Progress of Aluminum/Air Battery Development for SUSAN Electrofan Project

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I. Nomenclature

Wh/kg = watt-hour per kilogram, unit of specific energy to measure the gravimetric energy density
mAh/g = milliampere hours per gram, unit of specific capacity
mAh/cm^3 = milliampere hours per cubic centimeters, unit of volumetric energy density
mA/cm^2 = milliampere/per square centimeters, unit of current density
A/m^2 = ampere per square meters, unit of current density
E_o = electrochemical potential, a measure of the driving force for a redox reaction under standard condition
e^- = electron
$\mathrm{H_z}$ = hertz, unit of frequency
Ω = ohm, unit of resistance or impedance
Z' = a real part of impedance (resistance)
Z'' = an imagine part of impedance (reactance)
M = molarity, i.e. the number of moles of a solute dissolved per liter of solution, of electrolyte concentration

II. Abstract

Safe and high-performance battery technologies are demanded by the Subsonic Single Aft eNgine (SUSAN) Electrofan concept design project under National Aeronautics and Space Administration (NASA) electrified aircraft development program. Aluminum (Al)-air battery with very high theoretical specific energy density, is considered as promising battery chemistry which has the potential to meet the targeted specific energy goal of primary battery energy technology for the SUSAN project. In addition to having the exceptional electrochemical properties, aluminum is light weight, rich abundance, low cost, environmentally friendly, and has a good electrical conductivity and recyclability, which is among the key characteristics of SUSAN project on battery energy needs. A non-flammable aqueous electrolyte is used to prevent the fire and thermal runaway hazard for the safety of this battery chemistry. However, there are challenges for Al-air battery in practical application, mainly due to self-corrosion of Al and slow kinetics of oxygen reduction in air-cathode to impact the high-rate performance. Progress on addressing these challenges was made and some of the results were reported in our previous AIAA SciTech paper. In this paper, the focus is on the investigation of various factors, including electrolyte concentrations, temperature, and air-cathode loadings on ionic transport properties and discharge performance at different current densities. The results are discussed, and the progress is reported.

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III. Introduction

To meet the ever-increasing demand for safe and high-performance energy storage technologies, metal-air batteries are considered the potential leading energy storage technologies of the future [1-4]. Multivalent metal-air batteries with more electrons involved in the metal anode redox reaction, have attracted considerable interest recently [5-7]. Aluminum (Al)-air battery, having very high theoretical specific energy density (>8000 Wh/kg) [8-10], is considered as promising battery chemistry for safety and high capacity. A non-flammable alkaline solution is used to prevent fire and thermal runaway for safety. Aluminum anode has high gravimetric capacity of 2980 mAh/g (2nd highest, 77% of the highest capacity metal, lithium, with 3860 mAh/g), and very high volumetric capacity of 8046 mAh/cm^3 (the highest capacity metal), as well as sufficiently low redox potential of Al^{3+}/Al with -2.35V vs. standard hydrogen electrode (SHE) in alkaline electrolyte. In addition to having the exceptional electrochemical properties, aluminum is light weight, rich abundance, low cost, environmentally friendly, and has a good electrical conductivity and recyclability. All the materials for Al-air batteries can be domestically supplied, and there is no material supply chain issue, and is free from the geopolitical constrain. In addition, the discharge product is aluminum hydroxides or oxides, which is non-toxic and recyclable, thus Al-air battery is intrinsically safe, eco-friendly, and sustainable.

However, there are challenges for Al-air battery in practical application, mainly due to self-corrosion of aluminum anode and slow kinetics of oxygen reduction in air-cathode to impact the high-rate performance. The electrochemical reactions for the Al-air batteries in alkaline electrolyte are as follows [11]:

Anode reaction: $Al + 4OH^- \longrightarrow Al(OH)_4^- + 3e^-$ $E_o = -2.35V$ (1a)

$Al(OH)_4^- \longrightarrow Al(OH)_3 + OH^-$ (1b)

Cathode reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ $E_0 = 0.40V$ (2)

Overall reaction: $4Al + 3O_2 + 6H_2O \longrightarrow 4Al\,(OH)_3$ $E_0 = 2.75V$ (3)

