Development of Aqueous Electrolytes and Corrosion Inhibitors in Aluminium-Air Battery

Marliyana Mokhtar
Fuel Cell Institute, Universiti Kebangsaan Malaysia

Meor Zainal Meor Talib
Fuel Cell Institute, Universiti Kebangsaan Malaysia, Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia

Siti Masrinda Tasirin
Fuel Cell Institute, Universiti Kebangsaan Malaysia, Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia

Edy Herianto Majlan
Fuel Cell Institute, Universiti Kebangsaan Malaysia

Abstract

Aluminium-air battery is an attractive candidates for metal-air batteries because it has high theoretical electrochemical equivalent value, 2.98 Ah g⁻¹ which is higher than other active metals; magnesium (2.20 Ah g⁻¹) and zinc (0.82 Ah g⁻¹). One of the important components inside aluminium-air battery is electrolyte. Electrolyte is the conducting medium through which the two-way charges transfer occurs between the electrodes. The electrolyte also separates the anode and cathode to avoid short circuit and simultaneously provides hydroxide ion to maintain the electrochemical reactions. Aqueous electrolytes were widely used in metal-air batteries because their low cost, wide availability and high ionic conductivity. The main challenge that this battery encounter is aluminium anode self-corrosion. This paper reviews the development of the aqueous electrolytes selection based on their pH ranges which are acidic, neutral salt and alkaline solution. In order to reduce the self-corrosion, there are two methods that can be used which are to dope aluminium with other active metal elements or to modify the composition of electrolytes by adding corrosion inhibitors. Examples of active metal elements are Sn, Ga, In, Zn, Mg and Mn. For corrosion inhibitors, we can use either organic or synthetic inhibitors. This paper also proposes that the best material selection for outstanding Al-air battery performance is by using alkaline solution as the electrolyte, Al alloy as the anode and the addition of corrosion inhibitor to control the electrode corrosion problem.

Keywords: Aluminium-air battery, Aqueous electrolytes, Al alloys and corrosion inhibitor.

JEL: Q42.

1. Introduction

Aluminium (Al) is an attractive anode candidate material for metal-air batteries because it has high theoretical electrochemical equivalent value, 2.98 Ah g⁻¹ which is second highest after Lithium (3.86Ahg⁻¹) and higher than other active metals; Magnesium (2.20 Ahg⁻¹) and Zinc (0.82 Ahg⁻¹) (Li
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and Bjerrum, 2002; Linden, 2011; Agladze et al., 2012). Aluminium is also an inexpensive metal which is the second most abundant metallic element after silicon, environmental friendliness, non-toxic and high recyclable value (Schwarz, 2004). The theoretical specific energy of Al-air battery in alkaline electrolyte is up to 200 Wh/kg and for neutral salt solution is between 300 to 500 Wh/kg (Linden, 2011).

This battery comprises three main components which are an anode, a cathode and an electrolyte. The discharging battery is a galvanic cell and the cell drives electrical current in the external circuit. Electrolyte play an important role in this battery because it is the conducting medium through which the two-way charge transfer occurs between the electrodes (Linden, 2011). The electrolyte also separate the anode and the cathode to avoid short circuit and simultaneously provides hydroxide ion to maintain the electrochemical reactions (Zhang et al., 2014). Aqueous electrolytes are widely used in metal-air batteries because of their low cost, wide availability and high ionic conductivity. The aqueous electrolytes has been categorized based on the pH scale which are alkaline solution (7 < pH ≤ 13), neutral salt solution (pH = 7) and acidic solution (2 ≤ pH < 7).

Oxidation reaction at anode depend on the type of electrolyte take place in the reaction

Anode: \[ \text{Al} \rightarrow \text{Al}^{3+} + 3e \] (Equation 1.1)

Cathode: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \] (Equation 1.2)

Overall: \[ 4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3 \] (Equation 1.3)

Another undesired (parasitic) reaction occurs at anode because of water reduction reaction. The parasitic hydrogen generating reaction can be expressed as

Side reaction: \[ \text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \frac{3}{2}\text{H}_2 \] (Equation 1.4)

Linden (2011) reported that the equilibrium voltage range for aqueous electrolytes influence by the electrolyte concentration and temperature. In salt solution at room temperature, the reaction product in the battery appeared gelatinous, which made the resistance of the battery high and the output power low. It also had low polarization voltages which can be operated with coulombic efficiencies in the range of 50 to 80% (Linden, 2011). These phenomena did not exist in the alkaline solution. The efficiency of the battery using an alkaline solution was higher than that of the neutral salt solution and this happened because of the enhanced proton conductance of high pH electrolytes (Li and Bjerrum, 2002; Zhang et al., 2009; Linden, 2011; Egan et al., 2013). Therefore, in this paper, we discusses the development of the aqueous electrolyte that has been used in aluminium-air battery based on their performances and the techniques used to evaluate it.

In addition, there is one main obstacle that hinders Al-air battery to be deployed on a commercial scale is aluminium self-corrosion rate (Mohamad, 2008; Egan et al., 2013). There are three main processes occurring on the aluminium surface that hinder further oxidation reaction at the anode in aqueous based cell which are the formation of oxides films, Al2O3 and Al(OH)3, formation of corrosion products, Al(OH)3 and Al(OH)4 and parasitic hydrogen evolution, which lower the potential of the battery (Zhuk et al., 2006; Zeng et al., 2010). Because of this constraint, more efforts are needed to be developed to reduce the corrosion rate.

