Analysis of Mg(OH)$_2$ Deposition for Magnesium Air Fuel Cell (MAFC) by Saline Water

(Analisis Pemendapan Mg(OH)$_2$ untuk Sel Bahan Api Udara Magnesium (MAFC) oleh Air Masin)


ABSTRACT
Magnesium air fuel cell (MAFC) systems are eco-friendly fuel cells that use electrolytes of saltwater and oxygen from the air to produce power. However, MAFC cells face a critical problem, which is the deposition of side products on the surface of the Mg anode plate and the cathode electrode. Therefore, this study will focus on the analysis of factor on Mg(OH)$_2$ deposition by identifying the optimal seawater, Mg alloy, and surface roughness and additives solution. Magnesium plates AZ31 are used as the anode, and air electrode as the cathode. This study also considers physical characteristics such as SEM, EDX and corrosion test while chemical characterization by performance test with difference electrolyte, anode, and roughness. Catechol-3,5-disulfonic acid disodium salt (tiron) as anti-deposition used to reduce the deposition of Mg(OH)$_2$, on the anode and cathode surfaces and thus improve the performance of MAFC. From the performance study, the MAFC able to produce a power density of 27.54 mW/cm$^2$ which is high compare to the MAFC without tiron. Therefore, with the active area by 110.25 cm$^2$, the MAFC generates 2.93 W. The deposition of Mg(OH)$_2$, reduces the active area of magnesium oxidation, thus, reduce the electricity generation. With the knowledge of optimal seawater concentration and improvement of a single fuel cell system, this study is expecting to assist the fisheries and aquaculture sector as well as the coastal communities in terms of providing a better, safer, and cheaper alternative source of electricity.

Keywords: Anti-deposition; magnesium fuel cell; saline water

INTRODUCTION
With the accelerated economic growth, renewable oil is rapidly used, triggering a number of environmental problems, including acid rain and global climate change (Fadzillah et al. 2019). Thus, in the immediate future, green clean energy is expected especially in transportation,
industry, and energy resource for human (Hannan et al. 2017). Metal-air fuel cell (MAFC) provides a compelling option due to the battery’s high potential capacity, low-cost, and environmental benignity (Mokhtar et al. 2015). MAFC is increasingly gaining attention as renewable energy sources that can be benefited from very cheap seawater (salt water) and magnesium metal and has twice the volumetric energy density of lithium. MAFC used magnesium plate as anode, carbon electrode as cathode, and salt water (also used sea water) as electrolyte. One of the advantage of MAFC is the usage of materials from unlimited natural resources which attracted attention from researchers (Kim et al. 2018; Liang et al. 2008; Zhang et al. 2017). Magnesium is able to substitute or boost lithium ion as a battery based on studies. However, the theoretical magnesium relative to lithium as an anode material has half of the energy density per unit mass, with a volumetric density of about 50 per cent higher (32,731 versus 22,569 GJ/m³) relative with 18,8 versus 42,3 MJ/kg. Moreover, because of the abundance of magnesium on earth, magnesium dependent has a cost advantage on lithium.

On the other hand, the application of MAFC is also very important in the development of sustainable renewable energy alternative. Hahn et al. (2015) manage to develop the marine system using MAFC, which is direct to the ocean. The engineered MAFC device is dipped into the electrolyte of the seawater by a galvanic hydrogen producing cell. The planar magnesium anode is positioned between two electrodes with catalyst of hydrogen evolution and gas separation membranes. MAFC therefore represents a potential for substantial energy harvesting in future because of its high discharge level, large capacity and low environmental impact.

As Mg is immersed to salt water, the primary cathodic reaction is corrosion due to water reductions in hydrogen. However, Mg has a different behavior in aqueous environments, with the reaction rate of hydrogen evolution (HE) increasing with an increase up to anodic polarization of open circuit potential (OCV) (Liang et al. 2008), which contradicts norms in electrochemical kinetics. This phenomenon, which is known as anomalous HE, has long been observed (Hahn et al. 2015) but its mechanism of reaction is not understood and continues to be the subject to intense study. Majority of the anomalous HE originates in active dissolve areas.

