

# ANALYSIS OF A LITHIUM AIR BATTERY

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I pledge on my honor that I have not given or received any unauthorized assistance on this assignment.

## 1. INTRODUCTION

Lithium air cell is a metal air electrochemical cell that utilizes the oxidation of Lithium in the presence of excess oxygen to generate an electrochemical potential and induce current. This reaction chemistry can theoretically lead to batteries with very high specific energy (5-10 times higher than regular Li-Metal electrochemical cells). The specific energies are comparable to that of gasoline and hence these batteries have shown great potential to replace regular combustion engines in the automotive industry. The non-aqueous lithium-air battery, comprised of a lithium metal anode and an oxygen cathode, has been found to be the highest energy density battery that can be developed into a practical system. It promises to overcome the energy density limitations of the regular lithium ion batteries.

In recent years, we have realized the need for the electrification of transportation to reduce which would minimize our dependence on fossil fuels, thereby reducing the  $\text{CO}_2$ , which would have a drastic effect on climate change. In the past decade, a significant rise has been observed in Hybrid Electric Vehicles (HEVs) and Plug in Hybrid Electric Vehicles (PHEVs). About 40,000 of low cost battery operated vehicles which have a driving range of 50-100 miles, and about 20,000 of luxury vehicles (Tesla) having longer driving range were sold in 2013 in the United States. Most vehicle companies believe that the energy density of a cell plays a major role in the development of safe, long lived and cost-effective batteries for long range vehicles. This emphasis of energy density has attracted research interests on the Lithium – Air batteries.

### 1.1. CELL CHEMISTRY

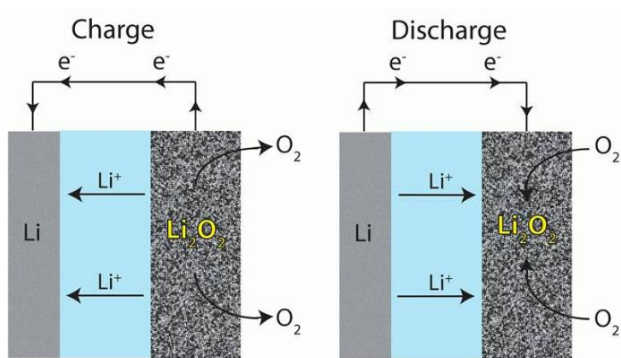
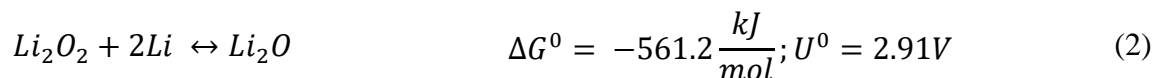
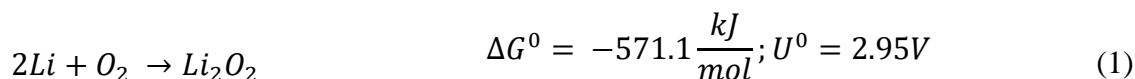


Figure 1: Schematic Representation of the Lithium Air Battery for charge and discharge cycles.

The electrochemical cell includes a lithium metal negative electrode (anode) and oxygen as a positive electrode (cathode). The setup is shown in figure 1, where the cathode is porous carbon which acts as a medium for the discharge reaction to occur. In most cases the cathode is a porous carbon structure and contains catalysts to facilitate the reaction.

## 1.2. NON-AQUEOUS LITHIUM-AIR BATTERY

During the operation of a non-aqueous Li-Air Battery, oxygen from external sources enters the porous carbon cathode, where it gets reduced to form lithium oxides. Various electrolytes have been used in the cells for research including various esters, ethers, alkyl carbonates, amides, nitriles and dimethyl sulfoxide (DMSO). Solid state cells generally employ Solid Polymer electrolytes (SPE) and Ceramic Solid Electrolytes (CSE). Due to the insolubility of the oxides in the electrolyte, they occupy the pores of the carbon cathode. The cell gets discharged once all the pores are occupied by the oxides leaving no space for oxygen to enter the system. The oxides formed are usually Lithium peroxide ( $\text{Li}_2\text{O}_2$ ) which may further get reduced to Lithia ( $\text{Li}_2\text{O}$ ) showing further reactions once the porous sites are completely occupied. The expected reaction mechanism can be written as:



Both the reactions in the above equations show a similar open circuit voltage of 2.9V, the specific capacity of the cell is about 3.861 Ah/(gram Li) resulting in a theoretical power of 11,238 Wh/(kg Li) assuming only the Lithium electrode is present in the battery. As seen from the cyclic voltammetry analysis discussed later, the oxygen reduction begins with a one electron reduction and additional reduction reactions take place to form the final product  $\text{Li}_2\text{O}$ .