Alloying Al with small amounts of other metals such as magnesium (Mg), zinc (Zn), lead (Pb), tin (Sn), gallium (Ga) and indium (In) is one way to suppress the corrosion (Paramasivam and Iyer, 2001; Paramasivam et al., 2003; El Abedin and Endres, 2004; Rashvand Avei et al., 2013). All these elements have lower melting temperatures than Al, have a degree of solubility in Al, soluble in alkaline electrolyte and have high hydrogen overpotential. The ions dissolved into the solution and redeposit on the cathodic surface to decrease the hydrogen evolution (Li and Bjerrum, 2002; Egan et al., 2013).

Addition of corrosion inhibitor in electrolyte such as synthetic, organic and ionic liquids can also exhibit good performance (Macdonald and English, 1990; Al-Rawashdeh and Maayta, 2005; Abdel-Gaber et al., 2010; Egan et al., 2013; Rashvand Avei et al., 2013). Corrosion inhibitors are used to prevent uncontrolled corrosion of Al electrode in the electrolyte during current discharge. The main mechanism of corrosion inhibition is by adsorption of inhibitor molecules on the corroding metal surface thus effectively lowering the corrosion reaction to a controlled level (Pyun and Moon, 2000).
Since usage of chemical inhibitors has been limited by environmental regulations because of the hazardous and toxicity issues, more attention is now on natural green extracts as alternative corrosion inhibitor materials. This paper also cover the recent successful inhibitor substances that can inhibit the Al corrosion in aqueous media which has been reported by some authors.

2. Aqueous Electrolytes

2.1. Acidic Solution Electrolyte

For pH range below 7 which known as acidic form, this aqueous electrolyte has been used since 90s. By alloying pure Al with other active metal elements helps to increase the performance of the aluminium-air battery in acidic electrolyte. Saidman and Bessone (1997) deposited In on the pure Al surface to form Al-In alloy and used 0.5 M chloride acid as the aqueous electrolyte solution. The reaction occurs at room temperature and the result showed that the activation process depend on the concentration of ion In$^{3+}$. At higher ion In$^{3+}$ concentration, for potentials more positive than -1.50 V, the electroreduction of ion In$^{3+}$ can be occurred while the electroreduction of ion InO$^{2-}$ on quasibare Al was occurred for potentials more negative than -1.50 V.

Besides alloy with Indium, Al also can be alloyed with Silicon (Si) and Mazhar et al. (2001) reported that by using polarization technique, it indicated that the higher composition of Si alloyed with Al gives more negative potential value and when increasing the acid concentrations, the values of potential were found more shift to the negative side which is between -0.8 to -1.0 V.

Recently, Flamini and Saidman (2012) alloyed Al with Zn and investigated the performance by using different types of acid which have same concentration, pH value and operating temperature. Tefal plots showed that the potential value for Al-Zn alloy in 0.5 M chloride acid was more negative compared to Al-Zn alloy in 0.5 M acetic acid, -1.02 V and -0.80 V respectively.

Furthermore, the development of ternary alloy for Al is has also been studied in acidic electrolyte. Munoz et al. (2002) and Ma et al. (2013a) studied the combination of Al-Zn-In alloys, Flamini and Saidman (2012) studied the combination of Al-Zn-Ga alloys and Al-In-Ga alloys and Ma et al. (2013b) studied the Al-Zn-Mg alloys combination.

The combination of Al-Zn-In alloys revealed the potential values were between -0.9 to -1.1 V when the reactions occur in the 0.5 M chloride acid while in the 1 M chloride acid, the potential value is around -0.7 V (Munoz et al., 2002; Ma et al., 2013a). Based on the results that they got, it can be conclude that in acidic solution, the alloys undergo low degree corrosion process.

For Al-Zn-Ga and Al-In-Ga alloys, the potential values are more towards negative values in 0.5 M chloride acid when we increase the composition of Ga element in the alloys. The potential values that stated in the report are between -0.97 V to -1.27 V for Al-Zn-Ga alloys and -1.64 V to -1.78 V for Al-In-Ga alloys (Flamini and Saidman, 2012). With the same composition of alloys, then they tested the alloys in acetic acid and the results presented that the potential values were lower than -1.0 V (Flamini and Saidman, 2012).

Ma et al. (2013b) recently investigated the potentials of Al-Zn-Mg alloy combination. The open circuit potential values are between -0.6 V to -1.0 V for chloride acid solution which the reaction operate at room temperature and the pH range are between pH 1 to pH 4. From the report also showed that this alloy undergoes the pitting corrosion and relatively low degree corrosion process. The performance of the acidic electrolyte for aluminium-air battery has been summarized as shown in Table 1.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Concentration (M)</th>
<th>Operation temperature (K)</th>
<th>Anode</th>
<th>Technique</th>
<th>Result / performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloride acid pH 3</td>
<td>0.5</td>
<td>298</td>
<td>Al-In</td>
<td>potentiostatic and</td>
<td>Activation process</td>
<td>Saidman and Bessone (1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>potentiodynamic techniques,</td>
<td>depends on the amount of In deposited at the bare Al surface,</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SEM</td>
<td></td>
<td></td>
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</table>

Table 1. Summary of acidic electrolytes for aluminium-air battery.
possibly forming an Al-In surface alloy where Cl- adsorbs. This In disposition reaction is also depend on the potential, the actual In3+ concentration, the Cl- concentration and the local pH.

