

Modeling of Electrochemical Processes in a Zinc-Air Battery Cathode

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Project Report

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Introduction

Metal-air batteries offer high specific energy density applicable to household-level storage and have been potentially used in various fields including electromobility, portable electronics and stationary grid applications^{1,2,3}. These batteries are open at the cathode and use atmospheric oxygen while the metal acts as the anode. Materials that have been used in this type of energy storage media are iron, zinc, magnesium, sodium and lithium. Elements with lower molecular weight provides higher energy density and lithium-air batteries are considered to provide the highest value among other options. However, the efforts for commercialization of this type of batteries have been hindered by several issues such as low electrolyte stability in presence of oxygen, and dissolution of lithium complexes in the electrolyte as well as shape-changing of lithium metal^{2,4}.

On the other hand, zinc is very cheap, abundant, non-toxic and very stable in aqueous electrolytes which makes it a promising candidate to be used as an anode in metal-air batteries. Therefore, zinc-air batteries (ZABs) offer high energy specific density, cheap and accessible design. Secondary zinc-air batteries are currently commercialized and being used historically as hearing aid button cell batteries. The theoretical specific energy density of zinc-air batteries amounts to high value of 1000 WHkg⁻¹. However, these cells have a short shelf-life and can endure only a few hundred cycles mainly due to degradation of alkaline electrolyte in contact with zinc anodes. The absorption of carbon dioxide from air into the electrolyte reduces the electrolyte pH value by irreversibly reducing the hydroxide concentration. This phenomenon effectively decreases electrolyte conductivity and increases the anode passivation. As a result, the cycle life will reduce to a very short few months without precautionary actions. Employing carbon dioxide absorbers⁵ as well as using new electrolyte alternatives such as aqueous neutral electrolytes⁶ and ionic liquids⁷ can mitigate this effect possibly.

A typical alkaline zinc-air is consisted of the following as shown in Figure 1:

- A porous anode normally made of Zinc powder attached to current collector
- A gas diffusion electrode (GDE) that facilitates the volume change of Zn anode
- Alkaline electrolyte such as potassium hydroxide

- Separator that disconnects the electric contact between electrodes
- Gas diffusion electrode acting as cathode that supplies the air oxygen to the cell¹

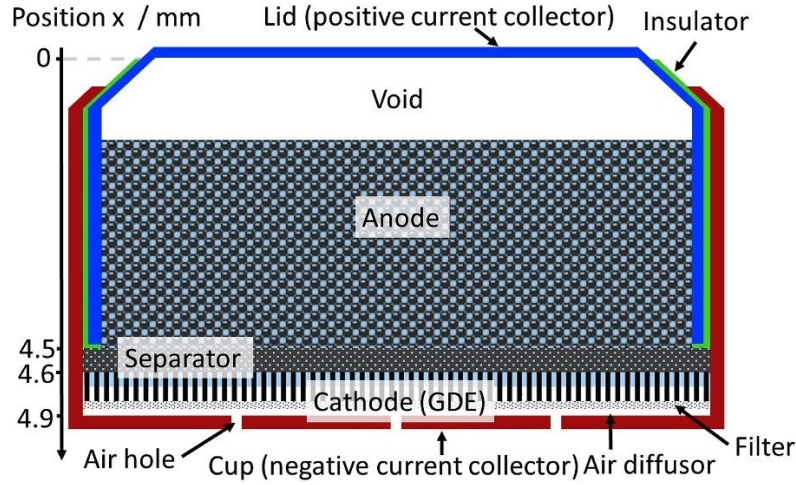


Figure 1 Structure of zinc-air button cell¹

For this project, I am hoping to show a very simplified model of ZAB. For simplicity, only air cathode has been chosen as the system of study. This model attempts to identify the effect of CO₂ addition in the air composition on the charge transfer as well as mass transfer components of electrochemical processes occurring in a typical ZAB by glancing over two different CO₂ concentration scenarios.

Model Formulation

In a typical ZAB during discharge, the anodic Zn is oxidized by dissolving into alkaline electrolyte according to Eq. 1. It has a relatively high solubility and it forms various hydroxide complexed of which, zincate, Zn(OH)₄²⁻ has a dominant concentration⁸. As the zincate concentration increases over its solubility limit, it will start to precipitate in the form Zinc oxide (ZnO) as shown in Eq. 2. If this reaction does not proceed as expected, the OH⁻ concentration will deplete rapidly and may cause cell voltage to rise unexpectedly.



In the GDL, the oxygen is dissolved in the electrolyte and will reduce to OH⁻ at the cathode surface following Eq. 3. However, the formation of carbonate (CO₃²⁻) due to the presence of CO₂ in the upcoming air is the primary source of degradation (Eq. 4) as the concentration of OH⁻ decreases and the conductivity reduces as a result.



Therefore, the overall reaction -neglecting reaction 4- is:



Certain assumptions have been considered to further simplify the thermodynamic model of cathode at the GDL.