Due to the high reactivity of aluminum in alkaline solution, severe spontaneous self-corrosion on aluminum surface also occurs, companying with the evolution of H_2 gas, as shown below:

Anode self-corrosion: $2Al + 6H_2O + 2OH- \longrightarrow 2Al(OH)_4^- + 3H_2$ (4)

This parasitic self-corrosion reaction has to be reduced or eliminated due to its consumption of aluminum, resulting in lower aluminum utilization and poor discharge efficiency, and further possible reduction of the anode potential and the overall performance of battery [12,13]. The sluggish oxygen reduction reaction (ORR) in air-cathode has to be addressed sine it results in low coulombic efficiency and poor rate capability.

In our previous paper [1], the investigation of approaches to address these challenges, including the impact of electrolyte concentration and additive(s) and electrolyte management on aluminum self-corrosion/gassing, and components on air-cathode design was reported. The results showed that lower electrolyte concentration helped reduction of aluminum self-corrosion but slowed the aluminum anodic dissolution reaction in half-cells. In the paper, the results of the impact of electrolyte concentration on ionic conductivity and discharge performance at full cells at various current densities are discussed. In addition, the investigation of factors including temperatures and air-cathode loadings on discharge performance are discussed and reported in this paper.

IV. Experimental

Electrochemical Impedance Spectroscopy (EIS) Measurement - Solartron potentiostatic/galvanostatic in combination with frequency response analyzer, with Zview/Zplot software control, were used for the measurement of electrolyte ionic conductivity and cell impedance assessment.

Electrolyte Ionic Conductivity Measurement - The ionic conductivity of the electrolyte was measured by sandwiching the glass fiber separator with the electrolyte between two stainless steel (SS) disks, and electrochemical impedance spectroscopy (EIS) tests were performed with a 10mV AC voltage, and the frequency range from 1Hz to 10^6 Hz. The ionic conductivity (σ) is calculated using the following formula:

$$\sigma = d/(R_e*A) \quad (5)$$

Where d and A are the thickness and area of separator, and R_e is the resistance which is deduced from the fitting from at high frequency end from EIS measurement

Discharge Performance Tests - The discharge performance of Al-air lab cells were tested by using Arbin-2000 cycler. The tests were carried out at room temperature with natural environment from ambient condition. The discharge profiles were recorded at various current densities. The cut-off voltage for the cells was 0.2V.

Materials and Fabrication of Al-air lab cells were described in the previous paper [1]. All the tests were conducted at room temperature and natural air-breathing environments (except as noted).

V. Results and Discussions

V.1 Electrolyte Ionic Conductivity

The electrolyte is among the key components for Al/air battery discharge performance. Al-air batteries typically use aqueous alkaline electrolytes, having the properties of high ionic conductivity, fast oxidation and reduction kinetics, low overpotential, as well as low cost and non-flammability. The electrolyte impacts aluminum anodic dissolution in alkaline solution, as shown in equation 1, and aluminum parasitic self-corrosion reaction simultaneously, as shown in equation 2.

$$Al + 3OH^- \longrightarrow Al(OH)_3 + 3e^- \quad (1)$$

$$2Al + 6H_2O + 2OH^- \longrightarrow 2Al(OH)_4^- + 3H_2 \quad (2)$$

The hydroxyl ions (OH^-) in the electrolytes are involved on both reactions on Al anode simultaneously. Lower electrolyte concentration reduces the aluminum self-corrosion, but also lowers aluminum anodic dissolution reaction [1]. The self-corrosion reaction consumes aluminum and lowers aluminum utilization, which needs to be minimized or prevented. Additives including metal oxides such as zinc oxide (ZnO) are introduced into the electrolyte to help reduce the self-gassing. The ionic conductivity of electrolyte is directly relevant to ionic transport properties. High ionic conductivity of the electrolyte for fast ionic transport is needed to discharge at high current densities for high power performance. The ionic conductivity of electrolyte, which was adsorbed on separator with electrolyte amount close to actual environment, was measured by electrochemical impedance spectroscopy (EIS), as shown in Figure 1.

