Journal of Tropical Resources and Sustainable Science

journal homepage: jtrss.org

A Sight of Zinc Corrosion in Various Alkaline Media

W.M.I.W. Ismail, N.S.W. Zulkefeli, M.N. Masri*

Advanced Materials Research Cluster, Faculty of Earth Science, University Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia

Received 15 December 2016
Accepted 25 December 2016
Online 30 December 2016

Keywords:
alkaline electrolyte, corrosion potassium hydroxide, sodium chloride, sodium hydroxide

⌧*Corresponding author:
Dr. Mohamad Najmi Masri,
Advanced Materials Research Cluster, Faculty of Earth Science,
University Malaysia Kelantan,
17600 Jeli, Kelantan, Malaysia.
Email: najmi.m@umk.edu.my

Abstract

This review concentrates on corrosion properties that expose to zinc by various alkaline media. The assumption has been advanced that zinc corrodes electrochemically in the first stage of exposition, but the chemical corrosion prevails after a longer time. Different types of electrolyte had been tested on zinc such as sodium chloride, sodium hydroxide and potassium hydroxide. Each of alkaline media can produced corrosion product such as zinc hydroxide chloride, zinc hydroxide carbonate, zinc oxide, and zinc hydroxide. The production of corrosion products is depending on the carbon dioxide content that introduced to the air. Potassium hydroxide is the highest and active alkaline where it contains the highest ionic conductivity potassium ions, K^+ after hydronium, H_3O^+ among the cations and hydroxide, OH^- has the highest ionic conductivity among the anions.

1. Introduction

Uses of zinc (Zn) as the main material is depending on few factor such as its properties, uses and its function. For example, usage of Zn as alloy and die casting are important to the industries. Furthermore, zinc oxide (ZnO) is widely used in the manufactured of many products such as battery, paint, inks and electrical equipment. This is due to its properties high discharge efficiency and high safety features associated with its manufacturing process and use (El-Sayed, Mohran, & Abd El-Lateef, 2012).

On top of that, Zn is chosen as an anode in alkaline battery because of its capability of excellent combination physical and electrochemical properties. In addition, Zn also have a high specific energy and power density (Szczesniak et al., 1998), rechargeable, zero emission, recyclable and sustainable (Nakata et al., 2016). Other than that, Zn in alkaline solution as it is functioning of current density, temperature, solution composition, and porosity of the electrode.

Furthermore, Zn is a material that can be an electrode that has a large surface area, fairly dense, volume consumption is about three times lower than for magnesium and the dimension of the Zn anode are correspondingly smaller. The corrosion undermines the coating is prevented and the coating remains firmly attached to give its maximum life. Moreover, the property which gives Zn this valuable corrosion resistance is its ability to form a protective layer consisting of ZnO and OH^-, or of various basic salts, depending on the nature of the environment (Goodwin, 2010).

The alkaline battery electrolyte is important as it is functioning as a catalyst that conducts or promote the movement of ions from cathode to anode during charge or in reverse on discharge. There are several types of electrolyte that can be used such as sodium hydroxide (NaOH), sodium chloride (NaCl) and potassium hydroxide (KOH). Basically, alkaline battery used the KOH as an electrolyte in battery system. KOH is chosen because it can act as a strong base that can conduct the movement of ions from cathode to anode.

2. Corrosion of Zn in Different Alkaline Media

2.1. Sodium Chloride

The corrosion layer that forms on the surface of Zn when it is exposed to NaCl media was characterized where the composition of ZnO, zinc hydroxide, $\mathrm{Zn(OH)_2}$ and Zn hydroxide chloride, $\mathrm{Zn_5(OH)_8(Cl)_2.2H_2O}$ (Mouanga et al., 2007, Mouanga et al., 2010). While, Zn hydroxide carbonate was presence $(\mathrm{Zn_5(OH)_6(CO_3)_2.2H_2O})$ during the exposure of Zn in NaCl solution. However, the $(\mathrm{Zn_5(OH)_6(CO_3)_2.2H_2O})$ layer can be considered as porous layer, according to the passive region is not observed during anodic polarization experiments conducted in an aerated NaCl solution (Lin et al., 2012).

