Influence of anodizing concentration and electric potential on surface morphology and corrosion behavior of anodized magnesium in seawater activated battery

Supriyono¹, R Oktavian¹, L P M I Wulaningfitri¹, J C Pradana¹ and I Feliana¹
¹Department of Chemical Engineering, Engineering Faculty, Brawijaya University, Jl. Mayjen Haryono number 167, Malang, postal code 6541, Indonesia
E-mail: rama.oktavian@ub.ac.id

Abstract. Magnesium is one of the newly developed anode materials for seawater activated batteries. Anodizing is usually performed to expand the surface of anode materials which can improve the battery discharge performance. This work used Oxalic acid with concentration varied from 0.1 to 0.3 as an anodizing agent with electric potential varied from 1.5 to 6.0 Volt for an anodizing process. Electric potential used in the anodizing was varied from 1.5 to 6.0 Volt. Microstructure and corrosion behavior of anodized magnesium used in this work as battery anode and graphite as a cathode in 3.5% NaCl electrolyte solution were studied. Anodized magnesium in 0.3 M oxalic acid has the most uniform pores of microstructures than those anodized at other concentrations. Anodized magnesium at electric potential from 1.5 Volts tend to has higher value of potential (Ecorr = -1.754 to -1.772 Volt) and corrosion current (Icorr = 2.790 to 11.690μA/cm2), and lower polarization resistance (Rp = 425.170 to 1024.700 Ω) than non-anodized magnesium (Ecorr = -1.649 Volt; Icorr = 10.984 μA/cm2; Rp = 895.510 Ω). Anodized magnesium at the potential from 3.0 until 6.0 Volt indicates the presence of oxidation on the surface which leads to the less good characteristic pattern of dynamic potential.

1. Introduction
Recently, seawater batteries have been gaining a considerable attention from several countries for addressing the problem increasing energy demand. The principle of this battery is utilizing seawater as an electrolyte solution. It contains electrolyte NaCl when it is dissolved in water (Koontz et al, 2002; Petter et al, 2012). NaCl in water is ionized into Na⁺ and Cl⁻ ions in which the existence of these ions can cause sea water becomes an electrolyte solution. The abundant amount of seawater becomes the advantage of the use of seawater as a electrolyte. Moreover, seawater battery can be used directly by fishermen in the sea since they can find an electrolyte easily.

Magnesium is considered as anode material for seawater battery. It is because magnesium has several benefits, such as: (1) Its relative negative standardized potential value is -2.367 Volt vs. Standart Hydrogen Electrode (SHE). This enables magnesium to generate relatively large potential electrode potential value; (2) It has high theoretical value of gravimetric charge density of 2.233 mAh/gram allowing magnesium to store large electric current; (3) Its high theoretical value density of volumetric density of 3.881 mAh/cm³ allowing magnesium to store large currents per small volumes; (4) Its abundant amount on earth. Magnesium alloys have been successfully used as marine battery anodes (Davis, 2006; Kun, et al 2012). These alloys were produced by liquefying magnesium, gallium, aluminum, zinc, lead, each having 99% purity at 973 K with atmospheric Ar₂+SFe conditions to prevent...
magnesium burning. An alloy consisting of Mg, 3% wt Ga, 2% wt Hg has larger current density discharge than AZ31 (Mg, 2.94% wt Al, 0.93% wt Zn) and AP65 (Mg, 6% wt Al, 5.08% wt Pb, 0.6% wt Mn). Wang, et al. (2012) also succeeded in using magnesium alloy as an anode of seawater battery. These alloys were produced by melting the magnesium, aluminum, zinc, lead metals each having 99% purity at 750°C under Ar atmosphere to prevent magnesium burning. Wang, et al. (2012) concluded that the AP65 microstructure is very influential on battery discharge performance. The more homogeneous the alloy microstructure the better the discharge performance. Cheng, et al (2013) successfully synthesized magnesium with the porous morphology which has better discharge performance than non-porous magnesium.