<table>
<thead>
<tr>
<th>Chloride acid pH 2</th>
<th>0.5</th>
<th>303</th>
<th>Pure Al, Al-7%Si, Al-11%Si, Al-22%Si</th>
<th>Chemical, polarization and EIS measurements, SEM</th>
<th>Capacitive behaviour of the oxide covered surface is replaced by resistive behaviour as immersion time increases in HCl solutions and the pitting by chloride ions initiates more readily in acidic media. The values of potential were found more shift to the negative side which is between -0.8 to -1.0 V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride acid pH 3</td>
<td>0.5</td>
<td>Room</td>
<td>Al-Zn-Ga and Al-In-Ga</td>
<td>EDX analysis, SEM</td>
<td>Saturated calomel electrode (SCE) Al–Zn–Ga alloys in chloride solution towards more negative values.</td>
</tr>
</tbody>
</table>

Flamini and Saidman (2012)
The presence of In in true electric contact with Al and Zn promotes Cl− adsorption at the Al–In–Ga alloys in chloride solution varies between −1.62 and −1.73 V.

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>pH 3</th>
<th>Room</th>
<th>Al-Zn-Ga and In-Ga</th>
<th>EDX analysis, SEM</th>
<th>SCE (V):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride acid</td>
<td>pH 5</td>
<td>298</td>
<td>Ternary alloy Al–5%Zn–0.02%In</td>
<td>The presence of In in true electric contact</td>
<td>Muñoz et al. (2002)</td>
</tr>
<tr>
<td>Chloride acid pH 4</td>
<td>0.6</td>
<td>Room</td>
<td>Al-(Zn-5.02%, Mg-0.9%, Mn-0.44%, Si-0.06%, Fe-0.001%, Ti-0.04%, Cu-0.03%, In-0.02%, C-0.05%)</td>
<td>Measurements of self-corrosion, potentiodynamic polarization, cyclic polarization experiment combined with OCP technique and SEM.</td>
<td>General and pitting corrosion occurred simultaneously in acidic media. The result revealed that the alloy undergoes two types of localized corrosion process, leading to the formation of hemispherical and crystallographic pitting. Hemispherical pitting is found to occur on the surface of this material under a simply exposure in chloride solution whereas for the formation of the crystallographic pits is for to polarize the alloy. The open circuit potential = -1.0 V</td>
</tr>
</tbody>
</table>

| HCl | 1 | Room | Al-(Zn-5.02%, Mg-0.9%, Mn-0.44%, Si-0.06%, Fe-) | Measurements of self-corrosion, potentiodynamic polarization, cyclic polarization experiment | The open circuit potential = -0.57 V | Mokhtar, M et al. |
In alloys and tested the alloys in 2 M NaCl solution. The potential value obtained was around 1.3 V to 1.4 V and also has strong anode dissolution that helps to reduce the electrode polarization (Gudić et al., 2010; Smoljko et al., 2012).

Another excellent alloy combination besides Al-In is Al-Sn alloy. Gudić et al. (2005) has been investigated the efficiency of Al-Sn alloy combination in 0.5 M NaCl solution by changing the composition of Sn. Based on the results, for anodic dissolution, they concluded that the most effective alloys were with 0.20% and 0.40% composition of Sn element (Gudić et al., 2005). El Shayeb et al. (2001) was also studied the performance of Al-Sn alloy and the potential value that he gained was around -0.98 V in 0.6 M NaCl solution. In 2 M NaCl solution, the potential value of this alloy is shift more towards the negative side which is around -1.45 V and also has strong anode dissolution that helps to reduce the electrode polarization (Gudić et al., 2010; Smoljko et al., 2012).

Combinations of the Al-Mg alloy and Al-Zn alloy are also has been studied. The potential value of Al-Mg alloy that reacted in 2 M NaCl solution was between -0.8 V to -0.9 V and its depend on the composition of Mg element (Nestoridi et al., 2008). The potential value increases with the increases of the Mg composition in the alloy. Al-Zn alloy combination also gave slightly high potential value which is -1.14 V, when this alloy has been tested in 0.6 M NaCl solution (El Shayeb et al., 2001).

Gudić et al. (2010) and Smoljko et al. (2012) also investigated the performance of ternary Al alloys (Al-In-Sn) in 2 M NaCl solution. The potential value obtained was around -1.46 V and undergoes rough surface corrosion. Next, the Al-In-Ga alloys also has been studied by Despić et al.

2.2. Neutral Salt Solution Electrolyte

Since early 70s, the effectiveness of the neutral salt solution electrolyte has been studied by the researchers. Majority of the researchers reported that the potential values of pure Al are between -0.65 V to -1.1 V which is react in sodium chloride (NaCl) solution (El Shayeb et al., 2001; El Abedin and Endres, 2004; Gudić et al., 2005; Nestoridi et al., 2008; Gudić et al., 2010; Akmal et al., 2013). The results showed that the potential values of Al were depending on the concentration of NaCl solution and the operating temperature. The potential values will increase when we increase the temperature and the concentration of NaCl solution (Nestoridi et al., 2008; Gudić et al., 2010; Akmal et al., 2013).

Similar with acidic solution, binary and ternary alloys of Al are also help to increase the performance of Aluminium-air battery in neutral salt solution (Despić et al., 1976; Aballe et al., 2000; Aballe et al., 2001; El Shayeb et al., 2001; El Abedin and Endres, 2004; Gudić et al., 2005; Han and Liang, 2006; Nestoridi et al., 2008; Nestoridi et al., 2009; Gudić et al., 2010; Fan et al., 2012; Smoljko et al., 2012; Wang et al., 2013; Ma et al., 2013a; Ma et al., 2013b).

