

A Sighting of Zinc Corrosion in Various Alkaline Media

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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.

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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 (Szczeniak 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, $Zn(OH)_2$ and Zn hydroxide chloride, $Zn_5(OH)_8(Cl)_2 \cdot 2H_2O$ (Mouanga et al., 2007, Mouanga et al., 2010). While, Zn hydroxide carbonate was presence ($Zn_5(OH)_6(CO_3)_2 \cdot 2H_2O$) during the exposure of Zn in NaCl solution. However, the ($Zn_5(OH)_6(CO_3)_2 \cdot 2H_2O$) 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:

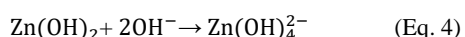
- (i) The cathodic reaction corresponds to the reduction of O_2
- $$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (\text{Eq. 1})$$

- (ii) The anodic reaction involves the dissolution of Zn
- $$Zn \rightarrow Zn^{2+} + 2e^- \quad (\text{Eq. 2})$$

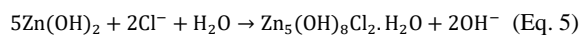
It can be expected that the Zn^{2+} and the OH^- react to produce zinc hydroxide.



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

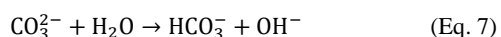
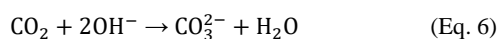


In the presence of NaCl, chloride ions (Cl^-) migrate to anodic sites where zinc hydroxide chloride, $Zn_5(OH)_8Cl_2$ is formed according to (5)



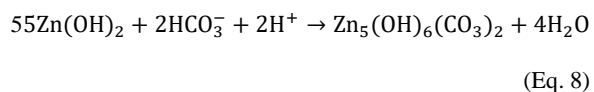
Boshkov et al., 2002 reported that Eq. (1) leads to a local increase in pH value in the depth of the corrosion damages and has, as result, the formation of $Zn_5(OH)_8Cl_2$ in the pits and their neighbourhood areas.

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).



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).

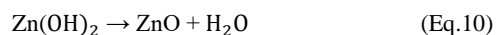
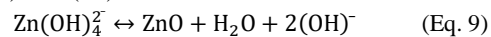


Considering the characterization of the corrosion layer formed on the top of zinc that reported by some authors in the literature, in the atmospheric conditions, $Zn_5(OH)_8Cl_2$ and $Zn_5(OH)_6(CO_3)_2$ are the main corrosion products of zinc.

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).



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).

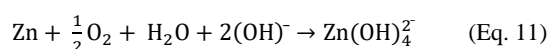
2.3. Potassium Hydroxide

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

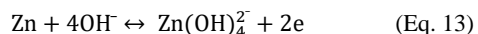
The Zn plate anode chemistry discharge in an alkaline electrolyte is represented by equation (11):



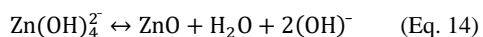
The reaction of Zn in Zn-air batteries during discharge are simultaneous and the use of an O₂ reducing catalyst in an air-cathode results in the reduction of the O₂ adsorbed from the surrounding air (Iyuke et al., 2003; Genies et al., 2003) The reactions are presented in equation (12):



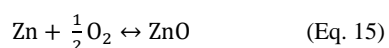
The reaction of the preliminary discharge at the Zn electrode can be expressed by equation (13) (Othman, 2002):



This reaction proceeds until the zincate [Zn(OH)₄²⁻] 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):



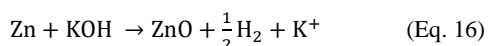
The overall battery reaction may be simplified as equation (15) (Kar et al., 2014):



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)₄²⁻. 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:



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 O₂ 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 H₂ 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 Zn₅(OH)₈Cl₂ and Zn₅(OH)₆(CO₃)₂. While, NaOH with corrosion products of ZnO, Zn(OH)₂ and Zn₅(OH)₆(CO₃)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.

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