Anodizing is an electrochemical process that is performed with help of the electric current to form pores on the metal surface. The metal is connected to the positive current (anode) from a power source, while an inert electrode is used as a cathode. This anodizing process causes anode metal turns into its oxide so that the surface of the anode will be eroded and will run out at a certain time. Therefore, the pores on the metal surface will emerge as an anodizing impact. Feiyue, et al (1998) succeeded in making porous aluminum by anodizing method in weak acid solution. This study aims to develop and evaluate the anodizing method on magnesium for its surface morphology and its discharge performance as an activated seawater battery anode material.

2. Experimental

2.1 Materials and Apparatus Research

The materials research used in this study include: (1) Magnesium foil with purity of 99.50%, with the dimension of 0.15-0.30 mm thickness, and 3 mm wide supplied by Merck was used as anode material; (2) Demineralized water was used as diluent of anodizing solvents and washers; (3) Oxalic acid with purity of 99% supplied by Sigma-Aldrich was used as anodizing electrolyte solution; (4) Sodium chloride aqueous solution with concentration of 3.5% wt. was used as electrolyte solution for battery performance test; and graphite with dimension of (5 x 1 x 0.5 cm) was used as cathode when anodized. The apparatus used in this study include: (1) Electrolysis vessel that was used as anodizing reactor; (2) Power supply with constant discharge current of 1200 mA that was used as electrical energy source in anodizing process; (3) Oven (Redline Brand Binder R153) was used as dryer.

2.2 Research procedure

Magnesium foil with purity of 99.5% was polished with 1000 grid Si-C emery paper, it was then rinsed with demineralized water to clean the dirt on the surface. Furthermore, magnesium foil was dried in oven at 105°C until constant weight. Anodizing was performed in 0.1 M oxalic acid solution using magnesium foil as anode and graphite as cathode. Two electrodes were immersed in electrolytic solution at depth of 2 cm. The distance of between two electrodes was set at 1 cm. Anodizing potential was varied from 1.5 to 6.0 Volts for 7 minutes. The schematic diagram for experimental set is shown in figure 1.

![Schematic Diagram](image)

**Figure 1.** Schematic diagram for experimental setup

After anodization process, magnesium was then cleaned by rinsing with demineralized water, and then it was stirred at the temperature of 105°C to constant weight. Surface morphology was observed using
3. Results and Discussion

3.1 Microstructure

SEM images of non-anodized and anodized magnesium anodes are shown in figure 2. It can be seen that there is anodized magnesium pore in all oxalic acid concentration variables. The anodized magnesium at 0.3 M oxalic acid concentration has the most pores among the other oxalic acid concentrations of 0.1 M and 0.2 M. The more pores on a battery anode will generate larger surface area. The larger surface area will increase the discharge performance of an anode battery. As the supporting data used data of linear polarization test results.

Figure 2. SEM photos of magnesium anode without anodizing (a) and it’s anodized at potential of 1.5 Volt for 7 minutes in 0.1 M Oxalic acid (b), 0.2 M (c), and 0.3 M (d)
3.2 Linear Polarization