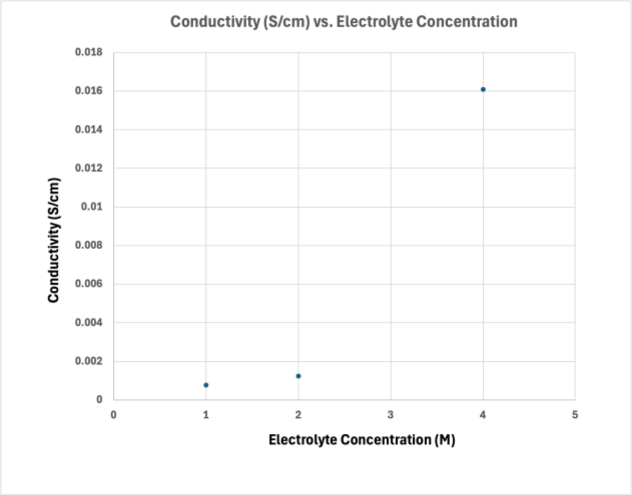

Figure 1. The ionic conductivity vs. concentration of electrolyte

The ionic conductivity increases as the electrolyte concentration increases from 1M to 4M. Although lower electrolyte concentration helps to reduce the aluminum self-corrosion, the lower ionic conductivity at lower electrolyte concentration may not provide adequate ionic transport properties needed for high current discharge performance.

V.2 Electrolyte Impact Discharge Performance

V.2.1 Full Cell Impedance Before Discharge

The ionic conductivity of electrolyte is an important factor to impact the ionic transport properties for discharge performance at high current densities. The ionic conductivity of electrolyte is impacted by the electrolyte concentration, as shown in Figure 1. The impedance of Al/air full cells before discharge, with electrolyte concentration being the only variable, showed that the cell internal resistances (R_s) are similar at different electrolyte concentrations, as shown at the high frequency end (left end with x-axis intercept) of Figure 2, however, the charge transfer resistance (R_{ct}), as induced from the fitting of semi-circle impedance spectrum, decreases with electrolyte concentration increases.

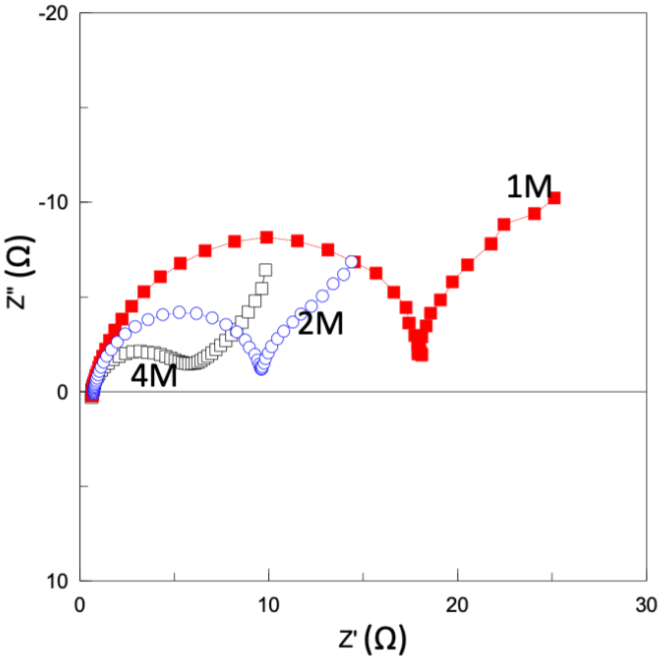

Figure 2. Full cell impedance before discharging at different electrolyte concentrations

As the electrolyte concentration increases from 1M to 2M, the R_{ct} reduces to about half, and as the electrolyte concentration increases from 2M to 4M, the R_{ct} further reduces about another half, as shown in Figure 2. Higher hydroxyl ions (OH^-) at higher electrolyte concentration increase the ionic transport properties, as indicated at higher ionic conductivity (Figure 1) and smaller charge transfer resistance indicates smaller interfacial resistance or fast kinetics (Figure 2). The discharge performance at high current densities is expected to be better at higher electrolyte concentrations.