Despić et al. (1976) reported that the potential values of Al-In alloys in neutral salt solution were between -1.4 V to – 1.7 V and the alloys corrosion rate were decreased compared to the pure Al. El Abedin and Endres (2004) also investigated the alloy in 0.6 M NaCl solution. The potential value of this alloy that they gained was around -1.2 V. Gudić et al. (2010) and Smoljko et al. (2012) also used Al-In alloys and tested the alloys in 2 M NaCl solution. The result indicated that this alloy undergoes random distribution of pitting corrosion and recorded the potential value around -1.3 V (Gudić et al., 2010). They were also stated that this alloy not only increased the anode efficiency but also help to reduce the hydrogen evolution rate (Smoljko et al., 2012).

The alloy undergoes pitting in acidic solutions and the open circuit potential = – 0.70 V.

### Table 2.1

| HCl | 1 | 298 | Al-(Zn-5.02% Mg-1.01% In-0.02% Si-0.09% Fe-0.001% Ti-0.05% Cu-0.02%) | cyclic polarization, self-corrosion and SEM. | Ma et al. (2013a) |

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(1976) and El Abedin & Endres (2004). The authors revealed that this ternary alloy exhibited more towards negative potential values compared to pure Al but slightly lower than Al-In alloys.

For ternary alloy that involve Al-Zn such as El Shayeb et al. (2001) investigated the Al-Zn-Sn alloy performance and Ma et al. (2013a; 2013b) investigated the Al-Zn-Mg alloy and Al-Zn-In alloy performances. Based on the results, it can be concluded that the potential values of these alloys increases in the following order: Al-Zn-In < Al-Zn-Mg < Al-Zn-Sn.

Nestoridi et al. (2008) has been studied the effectiveness of Al-Mg-Sn alloy and Al-Mg-Ga alloy in 2 M NaCl solution and the results showed that the potential values were increased with the composition of Mg element. The authors also reported that the potential value of Al-Mg-Sn alloy was slightly higher than the Al-Mg-Ga alloy. In addition, they also studied the combination of Al-Sn-Ga alloy and the potential value obtained was higher than Al-Mg-Sn alloy and Al-Mg-Ga alloy.

Other type of neutral salt solutions that also becomes promising electrolyte candidate is seawater. Akmal et al. (2013) reported that the open circuit potential value for pure Al in seawater solution at 303 K was 0.68 V. For aluminium-thallium-indium (Al-Tl-In) alloy studied by Mance et al. (1984), the potential value that the authors gained was around -0.9 V. Furthermore, the potential value can shift more towards negative side with increasing the temperature of seawater solution. Ezuber et al. (2008) revealed that by using weight loss technique, the Al alloys undergo pitting corrosion and the pit attack intensity increase when the operating temperature increase. Neutral salt electrolytes has been widely used in aluminium-air battery and Table 2 showed the summarization of the electrolyte result performance.

Table 2. Summary of neutral salt electrolytes for aluminium-air battery.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Concentration (M)</th>
<th>Operation temperature (K)</th>
<th>Anode</th>
<th>Result / performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td>Al-In and Al-Tl (up to 0.2%)</td>
<td>The potential values of Al-In alloys in neutral salt solution were between -1.4 V to – 1.7 V and the rate of corrosion of the alloys in neutral salt solutions is also decreased compared to that of pure aluminium.</td>
<td>Despić et al. (1976)</td>
</tr>
<tr>
<td>Neutral Salt</td>
<td>0.6</td>
<td>Al, Al-In and Al-Ga-TH</td>
<td>Result obtained showed the Al-In</td>
<td>The result exhibited a more negative rest potential than the Al-In alloy and a corrosion stability superior to that of the Al-Ga alloy. The negative difference effect was found to depend on the cation of the neutral salt in solution and the lowest effect was obtained in ammonium chloride solutions.</td>
<td>El Abedin &amp; Endres</td>
</tr>
</tbody>
</table>
In alloys the alloy exhibits the highest negative open circuit potential in 0.6 m NaCl and the corrosion resistance of the tested electrodes decreases in the following order: Al > Al-Ga-In > Al-In.