### Challenges:

These cells pose several limitations to the design of the cathode in the cells. Most of the common lithium ion cells have high vapour pressure and have a high evaporation rate. These would be very unstable in a Li-Air cell as the cathode is exposed directly to the air. Thus the low evaporation rate of the electrolytes becomes a crucial parameter. Most organic electrolytes pose a challenge to the operation of these cells as they wet the cathode pores and flood the air channels. Hence, only the dissolved oxygen participates in the oxygen reduction reaction. The dissolution of oxygen into these electrolytes play a major role in the availability of oxygen for the reaction and also diffusion of electrolyte through the air channels. Another challenge faced by the battery is that it has been seen to have much higher charge potentials than discharge potentials suggesting the presence of secondary reactions leading to lower electric efficiencies.

## 1.3. AQUEOUS LITHIUM-AIR BATTERY

The concept of a rechargeable aqueous Li-Air battery has taken importance in the past decade with the first proposed battery being based on a lithium anode, a water-stable NASICON type lithium-ion conducting solid electrolyte, an aqueous electrolyte and a carbon-air electrode with a catalyst. The calculated specific energy densities for these batteries are lower than those of the non-aqueous systems mainly due to the solvent (water) taking part in the electrochemical reaction in the aqueous system. Although, the mass specific energy density has been found to be about five times as

compared to the conventional lithium ion batteries and these have been seen to overcome several challenges faced in a non-aqueous Li-air battery system, such as electrolyte decomposition.

A few common reactions occurring in aqueous Li-air cells are:



The most important consideration for an aqueous system is the reaction occurring at the cathode. Most cells use a combination of carbon and a catalyst which influence the rate and the mechanism of the oxygen reduction reaction (for discharging) and the oxygen evolution reaction (for charging). The choice of the catalyst depends primarily on the nature of the electrolyte (acidic or alkaline) and is essential to ensure that the preferred four-electron mechanism dominates.

A common problem in aqueous Li-Air battery systems is that corrosion occurs at the active metal anode to produce hydrogen gas and hence exposure of the anode to the cathode must be prevented.

## 2. ANALYSIS OF A NON-AQUEOUS LITHIUM – AIR BATTERY

As seen in the previous section, the capacity of a lithium-air battery with unlimited oxygen supply is limited by the amount of Lithium metal present in the anode. For the reactions in equations 1 and 2, the specific energy of the cell has been evaluated as 11,238 Wh/kg (excluding the weight of oxygen), which is the highest for any metal-air battery. In addition, these offer a very high operating voltage, a flat discharge voltage profile, relatively long storage life and most importantly they are environmentally friendly.

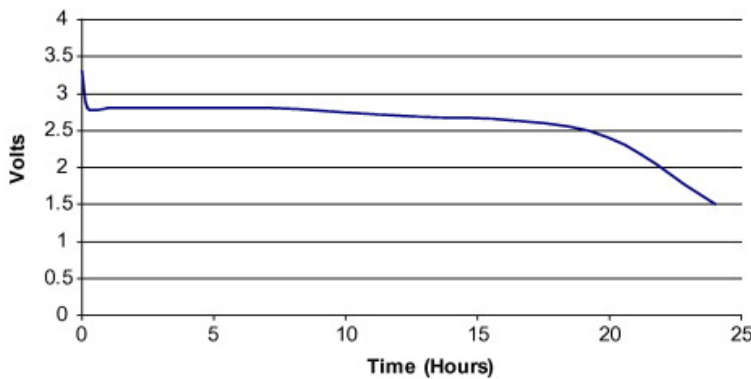


Figure 2: Discharge of a Li-Air cell using a Manganese-oxide catalyst in pure oxygen.

