$$N_{\text{C-grain}} = \frac{\Delta V_{\text{dischg product(s)}}}{V_{\text{dischg product on C-grain}}} \quad (42)$$

Note that  $\Delta V_{\text{dischg product(s)}} = \Delta V_{\text{Li}_2\text{O}_{2(\text{s})}}$  for  $\text{Li}_2\text{O}_{2(\text{s})}$  as the only discharge product and that  $\Delta V_{\text{dischg product(s)}} = \Delta V_{(\text{Li}_2\text{O}_{(\text{s})} + \text{Li}_2\text{O}_{2(\text{s})})}$  for  $\text{Li}_2\text{O}_{(\text{s})}$  and  $\text{Li}_2\text{O}_{2(\text{s})}$  as the discharge products.

The mass of a carbon grain of diameter,  $d_{\text{ave,C-grain}}$ , is given by:

$$m_{\text{C-grain}} = \left( \frac{\pi}{6} \right) (d_{\text{ave,C-grain}}^3) \rho_{\text{C-grain}} \quad (43)$$

where  $\rho_{\text{C-grain}}$  is the carbon grain mass density  $[\text{g m}^{-3}]$ .

The total mass of carbon grains in the cathode reaction layer is given by:

$$m_{\text{C-grains}}^{\text{total}} = m_{\text{C-grain}} N_{\text{C-grain}} \quad (44)$$

The total volume of carbon grains in the cathode reaction layer is given by:

$$V_{\text{C-grains}}^{\text{total}} = \frac{m_{\text{C-grains}}^{\text{total}}}{\rho_{\text{C-grain}}} \quad (45)$$

The mass of the binder in the cathode reaction layer is given by:

$$m_{\text{binder}} = r_{\text{binder}}(\text{mass of carbon grains in the cathode reaction layer}) = r_{\text{binder}} m_{\text{C-grains}}^{\text{total}} \quad (46)$$

where  $r_{\text{binder}}$  is the ratio of the mass of binder to the mass of the carbon grains in the cathode reaction layer.

The volume of the binder in the cathode reaction layer is given by:

$$V_{\text{binder}} = \frac{m_{\text{binder}}}{\rho_{\text{binder}}} \quad (47)$$

where  $\rho_{\text{binder}}$  is the binder density  $[\text{g cm}^{-3}]$ .

The mass of the polymer electrolyte in the cathode reaction layer is given by:

$$m_{\text{polymer electrolyte}} = r_{\text{polymer electrolyte}}(\text{mass of carbon grains in the cathode reaction layer}) = r_{\text{polymer electrolyte}} m_{\text{C-grains}}^{\text{total}} \quad (48)$$

where  $r_{\text{polymer electrolyte}}$  is the ratio of the mass of polymer electrolyte to that of the carbon grains in the cathode reaction layer.

The volume of the polymer electrolyte in the cathode reaction layer is given by:

$$V_{\text{polymer electrolyte}} = \frac{m_{\text{polymer electrolyte}}}{\rho_{\text{polymer electrolyte}}} \quad (49a)$$

where  $\rho_{\text{polymer electrolyte}}$  is the polymer electrolyte density given by:

$$\rho_{\text{polymer electrolyte}} = \frac{m_{\text{electrolyte}} + 1}{(m_{\text{electrolyte}}/\rho_{\text{electrolyte}} + 1/\rho_{\text{polymer}})} \quad (49b)$$

where  $m_{\text{electrolyte}}$  is the mass of the electrolyte, such as  $\text{LiPF}_6$  in an organic solvent mixture, e.g., propylene carbonate and 1,2-dimethoxyethane, per unit mass of a polymer, e.g., the polyacrylonitrile (PAN) holding the electrolyte.  $\rho_{\text{polymer electrolyte}}$  and  $\rho_{\text{polymer}}$  are the densities of the polymer electrolyte and the polymer, respectively  $[\text{g cm}^{-3}]$ .

It is assumed for this cell construction that some pore volume is available in the cathode for the air or oxygen access to the reaction sites even when the cell undergoes maximum discharge. The volume of the pore space available for air in the cathode layer at the end of the desired maximum discharge is:

$$V_{\text{air, end discharge}} = f_{\text{air, end discharge}} V_{\text{total}}^{\text{cathode}} \quad (50)$$

where  $f_{\text{air, end discharge}}$  is the volume fraction of the total cathode volume available for the presence of air in the pore space at the end of maximum discharge, and where  $V_{\text{total}}^{\text{cathode}}$  is the total cathode volume  $[\text{cm}^3]$ , that must accommodate the desired maximum cell

discharge. The total cathode volume is now expressed in terms of the required component volumes as:

$$V_{\text{total}}^{\text{cathode}} = (\text{volume of the solid discharge product(s)} + (\text{volume occupied by carbon grains}) \\ + (\text{volume occupied by binder}) + (\text{volume occupied by polymer electrolyte}) \\ + (\text{pore volume occupied by air at the end of maximum cell discharge}) \quad (51a)$$