The linear polarization testing method was used to determine the magnesium anode corrosion behavior in 3.5% NaCl solution. The dynamic potential polarization graph of the magnesium anode at varied oxalic acid concentration and anodizing potential are shown in figure 3. The anodic branch represents the oxidation process of the magnesium anode discharging during the anode polarization. The cathodic branch represents the reduction process of the hydration of the protons. The corrosion current is evaluated from the linear polarization graph using the extrapolation of the cathodic branch returning to the corrosion potential. The measured parameters of the dynamic potential polarization graph are shown in Table 1. These parameters are the corrosion potential (E_{corr}), the corrosion current density (I_{corr}), and the polarization resistance for the magnesium anode at 3.5% NaCl solution. The standard corrosion potential for magnesium is -2.57 Volt vs. Ag/AgCl, while for non-anodized magnesium the value is -1.649 Volt at steady state condition. This difference occurs due to film formation on the magnesium surface for non-anodized one and pore formation for anodized one. Magnesium with porous morphology has better discharge performance than non-porous Magnesium (Cheng et al., 2013). It is shown from this study that anodized magnesium has more negative value of corrosion potential compared to non-anodized magnesium. For anodized magnesium with anodized potential of 1.5 Volts showed more regular dynamic potential test pattern than the one with the potential of 3.0 to 6.0 Volts. At the anodizing potential of 3.0-6.0 Volts, corrosion on the magnesium surface occurs too rapidly so that the release rate of magnesium oxide from the magnesium surface is less than the corrosion rate. This will lead to the thickening of the insulator's corroded layer. This insulator layer is not expected when it is applied as an anode battery since it will degrade the performance of its discharges. At the anodizing potential of 1.5 Volts, anodized magnesium at 0.3 M of oxalic acid concentrations showed the most negative corrosion potential value (E_{corr} = -1.772 Volt vs Ag/AgCl) among all concentrations variable (0.1 M and 0.2 M with E_{corr} = 1.754 Volt and 1.765 Volt, respectively). This anodized magnesium also exhibits greater corrosion current density than both non-anodized magnesium and anodized magnesium at oxalic acid concentration of 0.1 M and 0.2 M. Of the two parameter (potential and corrosion current) shows anodized magnesium at potential of 1.5 Volt is the most activated in 3.5% NaCl solution rather than non-anodised and anodized magnesium from potential of 3.0 Volt to 6.0 Volt.

The corrosion rate is very much related to polarization resistance (Rp). High polarization resistance (Rp) value indicates low corrosion rate and vice versa. From Table 1 it can be seen that the anodized magnesium at anodizing potential of 1.5 Volt tends to have lower polarization resistance value (Rp = 425.170 until 1024.700 Ω) than the non-anodized magnesium (Rp = 895.510 Ω) and anodized magnesium at the anodizing potential of 3.0-6.0 Volt (Rp = 783.630 until 2388.100 Ω). The increasing value of polarization resistance (Rp) is directly proportional to the increasing potential used for anodizing. The value of polarization resistance on anodized magnesium that is relatively smaller than non-anodized magnesium. Low polarization resistance indicates the formation of the film on the surface of magnesium (Yu et al., 2011; Yu et al., 2012; Yu, et al., 2015). It is indicated by thinner film formation on the anodized magnesium anode surface compared to that of non-anodized magnesium anode. The polarization resistance value of anodized magnesium at potential of 1.5 Volts has smaller tendency than the anodized magnesium anode at the potential of 3.0-6.0 Volts. This shows that the film formed on the surface of the anodized magnesium anode at potential of 1.5 Volts is thinner than that of anodized magnesium anode at potential of 3.0-6.0 volts. The charge value of the polarization resistance (Rp) determines the corrosion behavior pattern of the magnesium anode. During corrosion process, the films formed allow to inhibit activation of magnesium in 3.5% NaCl electrolyte solution. The discharge process of the magnesium anode will be inhibited. At the anode magnesium anode at potential 1.5 V volt, the Mg^{2+} ion activation process is easier and faster than in the anodized magnesium anode at 3.0-6.0 Volt and non-anodized magnesium due to the thin film formed which is proved by the lowest polarization resistance (Rp) value.
Figure 3. Potensiodynamic polarization behavior of the magnesium anode in NaCl 3.5% wt at different anodizing potential: 1.5 Volt (a), 3.0 Volt (b), 4.5 Volt (c), 6.0 Volt (d)

4 Conclusion
This study shows that the anodized magnesium at anodizing potential of 1.5 Volt and 0.3 M in Oxalic acid concentration generates more pore than the anodized magnesium at concentrations of 0.1 M and 0.2 M. Anodized magnesium at anodizing potential of 1.5 Volts tends to have higher value of corrosion potential ($E_{corr} = -1.754$ until -1.772 Volt) and current ($I_{corr} = 2.790$ until 11.690 $\mu$A/cm$^2$), and lower polarization resistance ($R_p = 425.170$ to 1024.700 $\Omega$) than non-anodized magnesium ($E_{corr} = -1.649$ Volt; $I_{corr} = 10.984$ $\mu$A/cm$^2$; $R_p = 895.510$ $\Omega$). Anodized magnesium at the anodizing potential from 3.0 until 6.0 Volt indicates the presence of oxidation process on the surface which leads to the less good characteristic pattern of dynamic potential. Anodized Magnesium at anodizing potential from 1.5 Volt exhibited satisfactory discharge performance due to its microstructure and potential dynamic characteristics.
Table 1. The parameters obtained from the graph of dynamic polarization potential