The voltage of the cell is seen to start above 3V when the load is applied and soon becomes steady at around 2.8V and is seen to decrease sharply after three quarters of its life. This is a typical behaviour of any battery system. The discharge curve is relatively flat and can be seen to have applications in constant current applications.

## 2.1. REACTION MECHANISM OF THE OXYGEN REDUCTION REACTION

We would expect the reaction mechanism to follow equations 1 and 2 but the cyclic voltammetry curves show that the reduction of oxygen involves multiple steps.

The cyclic voltammetry data presented provides evidence of the sequential reduction of O<sub>2</sub>. The process begins with the formation of LiO<sub>2</sub> which gets reduced to form Li<sub>2</sub>O<sub>2</sub>. The final product formed is Li<sub>2</sub>O. The mechanism can be written as:

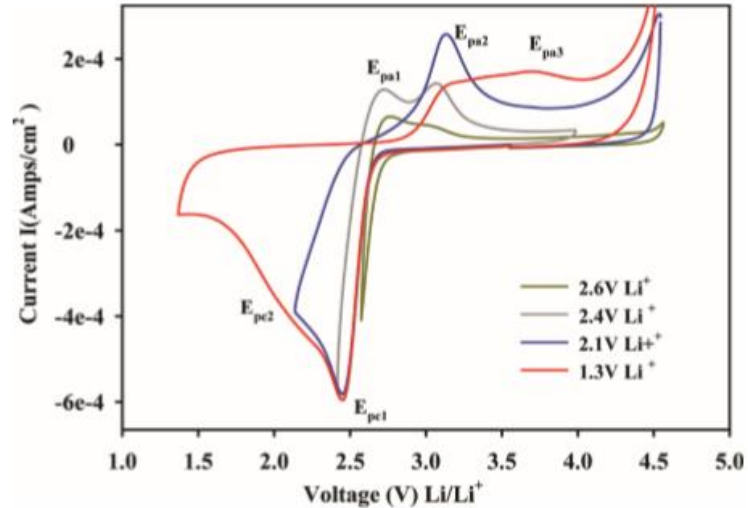
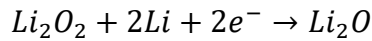
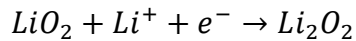
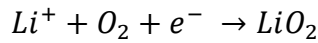


Figure 3: Cyclic Voltammetric Curves for the O<sub>2</sub> reduction reactions in 0.1M LiPF<sub>6</sub>/DMSO at various potential windows. For a glassy carbon working electrode for a scan rate of 100mV/s.

## 2.2. ELECTROCHEMICAL ANALYSIS OF THE CELL

The cell considered for analysis used an electrolyte of 1M LiPF<sub>6</sub> dissolved in acetonitrile. The cathode electrode thickness is 750mm with porosity of 0.73. The cell simulations have been performed for an operating temperature of 298.15 K. The data has been cited from the Journal of Power Sources.

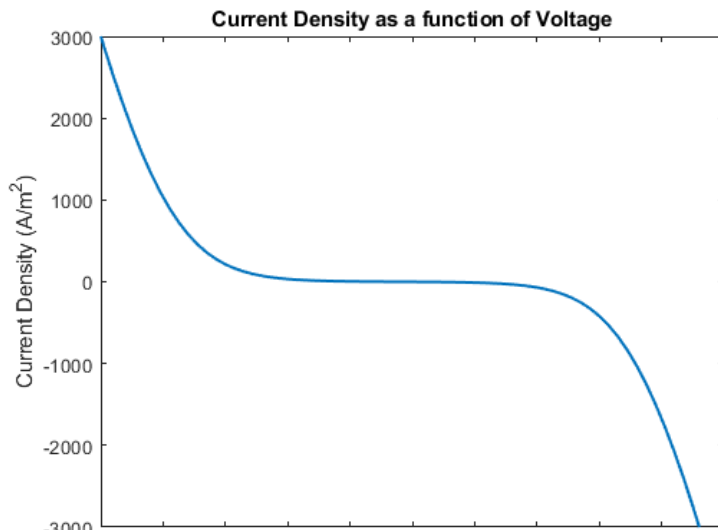


Figure 4: Current Density as a function of Voltage (over potentials).