Main limitation of Mg-Air fuel cell operation includes Mg anode corrosion which contributes to over potential of fuel cell and thus reducing its efficiency as well as formation of precipitates in the cell media. Factors influencing Mg anode corrosion includes hydrogen evolving reaction (HER) on Mg plates, negative difference effect (NDE) due to Mg metal property and galvanic corrosion due to impurities present in the Mg metal anode composition (Ma et al. 2019a). Formation of precipitate are reckoned due to formation of Mg(OH)₂, and MgO as product from redox reaction occurring at electrodes of the cells. Mg(OH)₂ are generally soluble in water, however, Mg(OH)₂ tends to precipitate at high concentrations of this salts. At a larger quantity, this precipitate tends to hinder ion flow between the electrodes of the cell, thus, reducing its electric power density out and overall efficiency of the cell. These precipitates also tends to block the gas pores of cathode layer which then prevents oxygen gas from diffusing into the cathode and reducing efficiency of ORR at cathode of the cell (Fadzilah et al. 2017; Höche et al. 2018; Majlan et al. 2018). The conventional Mg-air fuel cell used in power packs consist of AZ31 Mg metal alloy anode and cathode of noble metal, Pt. Other alloy of Mg also study in order to improve the performance such as AZ31b (Abdullah et al. 2015), AZ61 (Muhammad et al. 2011), and AZ91 (Li et al. 2018).

Issues in MAFC cells were thoroughly explored during writing based on credible literature sources. The restrictions of the MAFC listed directly restricted the efficiency of the MAFC cells, reducing the credibility of the entire MAFC electric generator. From the literature, there is no clear guidance for MAFC system in order to increase the performance by encounter the major problem in MAFC. In line with this, this study will emphasize on different cell performance enhancement approaches will be addressed and compared with energy density. Such strategies can be divided into four parts, namely hydrogen evolution, Mg alloy, grain size, and electrolyte additives in order to archives optimum performance.

**METHODS**

Hydrogen evolution tests of AZ31 were conducted in 3.5, 5, and 10 wt. % NaCl solution at room temperature that is prepared beforehand using the analytical grade of sodium chloride salt. An inverted burette with a measuring cylinder was used to collect and measure the volume of hydrogen produced. Magnesium alloy samples were cut into blocks with a dimension of 10 × 10 × 2 mm. The surface of the sample was ground with SiC sandpaper and cleaned with ethanol in an ultrasonic cleaner for 10 min. The samples were then sealed with resin, leaving an exposed area of 10 × 10 mm. Afterwards, this exposed surface was polished with sandpaper and diamond paste again, then rinse with ethanol and dry with cold air, immersed into electrolyte mentioned earlier for 48 h. The hydrogen volume of the sample production was determined. In the following formula, the average evolution rate for hydrogen was estimated, whereby \( \dot{\text{A}}_\text{H}_2 \) represents the average rate of hydrogen evolution (mL/cm² h), \( \text{VH}_2 \) is the total volume of hydrogen evolution (mL), \( s \) is the sample surface (cm²), and \( t \) is the immersion time (h) (Zheng et al. 2018). Three parallel tests were conducted to ensure good reproducibility of the data.

\[
\text{VH}_2 = \frac{\text{VH}_2}{st}
\]
The polarization curves and electrochemical impedance spectra (EIS) have been tested in an electrosystem workstation. The counter and a reference electrode was Pt wire and a saturated calomel electrode (SCE). Electrochemical samples with a surface area of 1 cm$^2$ with SiC abrasive paper were ground with exposure to 3.5, 5 and 10% by weight by NaCl aqueous solution by 298 + 1K. 3.5% concentration is used because, according to seawater concentration. It is to see the suitability of seawater as an electrolyte. Many other MAFC researchers use 5 and 10% is the maximum concentration used. As electrolyte in all electrochemical studies, the solution generated with deionized water and analytical reagents was used. After 10 min of immersion, the polarization curves were registered at a scan rate of 1 mV/s. After the initial 10 min delay, the EIS was calculated for a constant value of OCP. The frequency range tested was 100 to 1 Hz, and the voltage level was 5 mV. In order to ensure the replicability of the details, all electrical measurements have been carried out in triplicate.