<p>| NaCl | 0.5 | 298 | pure Al, Al-0.02% Sn, Al-0.09% Sn, Al-0.20% Sn, Al-0.40% Sn | The charge value decreases with the increase of the Sn content in the alloy. Based on the anodic current-time responses shape and the charge values indicate that the longer stay at the cathodic potential activates alloys with 0.20% and 0.40% Sn for anodic dissolution. |
| NaCl | 2   | 293 | Al (98%) : Al—0.1 % In, Al—0.2 % Sn and Al—0.1 % In—0.2 % Sn | The Al-In alloy exhibiting the most remarkable characteristics and the addition of In as an alloying component to aluminium reduces electrode polarization, decreases hydrogen evolution rate and increases the anode efficiency. |
| NaCl | 2   |     | Al (purity 99.8%) | The surface of smooth without any damages |
|      |     |     | Al—0.2% Sn | smooth surface without any damages |
|      |     |     | Al—0.1% In | smooth surface with large number of randomly distributed pits |
|      |     |     | Al—0.2% Sn—0.1% In | rough surface with a metallic luster |</p>
<table>
<thead>
<tr>
<th>NaCl</th>
<th>2</th>
<th>293</th>
<th>99.99% Al</th>
<th>OCP (mV) vs SCE = -800</th>
<th>Nestoridi et al. (2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-3% Mg</td>
<td>OCP (mV) vs SCE = -820</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Al-5% Mg</td>
<td>OCP (mV) vs SCE = -890</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.5% Mg 0.1% Sn 0.05% Ga</td>
<td>OCP (mV) vs SCE = -1530</td>
<td>Nestoridi et al. (2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.4% Mg 0.1% Sn</td>
<td>OCP (mV) vs SCE = -850</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.4% Mg 0.4% Sn 0.03% Ga</td>
<td>OCP (mV) vs SCE = -1510</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.4% Mg 0.03% Ga</td>
<td>OCP (mV) vs SCE = -800</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.4% Mg 0.1% Sn 0.03% Ga</td>
<td>OCP (mV) vs SCE = -1500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.6% Mg 0.1% Sn 0.05% Ga</td>
<td>OCP (mV) vs SCE = -1530</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al-0.4% Mg 0.07% Sn 0.05% Ga</td>
<td>OCP (mV) vs SCE = -1530</td>
<td></td>
</tr>
</tbody>
</table>

NaCl 2 293

| Al + (0.4 wt% Mg, 0.07 wt% Sn and 0.05 wt% Ga) | The limitation on the extent of constant current dissolution did not arise from changes to the electrolyte composition or to the formation of a protective surface anodic film. Nestoridi et al. (2009) |

NaCl 3.5 293

| aluminum alloy doped with Ga, In, Sn, Bi, Pb and Mn | The cell can discharge at 0.29 A for 140 h with the working voltage keeping over 1.1 V, the utilization ratio of aluminum anode is over 44%, and the life of battery is longer than 2400 h. Han and Liang (2006) |

NaCl 3.5 303

| AA5083 (Mg-4.9%, Mn-0.5%, Si-0.13%) | The potential of corrosion of the sample, −0.760 V, is close to that of the pitting nucleation, Aballe et al. (2001) |
Fe-0.3%Ti-0.03%Cu-0.08%Cr-0.13% $\to -0.720$ V. and this alloy undergoes two types of localized corrosion process, leading to the formation of hemispherical and crystallographic pits.

**NaCl 3.5**

3A21 (Mg-0.05%%Mn-1.3% Si-0.6% Fe-0.7%Ti-0.15% Cu-0.2% Zn-0.1%) Both alloys suffer from pitting corrosion and the corrosion of 7A09 is much more serious than 3A21. The EIS tests revealed that the high corrosion rate for 7A09 alloy and good corrosion resistance for 3A21 alloy.

7A09 (Mg-2.5% Mn-0.15% Si-0.5% Fe-0.5%Ti-0.1% Cu-1.6% Cr-0.23% Zn-5.5%) The open circuit potential = around -1.0 V and this alloy undergoes two types of localized corrosion process, leading to the formation of hemispherical and crystallographic pitting.

**NaCl 0.6**

Al- (Zn-5.02% Mg-0.9%%Mn-0.44% Si-0.06% Fe-0.001%Ti-0.04% Cu-0.03% In-0.02% C-0.05%) The open circuit potential = around -1.0 V and this alloy undergoes two types of localized corrosion process, leading to the formation of hemispherical and crystallographic pitting.

**NaCl 0.6**

Al- (Zn-5.02% Mg-1.01% In-0.02% Si-0.09% Fe-0.001%Ti-0.05% Cu-0.02%) This alloy undergoes relative light pitting in neutral solutions and the alloy exhibits a notable corrosion resistance in neutral chloride solutions which is well validated by Rp and Icorr measurement. The open circuit potential = -0.9 V

**NaCl 0.5**

Al OCP (V) = 0.66 *Akmal et al. (2013)*

Al OCP (V) = 0.67

Al OCP (V) = 0.65

Al OCP (V) = 0.75

Al OCP (V) = 1.1

Al OCP (V) = 0.92
The ternary alloy Al(T)-0.1% In-0.1% Tl is uniformly dissolved in sea water and has a potential of -0.9V (SCE) in the current density region of 1-10 mA cm^{-2}.

The breakdown potential of the two alloys decreased with an increase in test temperature with better corrosion resistance for alloy 1100.

2.3. Alkaline Solution Electrolyte

There are two types of alkaline solution that typically used in aluminium-air battery; potassium hydroxide (KOH) and sodium hydroxide (NaOH) solution. The proton conductance in alkaline solution has been widely studied for many years.

Wilhelmsen et al. (1991) used weight loss technique to study the anode corrosion rate in 4 M KOH solution and the result claimed that the addition of other active metal elements help to improve the corrosion resistance of the anode. Chu and Savinell (1991) also investigated the KOH solution at the same operating temperature, 333 K and indicated that there was no mass transfer effect although the KOH concentration and temperature were significant on the polarization characteristics.

Doche et al. (1999), Tang et al. (2004) and Choi et al. (2011) investigated the anode corrosion rate in 4 M NaOH solution. Doche et al. (1999) used steady state technique to identify the corrosion
dissolution of pure Al and the result showed that pure Al exhibited the passive state based on the delineated polarization curves. By using polarization techniques, Tang et al. (2004) and Choi et al. (2011) studied the corrosion potential of pure Al and the potential value gained was around -1.5 V.