The chemistry reaction that happen in Zn when it immersed in NaCl:

eISSN Number: 2462-2389

(i) The cathodic reaction corresponds to the reduction of O_2

$$O_2 + 2H_2O + 4\bar{e} \rightarrow 4OH^- \quad \text{(Eq. 1)}$$

(ii) The anodic reaction involves the dissolution of Zn

$$Zn \rightarrow Zn^{2+} + 2\bar{e} \quad \text{(Eq. 2)}$$

It can be expected that the Zn^{2+} and the OH^- react to produce zinc hydroxide.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad \text{(Eq. 3)}$$

The pH may be high enough at very active cathodic sites for zincate ions, $Zn(OH)_4^{2-}$ to form according to equation 4.

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad \text{(Eq. 4)}$$

In the presence of NaCl, chloride ions (Cl^-) migrate to anodic sites where zinc hydroxide chloride, $Zn_5(OH)_8Cl_2$ is formed according to (5)

$$5Zn(OH)_2 + 2Cl^- + H_2O \rightarrow Zn_5(OH)_8Cl_2.H_2O + 2OH^- \quad \text{(Eq. 5)}$$

Boshkov et al., 2002 reported that Eq. (1) leads to a local increase in pH value in the depth of the corrosion damages and has, as result, the formation of $Zn_5(OH)_8Cl_2$ in the pits and their neighbourhood areas.

Zinc hydroxide carbonate, $Zn_5(OH)_6(CO_3)_2$ was also detected on Zn surface after immersion in NaCl solution. Its formation depends on the absorption of atmospheric CO_2 into the surface electrolyte and the formation of bicarbonate and carbonate according to (6) and (7).

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \quad \text{(Eq. 6)}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad \text{(Eq. 7)}$$

Sodium ions (Na^+) at cathodic areas also react with carbonate ions to form sodium carbonate. Some of carbon detected on Zn surface is due to the presence of sodium carbonate on the sample surfaces.

The formation of $Zn_5(OH)_6(CO_3)_2$ is given by the reaction of $Zn(OH)_2$ and HCO_3^- according to (8).

$$55Zn(OH)_2 + 2HCO_3^- + 2H^+ \rightarrow Zn_5(OH)_6(CO_3)_2 + 4H_2O \quad \text{(Eq. 8)}$$

Considering the characterization of the corrosion layer formed on the top of zinc that reported by some authors in the literature, in the atmospheric conditions, $Zn_5(OH)_8Cl_2$ and $Zn_5(OH)_6(CO_3)_2$ are the main corrosion products of zinc.

2.2. Sodium Hydroxide

A passivation layer forms on the top of Zn surface during the immersion in concentrated NaOH electrolyte. This phenomenon well known, in the electrolyte of NaOH, where the dissolution of Zn produces the Zn hydroxide $Zn(OH)_2$ which is not soluble in water at high pH value near to 14 (Mouanga et al., 2010). The Chemical reactions of ZnO and $Zn(OH)_2$ were detected on Zn surface after immersion in NaOH solution. It can be expected that the zincate can produce ZnO or $Zn(OH)_2$. The overall reaction is given by (9) and (12).

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2(OH)^- \quad \text{(Eq. 9)}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad \text{(Eq.10)}$$

Zinc hydroxide carbonate was also detected on zinc surface after immersion in NaOH solution. This corrosion product is formed as proposed in Eq. (6)–(8). the main corrosion products formed on the zinc surface after immersion in NaOH solution are ZnO, $Zn(OH)_2$ and $zZn_5(OH)_6(CO_3)_2$. Corrosion products formed on the Zn surface in this work correspond well to those reported in the literature (Mouanga et al., 2007).