The discharge performance was evaluated using a battery testing system connected to a potentiostat. The commercial MnO$_2$/C catalyst served as the cathode. It allows the oxygen in the air diffuse into the electrolyte for the discharge reaction. The electrolytes were 3.5, 5, 10 wt. % NaCl solution, natural seawater, and 3.5% NaCl with Tiron as an additive for comparison. 3.5% of saline water is used. The reaction regions of both anode and cathode were 110.25 cm$^2$. The current density of 10 mA/cm$^2$ chosen for long term low-power battery systems was used to investigate the release efficiency of magnesium anodes. The discharge products were blocked by boiling chromic acid (200 g/L), and anodized effectiveness using the mass loss system was measured. The morphologies discharged, or discharge curve by scanning electron microscopy have been observed. Triplicate battery analyses have been conducted to ensure the results are reproducible.

To identify the efficiency of each alloy with a 3.5% NaCl solution, three different Mg alloys (AZ31, AZ61, and AZ91) were used. In the meantime, the magnesium layer is coated with 3-sided paper before the top coating is stripped and called as fine, moderate, and rough in order to determine the appropriate grain size. Five forms of additives using the commercial-grade of Sigma Aldrich have been tested for additive research.

A single cell of MAFC conducts with 10.5 $\times$ 10.5 cm of magnesium plate which is producing active area of 110.23 cm$^2$. The electrode which layered by Mn catalyst and stainless steel current collector also used the same active area then both immerse in NaCl solution with different concentration as shown in Figure 1. Then, the single cell performance test by using Potentiostat Galvanostat to produce the polarization curve. Before testing, the stability test conducts in 5 min due to the high corrosion rate in the anode.

**FIGURE 1.** Single cell of MAFC

**RESULTS AND DISCUSSION**

Corroded morphology of AZ31 after immersion test in different NaCl concentration is displayed in Figure 2. Based on observation, some differences can be spotted in discharge product morphology between the samples immerse in mentioned NaCl concentrations. As shown
in Figure 2(a), the sample is almost entirely covered by flaky discharge product. Both Figure 2(b) and 2(c) also have flaky features with additional protuberance morphology and large cracks can be found on the sample surface. It was suggested that the discharge product breaks off easily, thus, exposing anode surface to the corrosive saline condition but providing a larger surface area for reaction to occur. Hence, this indicates that the higher the electrolyte concentration used, the faster the magnesium erosion occurs and can cause cracking to occur. It will reduce the effective and optimal use of magnesium fuel in MAFC. Therefore, the appropriate concentration should be used to balance the reaction rate at the anode and cathode to produce the optimal power output. Figure 3 shows the electrode containing the corrosion product attached to the electrode surface. If the precipitation blocks the electrode or magnesium surface, it may reduce the effectiveness of the active area and affect the reaction rate. According to Figure 4, the predominant oxygen and magnesium peak indicating the discharge product is most probably consisting of Mg(OH)$_2$, a typical by-product produced from the overall reaction that precipitates on the anode surface forming a protective film which inhibits the further reaction. The same pattern result is obtained from AZ31 alloy immersed in 3.5 and 5% NaCl solution.