Besides pure Al, the effectiveness of alkaline solution by using Al alloys as the anode also has been studied since late 80s (Macdonald et al., 1988). Choi et al. (2011) investigated the corrosion potential of pure Al and the potential value gained was around -1.5 V. Besides pure Al, the effectiveness of alkaline solution by using Al alloys as the anode also has been studied since late 80s (Macdonald et al., 1988). Choi et al. (2011) investigated the corrosion potential of pure Al and the potential value gained was around -1.5 V.

Further, the combination of Al-Zn-In alloy and Al-Zn-Mg alloy were also has been studied by Ma et al. (2013a; 2013b) in 4 M NaOH solution. The reaction occurred at the room temperature and the results showed that the potential for Al-Zn-In alloy and Al-Zn-Mg alloy were around -1.65 V and -1.67 V respectively. The Al-Zn-Mg alloy undergoes hemispherical and crystallographic pitting corrosion while the Al-Zn-In alloy undergoes only crystallographic pitting corrosion. Based on the results obtained, the alloys undergo an intense corrosion process in alkaline solution due to the chemical dissolution by OH⁻.

Recently, Gao et al. (2013) investigated the effectiveness of Bismuth (Bi) element when it alloyed with Al-Mg-Sn-Ga alloy. By using gas-collecting method, the authors investigated the self-corrosion of this alloy in 4 M NaOH solution. The result showed that the potential value was shift more towards negative side when the weight composition percentage of Bi element was increased.

In addition, Wang et al. (2013) implemented a promising hybrid concept that can solved parasitic hydrogen evolution problem just by using ordinary kitchen aluminium foil and the value of open circuit potential gained by this system was around 1.45 V. This system also disclosed that by increasing the concentrations of alkaline solution, the power density were also increased. Table 3 summarized the alkaline electrolytes for aluminium-air battery that previously report by the authors.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Concentration (M)</th>
<th>Operation temperature (K)</th>
<th>Anode</th>
<th>Technique</th>
<th>Result / performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>4</td>
<td>253 and 333</td>
<td>pure Al and Al-In alloy</td>
<td>weight loss experiments and polarization measurements, SEM and energy dispersive X-ray spectrometry of the anode surfaces</td>
<td>weight loss experiments reveal that addition of 0.1 weight percent In greatly improves the corrosion resistance of the anode</td>
<td>Wilhelmsen et al. (1991)</td>
</tr>
<tr>
<td>KOH</td>
<td>333</td>
<td>Al</td>
<td>rotating aluminum cylinder electrode</td>
<td>This study indicated that the effects of KOH concentration, aluminate concentration and temperature on the</td>
<td>Chu and Savinell (1991)</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Temperature</td>
<td>Sample</td>
<td>Test Methodology</td>
<td>Electrochemical Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-------------</td>
<td>--------</td>
<td>-----------------</td>
<td>----------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>298 and 333</td>
<td>pure Al</td>
<td>steady state techniques and voltammetric analysis</td>
<td>The steady state polarization curves showed that aluminium exhibits a passive state at both 298K and 333K.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>room</td>
<td>pure Al</td>
<td>anodic polarizing curve, SEM, EDAX</td>
<td>The potential value gained was around -1.5 V.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>pure Al</td>
<td>potentiodynamic polarization tests and electrochemical impedance spectroscopy</td>
<td>In, Mn, Sn, and Mg decreased the corrosion rate of the Al alloys, while Ga enhanced corrosion significantly and accelerated consumption of the anode. Fe was not beneficial to improve the electrochemical properties of the Al anode in that it caused a decrease in the cell voltage and reduced corrosion rate slightly.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>room</td>
<td>Al-1Mg-0.1Sn-0.1Ga-xBi alloys ; xBi: 0.0, 0.05, 0.1, 0.1</td>
<td>SEM/EDAX and electrochemical measurements</td>
<td>The addition of Bi increases segregative phases which</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the self-corrosion was tested by using the gas-collecting method further activate the alloys to get more negative open circuit potentials, at the same time self-corrosion increases.

| NaOH | room | Al-5.02% (Zn-0.98% Mg-0.44% Mn-0.06% Fe-0.01% Ti-0.04% Cu-0.03% In-0.02% C-0.05%) | measurements of self-corrosion, potentiodynamic polarization, cyclic polarization and SEM. | The open circuit potential = -1.67 V Ma et al. (2013b) |
| NaOH | 298 | Al-5.02% (Zn-1.01% Mg-0.02% Mn-0.09% Si-0.001% Ti-0.05% Cu-0.02%) | cyclic polarization, self-corrosion and SEM. | The open circuit potential = -1.65 V and the alloy undergoes an intense corrosion process in alkaline solutions due to chemical dissolution by OH- Ma et al. (2013a) |
| NaOH | room | ordinary kitchen aluminum foil = Al purity of 97.6 wt% (impurities: O 1.13, Fe 0.68, and Ag 0.59 wt%). | volume and evolution rate of hydrogen collected in the measuring cylinder | The aluminum/air sub-cell has an open circuit voltage of 1.45 V. Wang et al. (2013) |

3. Corrosion Inhibitors
3.1. In Acidic Medium

Recently, Fares et al. (2013) investigated the polyethylene glycol (PEG) with the present of antibiotic ciprofloxacin as the additive for the inhibitor in acidic medium. The result obtained showed that the efficiency of PEG increased from 61% to 91% with the addition of ciprofloxacin. It also increased the kinetic thermodynamic parameters such as activation enthalpy and entropy of the Al
corrosion. These authors also has used pectin natural polymer in acidic media and claimed that the activation energy, enthalpy of activation and entropy increased when the concentration of pectin increased (Fares et al., 2012b). For both inhibitors, the authors used Langmuir adsorption isotherm to study the adsorption process on Al surface (Fares et al., 2012b; Fares et al., 2013).