Electrochemical kinetic analysis of the cell for the current density as a function of Voltage (over potentials) shows a curve similar to what is expected for a battery, higher over potentials lead to higher current densities. There is very little current for over potentials of approximately 0.6V above and below the equilibrium potentials. As a result, the battery needs to be operated at higher over potentials to for it to be functional in a circuit and provide sufficient energy.

The operation of the cell at higher currents leads to very large polarizations in the cell as seen in Figure 5. Large polarizations for relatively small current densities shows relatively poor performance. The model that has been developed can be used to evaluate the relative magnitudes for each of these losses as a function of current density. Evaluation of the figure shows that the polarization at the cathode is much larger than the anode and that the potential drop in the electrolyte increases linearly with current density in the electrolyte in the absence of concentration gradients.

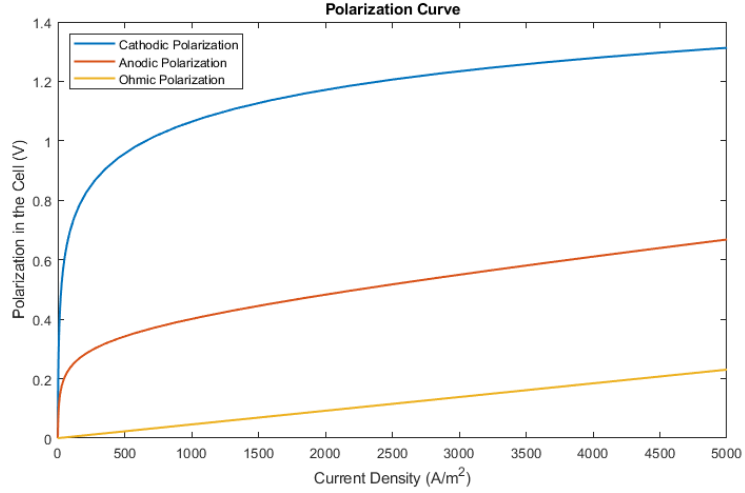


Figure 5: Cathodic, Anodic and Ohmic Polarization in the Cell.

### 2.3. POROUS ELECTRODES

The porous cathodes facilitate the oxygen reduction reaction due to the large surface area it provides. The figures below show the current density distribution along the length of the electrode and change in the current density distribution along the electrode. The plots have been made for the system analysed above in the absence of concentration gradients for an operating current density of 1000 A/m<sup>2</sup>. The current density for the model uses Tafel Kinetics and the following

equations were solved:

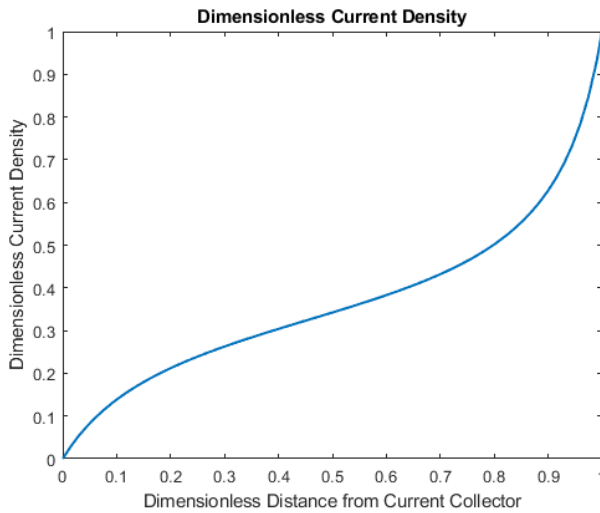


Figure 6: Distribution of current density through the porous cathode.

1.  $i_2 = -\kappa \frac{d\phi_2}{dx}$
2.  $i_1 = -\sigma \frac{d\phi_1}{dx}$
3.  $\nabla \cdot i_1 + \nabla \cdot i_2 = 0$
4.  $\nabla \cdot i_2 = ai_n$
5.  $i_n = i_0 \exp\left(-\frac{\alpha_c n F}{RT} (\phi_1 - \phi_2)\right)$

The solution requires solving a non-linear differential equation:

$$\frac{d^2 i^*}{dz^2} = \left( \frac{di^*}{dz} \right) \gamma \frac{I}{A} \left( \frac{1}{\sigma} + \frac{1}{\kappa} \right) \left( i^* - \frac{Kr}{Kr + 1} \right) \quad (6)$$