Writing Eq. (51a) in mathematical terms gives:

$$V_{\text{total}}^{\text{cathode}} = \Delta V_{\text{dischg product(s)}} + V_{\text{C-grains}}^{\text{total}} + V_{\text{binder}} + V_{\text{polymer electrolyte}} + f_{\text{air, end discharge}} V_{\text{total}}^{\text{cathode}} \quad (51b)$$

where  $\Delta V_{\text{dischg product(s)}} = \Delta V_{\text{Li}_2\text{O}_{2(\text{s})}}$  for  $\text{Li}_2\text{O}_{2(\text{s})}$  as the only discharge product when the discharge occurs by Eq. (3b) and  $\Delta V_{\text{dischg product(s)}} = \Delta V_{(\text{Li}_2\text{O}_{(\text{s})} + \text{Li}_2\text{O}_{2(\text{s})})}$  for  $\text{Li}_2\text{O}_{(\text{s})}$  and  $\text{Li}_2\text{O}_{2(\text{s})}$  as the discharge products when the discharge occurs, for example, by Eq. (3d) for the situation of equimolar formation of the solid product species. Eq. (51b) leads to the following expression for the estimation of the total cathode volume:

$$V_{\text{total}}^{\text{cathode}} \simeq \frac{\Delta V_{\text{dischg product(s)}} + V_{\text{C-grains}}^{\text{total}} + V_{\text{binder}} + V_{\text{polymer electrolyte}}}{(1 - f_{\text{air, end discharge}})} \quad (52)$$

One should note that all the terms in the numerator of the right-hand side of the equal sign in Eq. (52) are dependent on the desired cell maximum discharge and other parameters of the cathode reaction layer design, including the carbon grain average diameter and the maximum thickness of the solid discharge product film formed around each carbon grain.

The total pore volume fraction occupied by the gas phase in the cathode reaction layer before the start of the cell discharge,  $f_{\text{pore}}^{\text{total}}$ , is given by:

$$f_{\text{pore}}^{\text{total}} = \frac{V_{\text{pore}}^{\text{total}}}{V_{\text{total}}^{\text{cathode}}} = \frac{\Delta V_{\text{dischg product(s)}}}{V_{\text{total}}^{\text{cathode}}} + f_{\text{air, end discharge}} \quad (53)$$

### 3. Computed results

(a) Provided data:

- Concentration of the salt  $\text{LiPF}_6$  in an organic solvent such as a mixture of propylene carbonate and 1,2-dimethoxyethane = 1 M.
- Temperature of cell = 298.15 K.
- Dry oxygen partial pressure = 0.21 atm.

(b) Summary of the partial computed data:

- Reversible cell voltages:
  - Reaction (3b): 3.16 V.
  - Reaction (3d): 3.01 V.
- Effect of temperature on the reversible cell voltage at constant pressure of 1 atm and  $T_0 = 298.15$  K:
  - Reaction (3b):  $E = E^0 - (0.0005)(T - T_0) = 3.16 - (0.0005)(T - T_0)$  [V].
  - Reaction (3d):  $E = E^0 - (0.0006)(T - T_0) = 3.01 - (0.0006)(T - T_0)$  [V].
- Effect of pressure on the reversible cell voltage at constant temperature and gas phase composition ( $P$  = absolute pressure, atm;  $T = 298.15$  K):

- Reaction (3b):
 
$$\left(\frac{\partial E}{\partial P}\right)_{T, y_{\text{O}_2}} = \left(\frac{RT}{2F}\right) \frac{1}{P} = \frac{0.0128}{P} \quad [\text{V atm}^{-1}].$$

- Reaction (3d):
 
$$\left(\frac{\partial E}{\partial P}\right)_{T, y_{\text{O}_2}} = \left(\frac{1.5RT}{4F}\right) \frac{1}{P} = \frac{0.0096}{P} \quad [\text{V atm}^{-1}].$$

- Equilibrium reaction extent at 25 °C and 1 atm:

- For reaction (3b): Assume  $\xi_e / N_{\text{O}_2,0} = 1$ , where  $\xi_e$  is the extent of reaction at the equilibrium state with respect to reaction (3b) and  $N_{\text{O}_2,0}$  is the initial g mol of oxygen. Fractional conversion, if oxygen is the limiting reactant (in a batch reaction vessel), is:

$$x_{\text{O}_2} = \frac{N_{\text{O}_2,0} - N_{\text{O}_2,\text{eq}}}{N_{\text{O}_2,0}} = 1 - \frac{N_{\text{O}_2,\text{eq}}}{N_{\text{O}_2,0}} = 1 - \left(\frac{N_{\text{O}_2,0} - \xi_e}{N_{\text{O}_2,0}}\right) = \frac{\xi_e}{N_{\text{O}_2,0}} = 1 \quad (100\%).$$

- For reaction (3d):

$$\text{Assume} \\ \frac{\xi_e}{N_{\text{O}_2,0}} = \frac{1}{1.5}$$

and

$$x_{O_2} = \frac{N_{O_2,0} - N_{O_2,eq}}{N_{O_2,0}} = 1 - \frac{N_{O_2,eq}}{N_{O_2,0}} = 1 - \left( \frac{N_{O_2,0} - 1.5\xi_e}{N_{O_2,0}} \right) = \frac{1.5\xi_e}{N_{O_2,0}} = 1 \quad (100\%).$$

- Mass depletion and increase rates:

- $i_{geom} = 0.2 \text{ mA cm}_{geom}^{-2}$  [10].