Deng and Li (2012) investigated the extraction of Jasminum nudiflorum Lindl. leaves (JNLLE) as green corrosion inhibitor in hydrochloric acid (HCl) solution by using weight loss, polarization curves and electrochemical impedance spectroscopy (EIS) methods. Based on polarization curves, the result obtained showed that the JNLLE acted as the cathodic inhibitor and the adsorption followed the Langmuir adsorption isotherm. Ezeokonkwo et al. (2012) studied the Al surface adsorption process by applying Temkin adsorption isotherm and tested by using Eucalyptus citriodora extraction as the inhibitor in HCl solution. In this experiment, the authors also replaced the Al with mild steel to compare the inhibitor efficiency of both metals. The result revealed that there are better performance of corrosion inhibitor in Al compared to mild steel.

By using weight loss method, Yadav et al. (2013) has studied the Ziziphus mauritiana Fruit extract as green corrosion inhibitor for Al in HCl solution. It has been tested at room temperature and using different concentration of extraction, in the range between 0.0644 to 1.288 g/L. From the tests, it can be concluded that the efficiency of inhibitor increased with the increased in the inhibitor concentration. The corrosion inhibitor of aluminium alloy AA3001 in 0.1 M HCl solution by the extraction of Commiphora pedunculata (CP) gum has been evaluated by Ameh and Eddy (2013). By using gravimetric and thermometric methods of monitoring corrosion, the result showed that when the concentration of CP gum increased, the inhibition efficiency also increased but it decreased with the increasing temperature.

Halambek et al. (2013) has been investigated the ethanol solution of Ocimum basilicum L. oil as inhibitor for Al in 0.5 M HCl solution by using weight loss, potentiodynamic polarization and EIS methods. The result was found that the presence of basil oil in HCl solution was influenced on the decreasing of current densities and based on EIS result, it proved that this compound formed protective layer on Al surface. The silicate-based extracted from rice husk ash as the corrosion inhibitor for aluminium alloy Al 6061 in 0.5 M HCl solution has been studied by Othman et al. (2013). By using weight loss method, the result obtained indicated that the small addition of silicate-based help to exhibit the decreasing of Al 6061 weight loss.

Besides HCl solution, another acidic media that also has been studied was sulphuric acid, H$_2$SO$_4$. Obi-Egbedi et al. (2012) investigated the natural corrosion inhibitor for Al by Spondias mombin L. extraction in 0.5 M H$_2$SO$_4$. By using standard gravimetric technique, it was found that the inhibition efficiency increased when the concentration of extraction increased.

### 3.2. In Neutral Salt Medium

By using weight loss and polarization methods, Halambek et al. (2010; 2013) has been studied the effectiveness of Natural oil extracted from Lavandula angustifolia L. and ethanolic solution of Laurus nobilis L. oil as an inhibitor for Al alloy in the 3% NaCl solution. Based on the results, it can be concluded that both inhibitor provides good protection and help to hinder the pitting corrosion on Al alloy surface.

### 3.3. In Alkaline Medium

The corrosion inhibitor of leaves extract of Phyllanthus amarus on Al surface in 2 M NaOH solution has been studied by Abiola and Otaigbe (2009) using chemical technique. The result gained indicated that at highest concentration tested, the inhibition efficiency was around 76%. With the same technique and alkaline medium, the authors also tested the Gossypium hirsutum L. leave extracts (GLE) and seed extracts (GSE) as Al corrosion inhibitor (Abiola et al., 2009). It was found that the GLE extract was more effective than GSE extract since the efficiency of inhibition for both extracts obtained were 97% and 94% respectively.

Abdel-Gaber et al. (2010) has been evaluated cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and lupine seed extract as Al surface inhibitor in 2 M NaOH solution by using
 electrochemical technique and the result revealed that lupine seed extract was controlled both of Al anodic dissolution and hydrogen gas evolved at cathodic side.

Recently, in 1 M NaOH solution, the extraction of Solanum trilobatum leaves as Al corrosion inhibitor has been investigated by Geetha et al. (2013). It was found that at the highest concentration tested, the inhibition efficiency was around 94%. Irshedat et al. (2013) studied the Al inhibitor by Lupinus varius I. extract in 1 M NaOH solution. By using weight loss method, it can be concluded that the inhibition efficiency increased with increasing the extract concentration and decreased with increasing temperature. Furthermore, Table 4 summarized all the natural corrosion inhibitor for Aluminium in classified media which has been studied in a few years back.

3.4. Ion and Chemical Additives

In neutral salt media, the ion additives that has been studied were ion In\(^{3+}\), Sn\(^{3+}\) and Zn\(^{2+}\). El Shayeb et al. (1999) has been investigated the effectiveness of Al anode potential by adding ion In\(^{3+}\) as an additive in 0.6 M NaCl solution and the result obtained showed that the activation of pure Al and Al alloys was increased with the increasing of ion In\(^{3+}\) concentration. The authors also investigated the present of ion Sn\(^{3+}\) as additive in 0.6 M NaCl solution (El Shayeb et al., 2001). The SCE potential value for pure Al and Al alloys based on the experiments was in between -0.95 V to -1.1 V. Pure Al and Al alloys also has been tested by using ion Zn\(^{2+}\) as an additive in 0.6 M NaCl solution by El Abedin and Endres (2004). The result revealed that Al-In alloy exhibited the highest potential value compared to pure Al and Al-Ga-In since the value reported was -1.2 V, -0.8 V and -1.05 V respectively.