V.2.2 Electrolyte Impact on Discharge Performance at Various Current Densities

The impact of electrolyte concentrations on discharge performance at different current densities of 1 mA/cm^2 and 5 mA/cm^2 was investigated, with the electrolyte concentration is the only variable. As discharge at the current density of 1 mA/cm^2, which is equivalent to 10 A/m^2, the best discharge performance, i.e. the smallest initial voltage drop, highest discharge voltage and longest discharge time, is obtained at 4M electrolyte concentration, as shown in Figure 3. As the electrolyte concentration decreases from 4M to 1M, the ionic conductivity decreases (Figure 1) and charge transfer resistance increases (Figure 2). The immediate initial discharge voltage drop increases with lower electrolyte concentration is caused by the increase of interfacial resistance due to high charge transfer resistance. The subsequent lower discharge voltage at lower electrolyte concentration is caused from the lower ionic conductivity and higher interfacial resistance. The discharge voltage profile at 1M electrolyte concentration showed that the discharge voltage is slightly recovered from the initial drop after a few minutes, which is due to the slow anodic dissolution reaction at 1M electrolyte concentration, as shown in equation 1. The short discharge time at lower electrolyte concentration is due to the early precipitation of discharge product at lower electrolyte concentration, resulting in the passivation on aluminum anode surface and concentration polarization of difficulty for OH^- to passing through the formed discharge product.

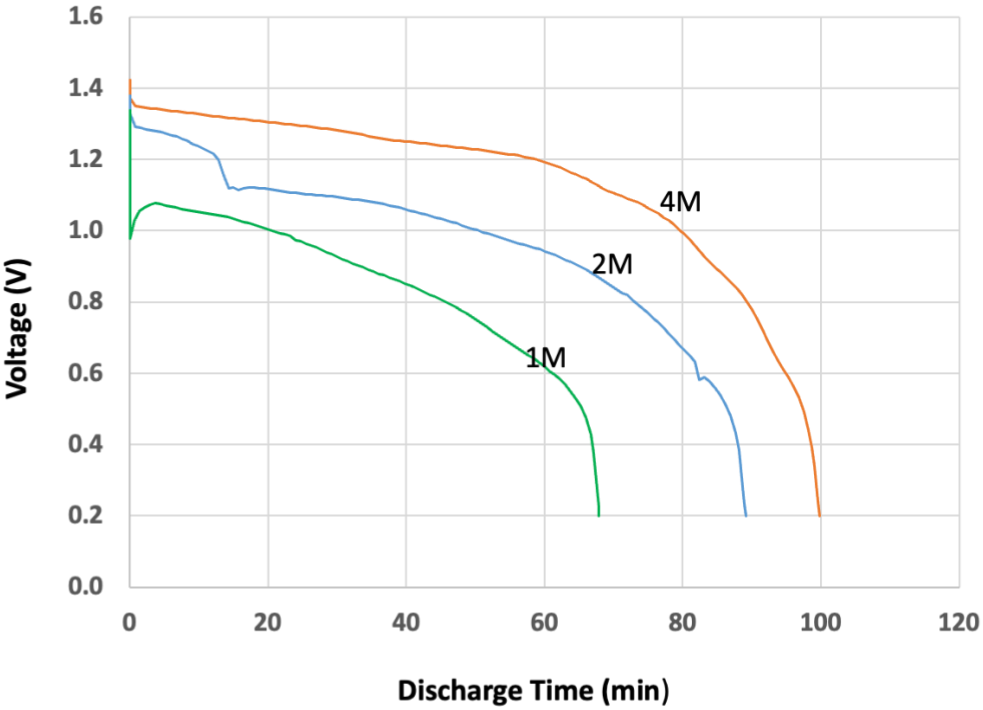

Figure 3. Discharge performance at different electrolyte concentrations at the current density of 1 mA/cm^2 (i.e 10A/m^2)

The results showed that the electrolyte concentration at 1M is low for discharge at the current density of 1 mA/cm^2.