- Total system mass increase rate is then:

$$\begin{aligned} \frac{dm_{sys}^t}{dt} &= 3.32 \times 10^{-8} \text{ [g s}^{-1} \text{ cm}_{geom}^{-2}], \text{ for reaction (3b).} \\ &\cong 2.49 \times 10^{-8} \text{ [g s}^{-1} \text{ cm}_{geom}^{-2}], \text{ for reaction (3d).} \end{aligned}$$

- Lithium metal consumption rate is:

$$\left( \frac{-dN_{Li(s)}}{dt} \right) = 2.07 \times 10^{-9} \text{ [g mol s}^{-1} \text{ cm}_{geom}^{-2}], \text{ for reactions (3b) and (3d).}$$

- Solid discharge product production rates are:

$$\begin{aligned} \frac{dN_{Li_2O_{2(s)}}}{dt} &\cong 1.04 \times 10^{-9} \text{ [g mol s}^{-1} \text{ cm}_{geom}^{-2}], \text{ for reaction (3b).} \\ &\cong 5.2 \times 10^{-10} \text{ [g mol s}^{-1} \text{ cm}_{geom}^{-2}], \text{ for reaction (3d).} \end{aligned}$$

- Cell heat removal rate for its isothermal operation at 25 °C, 1 atm:

- $I^t = i_{geom} = 0.2 \times 10^{-3} \text{ A cm}_{geom}^{-2}$  [10].

- $E_{actual}^{cell} = 2.65 \text{ V}$  (a typical value).

- $\dot{Q}_{r \times n(3b)} \cong -0.00013$  and  $\dot{Q}_{r \times n(3d)} \cong -0.0001 \text{ [J s}^{-1} \text{ cm}_{geom}^{-2}]$ .

- Theoretical discharge and maximum thermal efficiency:

- Theoretical discharge per gram of  $Li_{(s)}$  consumed is 3863.03 mAh g<sup>-1</sup>  $Li_{(s)}$ .

- Maximum thermal efficiency,  $\eta_{thermal,max} \cong 90\%$  for reaction (3b) and  $\cong 90\%$  for reaction (3d), using the thermodynamic data from [11].

#### 4. Concluding remarks

The developed/assembled mathematical formulation has been presented to compute the following:

- Reversible single electrode and overall cell reaction voltages for the formation of only  $Li_2O_{2(s)}$  as well as both  $Li_2O_{(s)}$  and  $Li_2O_{2(s)}$  as the solid discharge product species in the cathode reaction layer.
- Moles of species  $Li_{(s)}$ ,  $Li_2O_{(s)}$ , and  $Li_2O_{2(s)}$  as a function of time during the cell discharge period.
- Heat transfer rate between the cell and its surroundings for a desired total current at the actual cell voltage.
- Theoretical discharge capacity and thermal efficiency of the cell.
- The composite carbon cathode volume of the cell.

Some illustrative cell numerical data have been presented on the reversible cell voltages, the effect of temperature on the reversible cell voltage, the effect of pressure on the reversible cell voltage at constant temperature and gas phase composition, the equilibrium reaction extent at 25 °C and 1 atm, cell mass depletion and increase rates, cell heat removal rate for its isothermal operation at 25 °C, 1 atm, and the theoretical discharge and maximum thermal efficiency.

It is envisaged that the developed formulation will be useful in the design/development as well as in the performance analysis of a lithium/air or oxygen battery system.

#### References

- [1] E.L. Littauer, K.C. Tsai, J. Electrochem. Soc. 124 (1977) 850–855.
- [2] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1–5.
- [3] J. Read, J. Electrochem. Soc. 149 (2002) A1190–A1195.
- [4] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Iriedger, D. Foster, J. Electrochem. Soc. 150 (2003) A1351–A1356.
- [5] A. Doble, R. Rodriguez, K.M. S Abraham, Proceedings of the Electrochem. Soc. Joint International Meeting, Abstract No. 496, October 3–8, 2004.
- [6] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, J. Power Sources 146 (2005) 766–769.
- [7] G. Prentice, Electrochemical Engineering Principles, Prentice-Hall, Upper Saddle River, NJ, 1991, pp. 31, 36, 71.
- [8] J.S. Newman, Electrochemical Systems, Prentice-Hall Inc., 1991, pp. 98, 99, 103, 194.
- [9] J. Larminie, A. Dicks, Fuel Cell Systems Explained, John Wiley & Sons Inc., 2003, p. 59.
- [10] J. Read, J. Electrochem. Soc. 153 (2006) A96–A100.
- [11] D.R. Stull, H. Prophet, JANAF Thermochemical Tables, 2nd ed., National Bureau of Standards, Washington, DC, 1971.