- Temporal variations are small, therefore, no thermal energy transfer considered.
- The partial pressure, and subsequently mole fractions of air components are fixed.
- NO concentration gradient present over GDL dimension. There are only two nodes/states, one at beginning and the other at end of GDL length, available.
- Constant diffusion coefficient, independent of gas composition along the GDL length, is assumed.
- Gas properties are calculated based on ideal gas law.

Results and Discussion

The developed model is based on two different scenarios with various initial cathode component concentration. Scenario 1 (Table 1) assumes that there is no CO₂ present in the atmospheric air entering the GDL while scenario 2 assign a high concentration to the incoming CO₂ ($X_{\text{CO}_2} = 0.3$).

Table 1 GDL composition of two scenarios

Cathode components	Scenario 1. No CO ₂		Scenario 2. CO ₂ included	
	Node 1	Node 2	Node 1	Node 2
O ₂	0.20	0.40	0.20	0.45
H ₂ O	0.10	0.25	0.10	0.25
N ₂	0.78	0.2	0.58	0.3
OH ⁻	0.10	0.15	0.10	0.0001
CO ₂	0.000010	0	0.30	0
CO ₃ ²⁻	0.00	1e-8	0.00	1e-8

In the following, the gas species fluxes as well as electric potential corresponding each cell component will be calculated and compared for two scenarios. At first, the gas-diffusion in the GDL of the carbon cathode is modeled using Fick's law relations for gas diffusion and convection transport correlations developed in class. The effect of permeability of the cathode

on the flux due to the bulk convection as well as the effect of microstructure characteristics of the cathode on diffusion aspect were taken into consideration.

Figure 2 shows the calculated species flux of oxygen, nitrogen and water vapor between the 1st node at the beginning of GDL and the 2nd node at GDL-electrolyte interface. There is no change for the flux values of the oxygen and water as their concentration gradient between two nodes stayed similar for both scenarios. Considering similar convection for both gases, the flux remains constant in both scenarios as a result. However, having no CO₂ in scenario 1 means higher concentration of N₂ in the first node that stimulates a larger concentration gradient and higher diffusion flux accordingly comparing with scenario 2. This fact matched very well flux values from Figure 1.

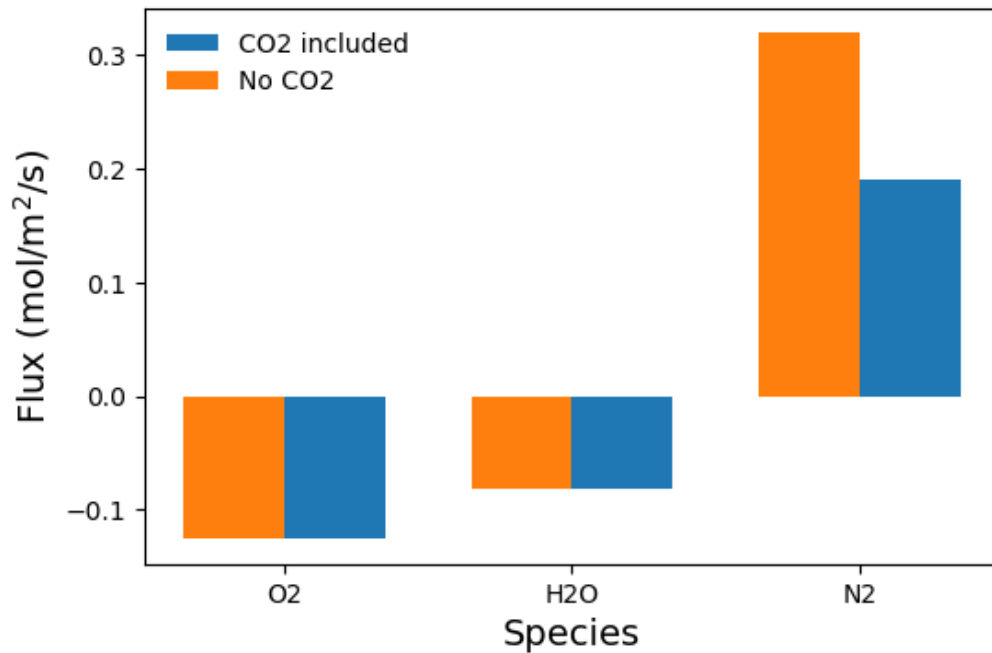


Figure 2 Calculated flux of oxygen, nitrogen and water vapor in the GDL.

Next, I modeled the charge transfer of the oxygen reduction at the GDL for both scenarios. First, based on the available kinetics data of oxygen reduction action, the cathodic exchange current density was calculated based on Butler-Volmer formulation. Further, the cathodic and electrolyte electric potential was calculated assuming a zero anodic potential by solving an ODE previously developed in class. Figure 2 shows the electric potential as function of time that indicates a similar potential for cathode and electrode in both scenarios. This is mostly due to the fact that the change in $\Delta\phi_{eq}$ calculated with different compositions is not that significant to affect the cathodic overpotential and finally the results of ODE for calculated potentials.