As discharge at the current density of 5 mA/cm^2, i.e. 50A/m^2, the discharge voltages become lower and the discharge times becomes shorter, as shown in Figure 4, in comparison with the discharge voltage curves at 1 mA/cm^2. The initial discharge voltage drop at 2M electrolyte concentration becomes as severe as at 1M electrolyte concentration. The discharge voltages are slightly recovered from the initial drop after a few minutes for both 1M and 2M electrolyte concentrations, which indicates that aluminum anodic dissolution reaction becomes slow initially at 2M electrolyte concentration, as 5 mA/cm^2 current density is applied. The subsequent discharge voltage is maintained at 2M electrolyte concentration, however, the subsequent discharge voltage at 1M is not maintained and drops quickly, which is due to slow ionic transport properties and slow kinetics, as well as concentration polarization of discharge product precipitation on aluminum surface at 1M electrolyte concentration.

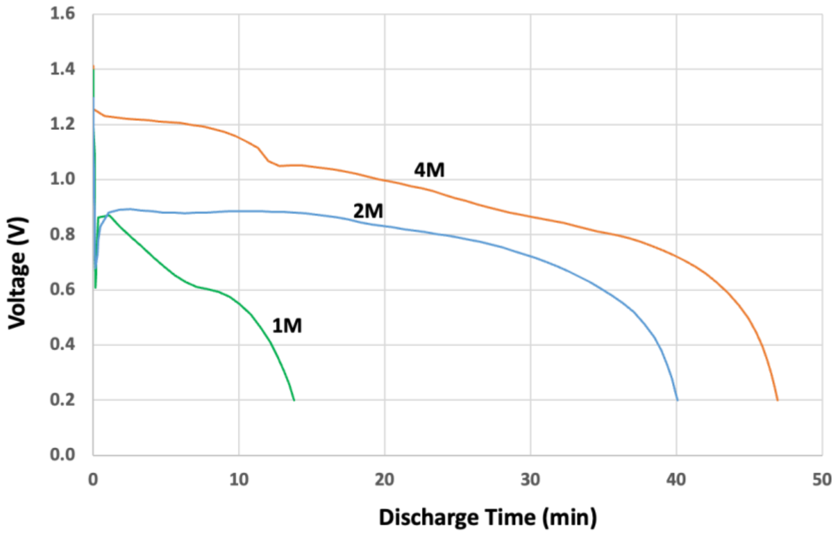

Figure 4. Discharge performance at different electrolyte concentrations at the current density of 5 mA/cm^2 (i.e 50A/m^2)

The results showed the electrolyte concentration at 1M is too low and 4M electrolyte concentration is appropriate at the tested electrolyte concentrations for discharge at the current density of 5 mA/cm^2. As the discharge current density increases, the discharge voltage drop caused by cell internal/ohmic resistance increases. In addition, the high ionic conductivity of electrolyte, the low cell impedance and charge transfer resistance, as well as low concentration polarization are among the important factors for the good discharge performance at high current density, which is needed for meeting the high-power discharge purposes. The factors that impact the high current density discharge include fast air/oxygen reduction reaction, low electrode resistance and electrode/electrolyte impedance, and high ionic conductivity of electrolyte and low concentration polarization.

V.3 Current Density Impact on Discharge Performance at Fixed Electrolyte Concentration

To help further understand the impact of current density on discharge performance, different current densities of 1 mA/cm^2 (i.e. 10A/m^2), 3 mA/cm^2 (30A/m^2) and 5 mA/cm^2 (50 A/m^2) were evaluated at fixed 2M electrolyte concentration. As current density increases at 2M electrolyte, the immediate initial voltage drop become bigger, the subsequent discharge voltage becomes lower, and the discharge time becomes shorter, as shown in Figure 5. Since the electrolyte concentration is at 2M electrolyte, the ionic conductivity of electrolyte and cell impedance are the same. The result showed that this 2M electrolyte can carry the current densities of 1mA/cm^2 and 3 mA/cm^2 but not well at 5 mA/cm^2. This 2M electrolyte does not take aluminum anodic dissolution fast at 5 mA/cm^2, as shown in the immediate initial voltage drop. The shorter discharge time at 5 mA/cm^2 also indicate that the concentration polarization at 5 mA/cm^2 is a factor for discharge performance fade quickly.