**FIGURE 2.** Corrosion morphology with discharge product of AZ31 after immersion test in a) 3.5% NaCl, b) 5% NaCl, and c) 10% NaCl solution

**FIGURE 3.** Corrosion product magnesium oxide (Mg(OH)$_2$) in MAFC electrode
TABLE 1. EDX results for EDX spectra of AZ31 alloy surface immersed in 10% NaCl solution for 48 h

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>0.74</td>
<td>1.24</td>
</tr>
<tr>
<td>O K</td>
<td>48.81</td>
<td>61.58</td>
</tr>
<tr>
<td>ZnL</td>
<td>1.89</td>
<td>0.58</td>
</tr>
<tr>
<td>NaK</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>MgK</td>
<td>33.98</td>
<td>28.22</td>
</tr>
<tr>
<td>AlK</td>
<td>1.02</td>
<td>0.77</td>
</tr>
<tr>
<td>SiK</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>ClK</td>
<td>11.31</td>
<td>6.44</td>
</tr>
<tr>
<td>CaK</td>
<td>2.05</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Figure 5 shows the hydrogen evolution rate curves of AZ31 alloy sample as a function of immersion time in 3.5, 5, and 10% NaCl solution which is used to represent the corrosion rate of magnesium alloy in respective saline solution. As shown in Figure 5, the difference of hydrogen evolution rates of AZ31 in three different concentration of the saline solution was indistinct at the primary stage of immersion but became apparent after 4 h. The corrosion rate of AZ31 immersed in 10% NaCl solution is the highest, followed by AZ31 immersed in 5% NaCl solution and AZ31 immersed in 3.5% NaCl solution has the lowest rate of corrosion. The finding suggests that the AZ31 Mg alloy samples immersed in 3.5% NaCl solution has better corrosion resistance compared to the one immersed in 5 and 10% NaCl solution. The result is also supported by previous work which finds that the activation
energy value decreases as the concentration of salt increase, implying that the corrosion is thermodynamically more favoured in a higher concentration of the saline solution. Hence, the rate of deterioration of AZ31 is the highest is 10% NaCl solution.

Dhanapal et al. (2012) clarified that increased corrosion rate with increasing chloride ion concentration was due to chloride ion involvement in the dissolution reaction. The more chloride ion in NaCl solution, the faster ion (Cl⁻) transferred through the outer layer and penetrated the alloy surface substratum, thereby increasing corrosion rate. As the Cl⁻ has an aggressive property that could penetrate the alloy surface, it contributes to the initiation and production of pitting corrosion and localized corrosion. Thus, it may cause Mg(OH)₂ film to dissolve when adsorbed on the anode surface (Shi et al. 2017; Yang et al. 2016). Therefore, the corrosion product is quickly removed from the exposed region in Figure 1(b) and 1(c) compared with Figure 1(a) and is still protected with a corrosion product that serves as a protective film.

AZ31 magnesium alloy was adopted as the anode for Mg-air fuel cell incorporated with MnO₂ catalyst on the air cathode to evaluate their discharge performance in 3.5, 5, and 10% NaCl solution. The curves of voltage and power density vs current density are presented in Figure 6(a) and 6(b), respectively. The presence of tiron into NaCl solution has improved the power output of MAFC from 22.3 to 24.9 mW/cm². However, the current density at maximum power output decreased from 35 to 30.1 mA/cm². It is due to the presence of tiron, which also reduces Mg erosion and decreases the amount of current generated. This results was also supported by Hoche et al. (2018) although the optimum power out is still high compared to others.