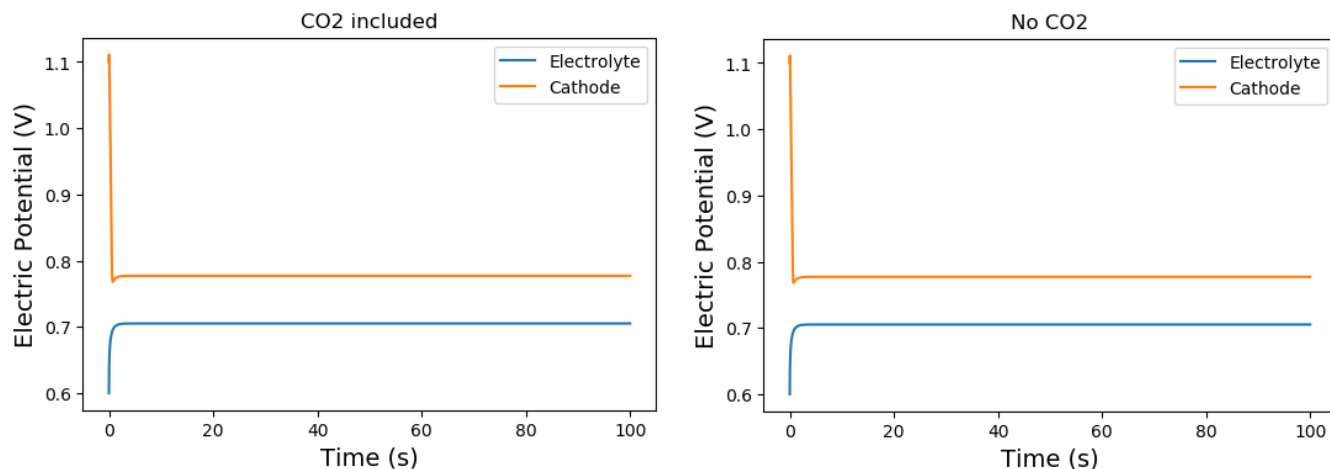


Figure 3 Electric potentials (V) for both electrolyte and cathode as a function discharge time (s).

The effect of CO_2 inclusion in the gas phase on the cell voltage while varying the external current was also investigated. Figure 4 shows the calculated cell potential with no ohmic or ionic overpotential as a function of external current for both scenarios. As mentioned previously, depletion of OH^- , the main charge carrier, results into a sudden increase in the cathodic potential while the electrolyte potential remains constant. Consequently, the cell potential in the presence of CO_2 is typically higher at low current values but will approach to a steady state value (electrolyte potential) as the current increases.

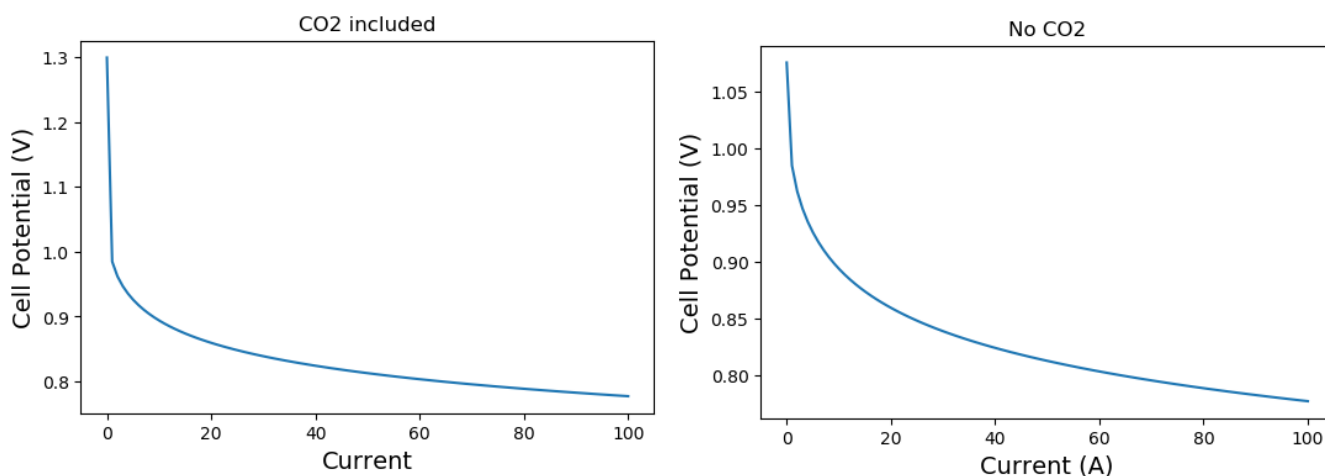


Figure 4 Full cell potentials (V) of both scenarios as a function external current (A).

Conclusion

In summary, a very simplistic model of charge transfer and gas transport in gas diffusion layer of an air cathode in a zinc-air battery is presented. In this mode, the effect of CO₂ presence on various mass transfer properties such as individual molar fluxes as well as cell electrochemical properties including full cell potential with varying time and current was investigated.

References:

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