2.3. Potassium Hydroxide

Strong base is a substance that increasing the concentration of OH^- where hydrolyses completely can accept proton and donate a pair of electrons. Strong base usually used as electrolyte. Electrolyte is a substance that containing a free ion which are carrying electric current in the electrolyte. KOH is chosen as an electrolyte because of it character as a strong base that allow the current to flow, do not gas off and remain in the cell. Besides, it contained loosely bound semi-solid jelly granules and limited amount of free KOH electrolyte available to the Zn electrode due to the high water retentivity of the gel (Othman, 2002b). However, (Iwakura et al, 2002) reported that the highest conductivity in polymer gel-KOH mixtures are achieved at 6 M KOH concentration and give maximum impact on corrosion behaviour. Besides, the failure of anode is due to capacity of ionization (OH^-) ions. Based on the previous study the failure of the anode is due to the oxidation of Zn which formed ZnO layer (Mohamad, 2006).

Researcher reported that 6 M of KOH is the maximum concentration due to the very high ionic conductivity and high mobility of OH^- anion in water solutions. KOH is mostly used because apparently K^+ is the highest ionic conductivity after H_3O^+ among the cations and OH^- has the highest ionic conductivity among the anions. Thus, KOH proposed in literature that chloride ions may react with zincate to form Zn hydroxychloride complex that has a higher solubility that zincate, thus it make hinder formation of ZnO and increase utilization (Ippolito et al., 2016). The chemistry reaction:

i) Zinc Plate in Potassium Hydroxide Electrolyte

The Zn plate anode chemistry discharge in an alkaline electrolyte is represented by equation (11):

$$Zn + \tfrac{1}{2}O_2 + H_2O + 2(OH)^- \rightarrow Zn(OH)_4^{2-} \quad \text{(Eq. 11)}$$

The reaction of Zn in Zn-air batteries during discharge are simultaneous and the use of an O_2 reducing catalyst in an air-cathode results in the reduction of the O_2 adsorbed from the surrounding air (Iyuke et al., 2003; Genies et al., 2003) The reactions are presented in equation (12):

$$O_2 + 2H_2O + 4e \leftrightarrow 4OH^- \quad \text{(Eq. 12)}$$

The reaction of the preliminary discharge at the Zn electrode can be expressed by equation (13) (Othman, 2002):

$$Zn + 4OH^- \leftrightarrow Zn(OH)_4^{2-} + 2e \quad \text{(Eq. 13)}$$

This reaction proceeds until the zincate $[Zn(OH)_4^{2-}]$ ion reaches saturation point because the super saturation rate is time dependent. This effect is caused by the solubility of the anion in the electrolyte. Thus, the stable solubility stage is exceeded upon complete discharged, which results in the formation ZnO precipitate (Alias et al., 2010; El-lateef et al., 2015). This reaction can be presented as equation (14):

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2(OH)^- \quad \text{(Eq. 14)}$$

The overall battery reaction may be simplified as equation (15) (Kar et al.,2014):

$$Zn + \frac{1}{2}O_2 \leftrightarrow ZnO \quad \text{(Eq. 15)}$$

The tendency of Zn to corrode during battery storage remains difficult problem that should be addressed. Hence, researches have investigated the electrochemical reaction involved in alkaline solution. The predominant oxidized products of the aforementioned reactions are generally believed to be $Zn(OH)_4^{2-}$. Nevertheless, most researchers believe that the passive film contain ZnO.

ii) Reaction in the Electrolyte

Where the reaction at the electrolyte is given as following:

$$Zn + KOH \rightarrow ZnO + \frac{1}{2}H_2 + K^+ \quad \text{(Eq. 16)}$$

When the Zn is immersed into the electrolyte, the reaction of this strong base electrolyte to the Zn is reacted. The KOH break their bond where the O_2 is deposited at the surface of the Zn. Which the form of ZnO is the passive film that function as to protect the Zn itself from corrode. The K^+ remain in the solution. Its due to its properties that high in ionic conductivity. The production of H_2 in the electrolyte will release to the air.