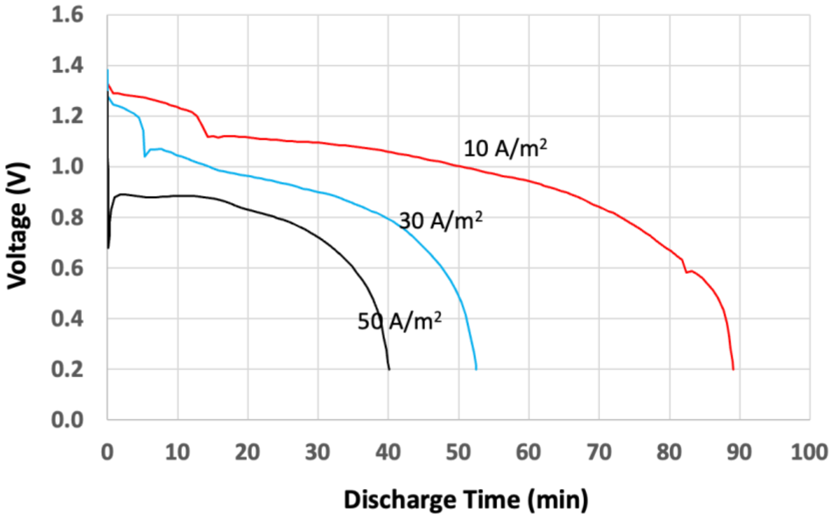

Figure 5. Discharge performance of different current densities at 2M electrolyte concentration

The result showed that the discharge voltage is lowered and discharge time is shortened as current density increases. The immediate initial voltage drop is obviously seen at higher density discharge. The factors that impact the high current density discharge include fast air/oxygen reduction reaction, low electrode resistance and electrode/electrolyte impedance, and high ionic conductivity of electrolyte and low concentration polarization.

V.4 Temperature Impact

To improve the ionic transport properties and enhance the kinetics, the impact of temperature on discharge performance was investigated. The full cell impedance with 2M electrolyte concentration before discharge shows that the cell impedance becomes smaller and the charge transfer resistance is reduced by ~25% as the temperature is increased from room temperature to 40°C, as shown in Figure 6. It is obvious from the impedance that the increase of temperature enhances the kinetics.

The impact of temperature on discharge performance of the cells are shown in Figure 7. The discharge voltage profile at 40°C is higher and flatter in comparison with the voltage profile at room temperature, which is due to the reduced charge transfer resistance and enhanced kinetics and the reduction of concentration polarization on aluminum electrode at 40°C. However, the discharge time is shorter at 40°C. This is because the full cells were put into the environmental chamber with the chamber door closed to maintain the temperature, but the air flow is limited.

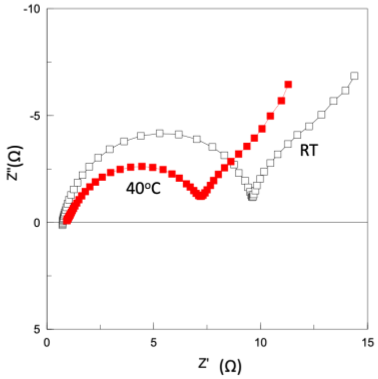

Figure 6. Full cell impedance before discharge at room temperature and at 40°C

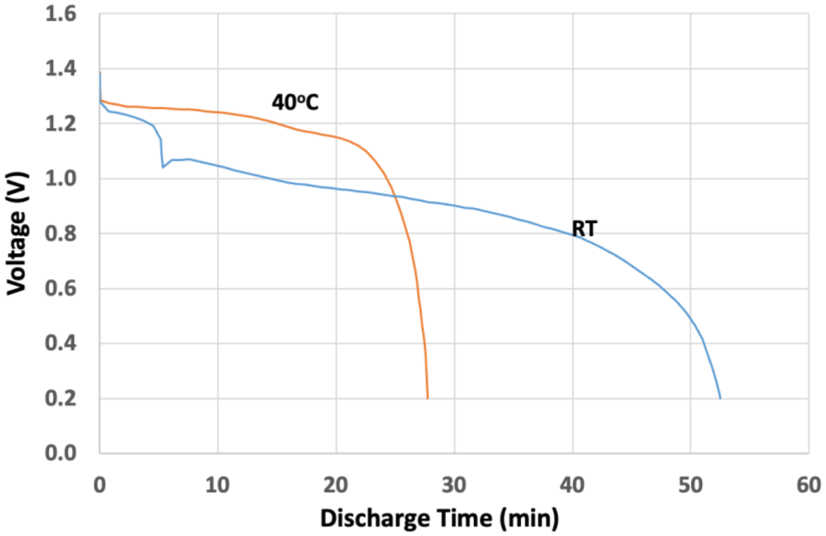

Figure 7. Discharge performance at room temperature (25ºC) and at 40ºC, at current density of 3mA/cm^2