It is shown that the Mg-air fuel cell using 10% NaCl solution exhibits the highest cell voltage and peak power density which is 1.7 V and 27.54 mW/cm², respectively, despite having the lowest corrosion resistance as analyzed compared to 5 and 3.5% NaCl. Furthermore, the lowest cell voltage and power density produced is Mg-air fuel cell using natural seawater as the electrolyte. However, Yang et al. (2018) find that alloy AZ63 immersed in natural seawater has lower corrosion potential and corrosion current density compared to immersed in 3.5% NaCl solution. It is implied that magnesium alloy tends to erode more severely in the salt solution than in natural seawater. The results also showed that the addition of Tiron in 3.5% NaCl solution has to improve the performance of Mg-air fuel cell compared to performance without the additive in 3.5% NaCl solution. Addition of Tiron enhances the discharge potential by suppressing the Fe enrichment and preventing the precipitation of Mg(OH₂) exposing fresh and active anode surface for further reaction (Vaghefinazari et al. 2020). It is clearly shown that all the electrolytes without any additive exhibit fluctuation in cell voltage and power density, indicating the formation and breaking off of the discharge product on anode surface over time (Ma et al. 2019b).
Mg metal as a MAFC anode as per discussed in the previous sections is associated with active corrosion issues. The functional degradation of Mg anode metal in the cell is due to two main factors, which is the negative impact of the electrode (NDE) which results in the reaction of hydrogen gas (HER) evolution and Mg anode displacement. It reduces the cell’s efficiency with regards to anode use, as the cell maintains its own (Wang et al. 2019). Therefore, several strategies for reducing the rate of active corrosion in the cell anode will be discussed and compared, including Mg metal alloying and Mg alloy microstructure modification. A detailed analysis of the Mg alloy most appropriate for the application of Mn-Al-Zn-si elements has been described as supporting the best anodic Mg anodic discharge properties in MAFC cells compared to other alloys, such as Mg-Al-Zn-Pb and Mg-Al-Mn-Ca alloys (Hamlen et al. 1969). Mg-Al-Mn-Zn-Si alloys are characterized as Mg alloy of AZ series. There are three different AZ series Mg alloys which include AZ31, AZ61, and AZ91 with different MAFC performance-boosting potential. The summary of MAFC cell performance with different AZ series Mg alloy, as shown in Figure 7 is compared and discussed.

The Mg-air fuel cell with the alloy of Mg AZ61 alloy has a higher emission potential than alloy Mg and alloy AZ31 and AZ91 at the same current density. In the case

FIGURE 6. Performance of Mg-air fuel cell using different concentration of NaCl solution as an electrolyte: a) Cell voltage vs current density and b) Power density vs current density. The cathode is a commercial air electrode with MnO₂ catalyst and AZ31 as the anode.
of AZ61 anode, the anode usage factor can reach as high as 41% at a current density of 10 mA/cm² for 5 h. The AZ61 alloy has better discharge properties in terms of discharge voltage and anode utilization factor (Ma et al. 2019a). It is due to the precipitate product released inhibits the active erosion of Mg anode due to the hydrogen evolution reaction of the Mg AZ61 anode that shows higher anodic efficiency than the pure Mg anode and the Mg AZ31 and AZ91 alloys. The results of the anode surface morphology results show that the discharge product is quickly accumulated on the surface of the AZ61 alloy compared to the other Mg alloys. Therefore, the Mg AZ61 alloy anode shows the lowest erosion current density (jcorr) and highest alloy anode utilization (Zhao et al. 2018). However, given the cost of AZ61 in the market is three times the price of AZ31. Then, in this study, we will use AZ31 because the performance shown by AZ31 is not much different from AZ61 and AZ91.

Besides alloying Mg anode, Mg anode microstructure is also known to have a significant effect on the mechanical properties and electrochemical performance of magnesium alloys (Wong et al. 2015). Therefore, modifying the Mg anode microstructure is an excellent way to improve the performance of the Mg anode discharge. Figure 8 shows the MAFC performance using different grain size of Mg alloys. Grain size has a significant influence upon corrosion behaviour in Mg anode and Mg anodynes electrochemical operation, which may have substantial effects on the output of Mg air because of their impact on the erosion rate of Mg anode and the

polarization of Mg anode (Zhao et al. 2018). In the writings of Zhao et al. (2018), the effects of three average grain size measurements using the Mg alloy of the AZ series as Mg anode have been studied in terms of anode utilization as well as average charge voltage.