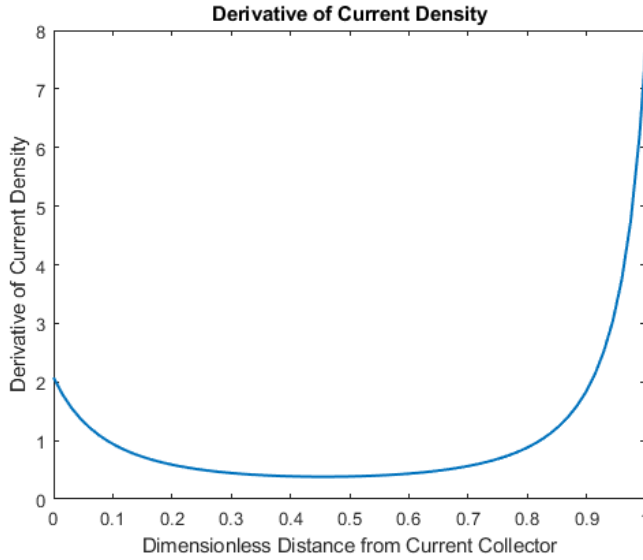


Figure 7: Derivative of Current Density along the length of the cathode.

Where,

$$i^* = \frac{i_2}{I}$$

$$\gamma = -\frac{\alpha_c n F}{RT}$$

$$Kr = \frac{\kappa}{\sigma}$$

Figure 6 and Figure 7 show that the current density is non-uniform and that the reaction is relatively non-uniform across the electrode shifting away from the centre of the electrode and that the reaction is more likely to occur at the front and the back of the electrode. The non-uniformity of the reaction within the electrode would significantly

impact the current generation in the cell as the porous sites towards the edges get occupied relatively early as the reaction proceeds. This would in turn affect the reaction rate and the diffusion of lithium ions through the porous electrode.

## 2.4. OPEN AND CLOSED SYSTEMS

Our analysis so far demonstrates the use of the Li-air cell as an open system which consumes oxygen from the ambient atmosphere as the reactant at the cathode. Even though this cell gives the highest possible specific energy, it faces multiple challenges. The presence of CO<sub>2</sub> and H<sub>2</sub>O in the atmosphere cause secondary reactions in the system to form Li<sub>2</sub>CO<sub>3</sub> and LiOH.H<sub>2</sub>O. These products significantly reduce the ability of the cell to recharge. The open system also requires additional mechanical components such as compressors, separation processes to remove water, carbon dioxide and other impurities. Flow channels within the cell must be installed to enable convective air transport. These components not only add up to the cost and weight of the system but also increase the power requirements.

The closed system on the other hand uses a cell stack within a pressure vessel containing pure oxygen. This eliminates the possibility of secondary reactions and eliminates the need for costly components and significantly more efficient batteries as parasitic power requirements are eliminated. This configuration also faces several challenges, most common being the exposure of

pressurized oxygen to a highly flammable electrolyte, which becomes a safety hazard. Other factor that needs to be considered is the ability of the vessel to withstand the high pressures. Also, heat transfer through the cell is governed by conduction through the heat sinks.

### **3. CONCLUSION**

In the report, we have quantitatively analysed the Li-air electrochemical system and it shows good promise for its applications in high energy applications specifically the automotive industry. We can conclude that a closed Li-Air battery system for a battery stack in a pressurized vessel is more likely to achieve the performance and life goals for an automotive system. The analytical framework presented above with a better understanding of system components and architecture will provide a very good estimate of possible specific energies and cost for the system. Theoretically calculated energy and cost estimates show that these have higher specific energy and lower costs when compared to the commonly used Li-ion electrochemical batteries.

This configuration is presently not a very attractive prospect for automotive manufacturers but has shown an enormous scope for research and development in terms of the electrode designs, uses of electrolytes, polymers, and separation membranes. The mechanical aspects of these systems are also being studied in great detail. The next step in the development of a cost effective, high energy density lithium-air cells would be to study the working and efficiency of the cell stacks in closed pressurized vessels containing pure oxygen and the development of electrodes and electrolytes to suit the configuration. These studies would ensure that the system would achieve its potential to be an economically viable and safe system in the upcoming years.

## 4. BIBLIOGRAPHY

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