3. Conclusion

In conclusion, it can have been stated that the corrosion products formed on Zn sample in three types of alkaline media which were NaCl with corrosion products of $Zn_5(OH)_8Cl_2$ and $Zn_5(OH)_6(CO_3)_2$. While, NaOH with corrosion products of ZnO, $Zn(OH)_2$ and $Zn_5(OH)_6(CO_3)_2$ and KOH with corrosion products of ZnO. Based on this three it can be compared by their behaviour in this three media of alkaline, the corrosion layer that formed on the Zn surface that immersed in NaOH more compact that the others solution.

Acknowledgements

This work was supported by Research Accularation Grant Scheme (R/RAGS/A08.00/01136A/001/2015/000197). Authors also would like to thank to Faculty of Earth Science to provide characterization equipment during characterization.

References

Alias, S. S., Ismail, A. B., & Mohamad, A. A. (2010). Effect of pH on ZnO nanoparticle properties synthesized by sol – gel centrifugation. Journal of Alloys and Compounds, 499(2), 231–237.

El-lateef, H. M. A. B. D., & Mohran, H. S. (2015). Role of nickel alloying on anodic dissolution behavior of zinc in 3 . 5 % NaCl solution . Part II : Potentiodynamic , potentiostatic and galvanostatic studies. Transactions of Nonferrous Metals Society of China, 25(9), 3152–3164.

El-Sayed, A. R., Mohran, H. S., & Abd El-Lateef, H. M. (2012). Corrosion study of zinc, nickel, and zinc-nickel alloys in alkaline solutions by Tafel plot and impedance techniques. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 43(2), 619–632.

F.E.Goodwin. (2010). Corrosion of Zinc and its Alloys. International Lead Zinc Research Organization, 1, 2078–2093. Journal Article.

Genies, L., Bultel, Y., Faure, R., & Durand, R. (2003). Impedance study of the oxygen reduction reaction on platinum nanoparticles in alkaline media, 48, 3879–3890.

Ippolito, N. M., Belardi, G., Medici, F., & Piga, L. (2016). Utilization of automotive shredder residues in a thermal process for recovery of manganese and zinc from zinc – carbon and alkaline spent batteries. WASTE MANAGEMENT.

Iyuke, S. E., Bakar, A., Amir, A., Kadhum, H., Daud, W. R. W., & Rachid, C. (2003). Improved membrane and electrode assemblies for proton exchange membrane fuel cells, 114, 195–202.

Kar, M., Simons, T. J., & Macfarlane, D. R. (2014). Ionic liquid electrolytes as a platform for rechargeable metal – air batteries : a perspective. Physical Chemistry Chemical Physics, 16, 18658–18674.

Lin, Z., Li, X., & Xu, L. (2012). Electrodeposition and Corrosion Behavior of Zinc-Nickel Films Obtained From Acid Solutions : Effects of TEOS as Additive, 7, 12507–12517

Mohamad, A. A. (2006). Zn/gelled 6 M KOH/O2 zinc-air battery. Journal of Power Sources, 159(1 SPEC. ISS.), 752–757.

Mouanga, M., Berçot, P., & Rauch, J. Y. (2010). Comparison of corrosion behaviour of zinc in NaCl and in NaOH solutions . Part I : Corrosion layer characterization. Corrosion Science, 52(12), 3984–3992.

Nakata, A., Arai, H., Yamane, T., Hirai, T., & Ogumi, Z. (2016). Preserving Zinc Electrode Morphology in Aqueous Alkaline Electrolytes Mixed with Highly Concentrated Organic Solvent Cdl Re Rct Zw, 163(2), 50–56.

Othman, R., Yahaya, A. H., & Arof, A. K. (2002). Zinc-Air Cell with KOH-Treated Agar Layer between Electrode and Electrolyte Containing Hydroponics Gel. Journal of New Materials for Electrochemical Systems, 5(3), 177–182.

Szczesniak, B., Cyrankowska, M., & Nowacki, A. (1998). Corrosion kinetics of battery zinc alloys in electrolyte solutions). Science, 130–138.