| Materials | Ecorr (Volt) | Icorr (μA/cm²) | Rp (Ω) |
|-----------|-------------|----------------|--------|
| Mg without anodizing | -1.649 | 10.984 | 895.510 |
| 0,1 M; 1,5 Volt | -1.754 | 2.790 | 1024.700 |
| 0,1 M; 3,0 Volt | -1.755 | 5.916 | 1147.200 |
| 0,1 M; 4,5 Volt | -1.792 | 8.340 | 936.900 |
| 0,1 M; 6,0 Volt | -1.593 | 1.957 | 2388.100 |
| 0,2 M; 1,5 Volt | -1.765 | 9.586 | 425.170 |
| 0,2 M; 3,0 Volt | -1.765 | 6.101 | 970.870 |
| 0,2 M; 4,5 Volt | -1.723 | 23.117 | 783.630 |
| 0,2 M; 6,0 Volt | -1.744 | 3.908 | 1116.300 |
| 0,3 M; 1,5 Volt | -1.772 | 11.690 | 586.330 |
| 0,3 M; 3,0 Volt | -1.751 | 9.599 | 1037.400 |
| 0,3 M; 4,5 Volt | -1.723 | 22.37 | 1166.600 |
| 0,3 M; 6,0 Volt | -1.655 | 1.583 | 1037.400 |

5 References
[1] Chen B, Wang R, Peng C, Feng Y, Wang N 2013 Influence of Al-Mn master alloys on microstructures and electrochemical properties of Mg-Al-Pb-Mn alloys Transaction of Nonferrous Metals Society of China 24 p 423-430
[2] Li F, Zhang L, Metzger R M 1998 On the Growth of Highly Ordered Pores in Anodized Aluminum Oxide Chem. Mater 10 p 2470-2480
[3] Davis J R 2006 Handbook of Materials for Medical Devices [M] ASM international OH: ASM International p 359–377
[4] Koontz R F, David L R 2002 Water Activated Batteries United States of America: McGraw-Hill inc.
[5] Ning G, Haran B, Popov B N 2002 Capacity fade study of lithium-ion batteries cycled at high discharge rates J. of Power Sources 117 p 160–169
[6] Petter S A, Fride V 2012 Alloys as Anode Materials in Magnesium Ion Batteries Norwegian University of Science and Technology: Department of Materials Science and Engineering
[7] Wang N, Wang R, Peng C, Feng Y, Chen B 2012 Effect of hot rolling and subsequent annealing on electrochemical discharge behavior of AP65 magnesium alloy as anode for seawater activated battery Corrosion science 64 p 17-27
[8] Yu K, Tan X, Hu Y, Chen F, Li S 2011 Microstructure effects on the electrochemical corrosion properties of Mg – 4.1% Ga – 2.2% Hg alloy as the anode for seawater-activated batteries Corrosion Science 53 p 2035–2040
[9] Yu K, Huang Q, Zhao J, Dai Y 2012 Electrochemical properties of magnesium alloy anodes discharged in seawater Transaction of Nonferrous Metals Society of China 22 p 2184-2190
[10] Yu K, Xiong H, Wen L, Dai Y, Yang S, Fan S, Teng F, Qiao X 2015 Discharge behavior and electrochemical properties of Mg-Al-Sn alloy anode for seawater activated battery Nonferrous Met. 25 p 1234-1240
[11] Zhao J, Yu K, Hu Y, Li S, Tan X, Chen F, Yu Z 2011 Discharge behavior of Mg–4 wt%Ga–2 wt%Hg alloy as anode for seawater activated battery Electrochimica Acta 56 p 8224-8231