Electrolyte additive techniques primarily focus on adding chemical additives which are usually non-degradable chemicals and stay in the electrolyte (Wong & Daud 2015). Various chemical electrolyte additives that could enhance MAFC cell efficiency have been identified to date, as stated in previous review papers. This study will concentrate on four potential additives to boost the efficiency of MAFC and compare them. It included salicylate, nitriloacetate (NTA), glucoside decyllate (DG), and sodium dodecylbenzosulfonate (SDBS). The capacity to boost efficiency is outlined in Figure 9 and Table 2 for better comparison.
FIGURE 8. MAFC performance using different grain size of Mg alloys

FIGURE 9. MAFC performance by using difference electrolyte additives

TABLE 2. Summary of MAFC performance using chemical electrolyte additive

<table>
<thead>
<tr>
<th>Electrolyte additive</th>
<th>Anode utilisation (%)</th>
<th>Precipitate inhibition efficiency (%)</th>
<th>Average discharge volt (V)</th>
<th>Durability (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference NaCl</td>
<td>13.5</td>
<td>-</td>
<td>1.47</td>
<td>4.1</td>
</tr>
<tr>
<td>Salicilate</td>
<td>27.2</td>
<td>94</td>
<td>1.61</td>
<td>5.7</td>
</tr>
<tr>
<td>NTA</td>
<td>6.5</td>
<td>-</td>
<td>1.68</td>
<td>1.9</td>
</tr>
<tr>
<td>DG</td>
<td>39.4</td>
<td>-</td>
<td>1.39</td>
<td>6.1</td>
</tr>
<tr>
<td>SDBS</td>
<td>49.1</td>
<td>65.1</td>
<td>1.15</td>
<td>6.3</td>
</tr>
</tbody>
</table>
The efficiency of highlighting chemical electrolyte additives that include anode usage, corrosion inhibition efficiency and peak voltage discharge, are the main parameters used in the determination of MAFC performance. The operating conditions of almost all alloys using Mg anode series AZ alloy with 3.5 wt. % NaCl electrolyte were compared with those additives at room temperature and pressure. The result in Table 2 showed that salicylate is the perfect electrolyte additive to enhance MAFC autonomy. It is because this agent demonstrates high medium usage of the anode with a small output volume. Furthermore, it has been shown that salicylate prevents the formation of sediment inhibiting cell flow compared to SDBS and DG, which do not offer such properties (Höche et al. 2018). The ideal MAFC cell needs a high anode consumption and a high energy output. Still, the limitations of the MAFC cell themselves mean that both features are inconsistent and difficult to achieve. The selection of the most efficient electrolyte additives must, therefore, match the anode usage characteristics and energy production rate (Li et al. 2018).

CONCLUSION
This article analyses various parameters to increase the MAFC’s power generator performance. Based on the results obtained, it can be concluded that using a 10% NaCl solution as a MAFC electrolyte produces higher power density. By contrast, having the highest concentration lead to the highest corrosion rate due to higher Cl⁻ compared to lower NaCl concentration. However, incorporating anti-deposition like Tiron obviously improves the performance of Mg-air fuel cells by suppressing deposition of the discharge product and increasing anode surface area, although it reduces the optimum current density. Comparing Mg plate, AZ31, AZ61 and AZ91 as an anode, AZ61 provides high current density compared to other plates. It is due to the precipitate product released that inhibits Mg anode active erosion due to the Mg AZ61 anode’s hydrogen evolution reaction, which shows higher anodic efficiency than pure Mg anode and Mg AZ31 and AZ91 alloys. However, due to cost consideration, AZ31 is highest in generating performance per cost. Fine-grain size has a significant impact on corrosion behaviour in Mg anode and Mg anodynes electrochemical activity compared to rough and medium. Finally, in additive research, salicylate displays the most excellent additive in preventing the development of sediment-inhibiting cell flow compared to SDBS and DG that do not exhibit these properties.

ACKNOWLEDGEMENTS
Universiti Kebangsaan Malaysia funded this research under Research University Grant GUP-2018-039 and PP-SELFUEL-2020. We also appreciate the fruitful cooperation by Persatuan Nelayan Sepang.

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Received: 5 August 2020
Accepted: 11 September 2020