The result shows that the temperature increase enhances kinetics and reduces concentration polarization on electrode surface to minimize the voltage drop and maintain higher and flatter discharge curve at 40ºC. The result also shows that continuation of supply of air at high temperature environment is important to maintain the discharge performance since air is part of reactant in the air-cathode.

V.5 Impact of Air-Cathode Loading

Air-cathode is an important and vital component in metal-air batteries. Air-cathode has the functions of breathing in air and converting it into hydroxyl ion (OH^-) via oxygen reduction reaction (ORR). Air-cathode is considered among the limiting factors for high power/high current discharge due to sluggish ORR. The investigation on the components and design of air-cathode including substrates, carbon materials and catalysts were conducted, and the preliminary results were discussed in our previous paper [1].

The loading in air-cathode is also considered an important factor for the kinetics. If the loading of electrode material coating layer on air-cathode, including carbon material, catalyst and binder, is too high, the air-cathode electrode layer becomes thick, which reduces the ionic transport, slows the kinetics and becomes less efficient. If the air-cathode coating layer is too thin, then the air-cathode is adequate and shorten the discharge time. Two different air-cathode loadings, 5.8 mg/cm^2 (high loading) and 3.6 mg/cm^2 (low loading) were investigated with 2M electrolyte concentration. The discharge performance at current density of 3 mA/cm^2 is shown in Figure 8.

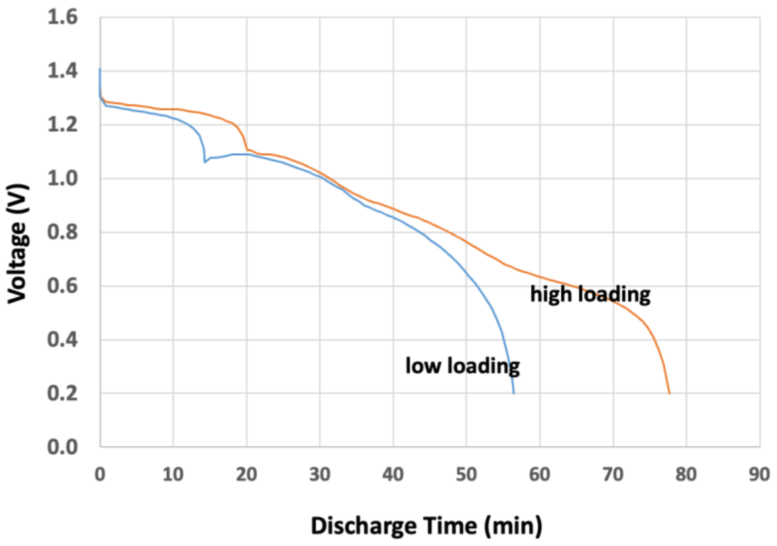

Figure 8. Discharge performance at different air-cathode loadings at current density of 3 mA/cm^2

The different loadings on air-cathodes have not much impact on the initial part of discharge performance at current density of 3 mA/cm^2, however, they have impact on discharge time. The cells with high loadings on air-cathodes have longer discharge times. The impact of different loadings on air-cathode at other different current densities is still under investigation. It is important to optimize the air-cathode loading and to maximize the efficiency of air-cathode in the Al/air cathode design.

VI Summary

This paper is focused on the investigation of factors to enhance kinetics and discharge performance at various current densities. Progress has been made in the research and development, and understanding the impact of different factors, including electrolyte concentration, temperature and loading of electrode material on air-cathode, on ionic transport properties, kinetics and discharge performances at different current densities. These factors need to be further optimized and integrated for the Al/air design and scale up for the large format cells. Currently, the test of Al/air cells are conducted at natural-air environment. The impact of the forced air flow to air-cathode on the kinetics is also to be investigated.

Acknowledgment

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