Besides ion as an additive, Tang et al. (2004) studied the potential effect by adding zinc chloride (ZnCl\(_2\)) in 0.5 M NaCl solution. The result gained showed that the addition of ZnCl\(_2\) help to increase and improved activation potential of pure Al and Al alloys. Then, cerium (III) chloride (CeCl\(_3\)) also has been evaluated as an additive in 3.5 M NaCl solution by Zhou et al. (2007) and the result indicated that the discharge performance of Al anode with addition of CeCl\(_3\) in NaCl solution was better than without it.

In alkaline media, the chemical additives that frequently used were zinc oxide (ZnO) and sodium stannate (Na\(_2\)SnO\(_3\)). Wang et al. (2011) and Martin and Zhu (2012) evaluated the present of ZnO as an additive in KOH solution while Rashvand Avei et al. (2013) evaluated it in NaOH solution. All authors claimed that an addition of ZnO help to hinder the Al corrosion and improved the performance of Al anode. For Na\(_2\)SnO\(_3\), Doche et al. (1997) has studied its present in NaOH solution while Chang et al. (2008) and Zeng et al. (2010) added it in KOH solution. The results revealed that with stannate, the potential values were shift more towards negative side. Other chemical additives that has been explored were BMIMBF4, polyethylene glycol, NaSnO3, alkaline citrate and more (Macdonald and English, 1990; Al-Suhybani et al., 1991; Kapali et al., 1992; Wang et al., 2009; Wang et al., 2011; Zhang et al., 2013). For further information, there are some reviews previously that has been explained in details about the additives used in alkaline medium for Al (Li and Bjerrum, 2002; Zhang et al., 2009; Egan et al., 2013).

4. Conclusion

Aluminium-air battery promising a great future battery due to their potential abilities as good for alternative power sources. As one of important part in this battery, the development of electrolytes should be viewed much more closer and deeper. Each aqueous electrolyte has its own benefits and challenges. In general, all aqueous electrolyte were needed to encounter the twin challenge which are Al anode corrosion and hydrogen evolution. In this paper, we discusses the performance of each types of aqueous electrolyte based on the different applied techniques. It can be concluded that the alkaline solution showed the most outstanding performances compared to the acidic and neutral salt solution. The performances were much more better when Al alloys either binary or ternary were used as anode. The addition of corrosion inhibitors into the aqueous electrolyte has also found help to increase the battery performance.
Table-4. Summary of natural corrosion inhibitor for aluminium in classified media.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Inhibitor</th>
<th>Additive</th>
<th>Technique</th>
<th>Adsorption isotherm</th>
<th>Performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2M NaOH solution</td>
<td>extract of <em>Phyllanthus amarus</em> leaves</td>
<td>chemical technique</td>
<td>Langmuir adsorption isotherm</td>
<td>75% efficiency at the highest concentration in the alkaline environment and the inhibition efficiency increased with increasing concentration of the extract</td>
<td>Abiola and Otaigbe (2009)</td>
<td></td>
</tr>
<tr>
<td>2M sodium hydroxide (NaOH) solution</td>
<td>Gosypium hirsutum L. leaf extracts (GLE) and seed extracts (GSE)</td>
<td>chemical technique</td>
<td>Langmuir adsorption isotherm</td>
<td>The inhibition efficiency increased with increasing concentration of the extracts. The GLE gave 97% inhibition efficiency while the GSE gave 94% at the highest concentration.</td>
<td>Abiola et al. (2009)</td>
<td></td>
</tr>
<tr>
<td>2M sodium hydroxide solution</td>
<td>cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and lupine seed extract</td>
<td>electrochemical techniques and chemical gasometry measurements</td>
<td>Langmuir adsorption isotherm</td>
<td>The inhibition efficiency was found to increase with the azo dye concentration but not with temperature.</td>
<td>Abdel-Gaber et al. (2010)</td>
<td></td>
</tr>
<tr>
<td>1M NaOH solution</td>
<td>Solanium trilobatum leaves extract</td>
<td>weight loss technique</td>
<td>mixed type inhibitor</td>
<td>94% efficiency at the highest concentration in the alkaline environment and the inhibition efficiency increased with increasing concentration of the extract.</td>
<td>Geetha et al. (2013)</td>
<td></td>
</tr>
<tr>
<td>1M NaOH solution</td>
<td>extract of Lupinus varius L.</td>
<td>weight loss technique</td>
<td>Langmuir and Temkin adsorption isotherms</td>
<td>The inhibition efficiency increased with increasing the concentration of the extract and decreased with increasing temperature.</td>
<td>Irshad et al. (2013)</td>
<td></td>
</tr>
<tr>
<td>basic medium naphthol compound, 4-(4-nitrophenylazo)-1-naphthol (4NIN)</td>
<td>classical chemical (gravimetric and spectrophotometric (UV-Vis and FTIR) methods</td>
<td>Langmuir adsorption isotherm</td>
<td>The inhibition efficiency was found to increase with the azo dye concentration but not with temperature.</td>
<td>Edox et al. (2013)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Acknowledgement

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