

The effect of zinc on the aluminum anode of the aluminum–air battery

Yougen Tang^a, Lingbin Lu^a, Herbert W. Roesky^{b,*}, Laiwen Wang^a, Baiyun Huang^a

^a Institute of Chemical Power Source and Material, Central South University, Changsha 410083, China

^b Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

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Abstract

Aluminum is an ideal material for batteries, due to its excellent electrochemical performance. Herein, the effect of zinc on the aluminum anode of the aluminum–air battery, as an additive for aluminum alloy and electrolytes, has been studied. The results show that zinc can decrease the anodic polarization, restrain the hydrogen evolution and increase the anodic utilization rate.

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1. Introduction

The aluminum–air battery which is mainly made of aluminum has many advantageous properties, such as abundance, low cost, innocuousness, high power density, high energy density, etc. [1]. A comparison of the metal hydride nickel battery and the lithium ion battery with the aluminum–air battery resulted in an enormous advantage of the battery technology and power supply [2]. However, the aluminum–air battery cannot be applied on a commercial scale, due to the high corrosion and hydrogen evolution of aluminum in the electrolyte, which leads to a sharp reduction of the anodic efficiency. Moreover an oxide film that covers the surface of aluminum decreases the anodic voltage efficiency, and cumbrous cell reactions are going on. Hence, to improve its performance some trace elements often are added. There are two routes to prepare the alloys: firstly the minor elements are added directly to the melt of the alloy [3], secondly the additives are introduced into the electrolyte [4]. We investigated the effect of zinc on the aluminum anode using various physical methods. This paper mainly reports on the effect of adding zinc to the Al–In alloy anode of the aluminum–air battery.

2. Experimental methods

In a resistance furnace with a corundum crucible two kinds of Al–In–Zn alloys were prepared in the temperature range of 750–800 °C. For the first alloy the contents of In and Zn are 0.10% and 3.48% respectively, whereas those of the second alloy are 0.22% and 3.00%. The alloys function as the aluminum anode. The purity of aluminum (99.99%) is lower compared to that of In (99.999%) and Zn (99.999%). The thickness of the electrode is about 1 mm, and the working area 1 cm². The nonworking area is covered by AB gum (a commercially reagent). The working area was polished step by step with different grain sizes of sand paper, the oil was removed with acetone, washed with distilled water, and dried in vacuum. A nickel slice acted as the counter electrode, whereas a saturated Hg/HgCl₂ electrode was used as the reference electrode. The electrolyte consists of an aqueous NaOH (4 mol L⁻¹) and NaCl (0.5 mol L⁻¹) solution and ZnCl₂ as an additive.

2.1. Determination of the surface of the aluminum electrodes

The surface of the investigated electrodes was analyzed by a KYKY-2800 type electronic microscope (SEM), for producing surface images with high resolution The Finder1000

* Corresponding author. Tel.: +49 551 393001; fax: +49 551 393373.
E-mail address: hroesky@gwdg.de (H.W. Roesky).

apparatus (EDAX) was used for analyzing the segregative phase of the aluminum alloy and the composition of the surface.

2.2. Determination of the aluminum anodic polarizing curve, cyclic voltammetry curve and ac resistance diagram

The anode polarizing curve, cyclic voltammetry curve and ac resistance diagram were tested using the Electrochemistry Work Station CHI660A of Shanghai Zhenghua Instrument Company. The three-electrode electrolytic cell system (Fig. 1) was used. The scanning scope of the anodic polarizing curve was 0.0–2.0 V, while the scanning speed was 0.002 V s^{-1} . The scanning scope of the cyclic voltammetry curve was 0.005 V s^{-1} . The ac impedance spectrum has been tested under the cut-off voltage of the electrode.

2.3. Determination of the aluminum anode hydrogen evolution curve

2.3.1. Determination of the aluminum anode hydrogen evolution curve in alkaline solution

The hydrogen evolution rate of the aluminum alloy was measured using a capacity flask with a graduated tube in alkaline solution. The hydrogen evolution rate is represented by the volume of hydrogen that was released from the consumption of aluminum alloy.

2.3.2. Determination of the aluminum anode hydrogen evolution curve in neutral solution

A funnel was placed above the operational electrode and connected with a graduated tube to collect the released hydrogen and to measure its volume. The measurements were completed under constant electric current at the operational electrode. The volumes of hydrogen were measured after each electrode had been polarized for about 32 min, and which were converted to hydrogen evolution current density

using the following equation:

$$i_{\text{H}_2} = \frac{2PVF}{RTSt} = \frac{Q}{St} = 127.5 \frac{V}{t} \quad (1)$$

where i_{H_2} is the hydrogen evolution current density (mA cm^{-2}); S , the area of the aluminum electrode (cm^2); t , time of collecting H_2 (h); V , volume of collected H_2 (mL); T , temperature of experiment ($^\circ\text{C}$); P , air pressure (1 atm); R , ideal gas constant; F , Faraday constant.

3. Results and discussion

3.1. The surface status of aluminum alloy electrodes

The purpose of adding indium and zinc to the aluminum electrodes is to produce holes in the oxide film of aluminum, and hence decrease the resistance. Furthermore elements such as indium and zinc can form a low-melting alloy with aluminum, and improve the aluminum electrode in such a way that the discharge can occur under high-rate current. In addition zinc as an alloying component can promote alloying of indium with aluminum. Finally, zinc can increase the hydrogen evolution potential of the aluminum electrode, which results in a decrease in hydrogen evolution and lowering of the aluminum corrosion.

In Figs. 2 and 3 the SEM photograph and the corresponding EDAX diagram are shown. Indium and zinc exist in the Al–In–Zn alloy in form of a segregative phase, and are homogeneously distributed. A segregative phase is the origin of the corrosion of the alloy, and it is also the origin of the activation of the aluminum anode. In an early state of dissolving the alloy, the indium enriched segregative phase is dissolved at the anode firstly under exposing the aluminum-matrix. The activation of the aluminum has been thus promoted. Afterwards the segregative phase separates and sheds from the aluminum base. The shedding of the segregative phase is one

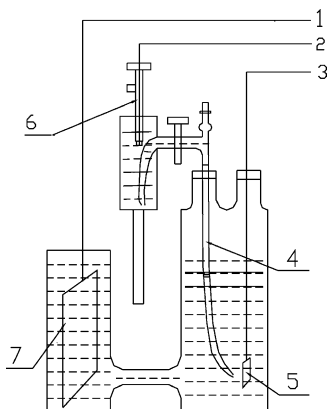


Fig. 1. The three-electrode electrolytic cell system Figure. (1) Connection to the counter electrode; (2) connection to the reference electrode; (3) connection to the operational electrode; (4) Luggin capillary; (5) Al alloy; (6) Hg/HgCl₂ electrode; (7) nickel slice.

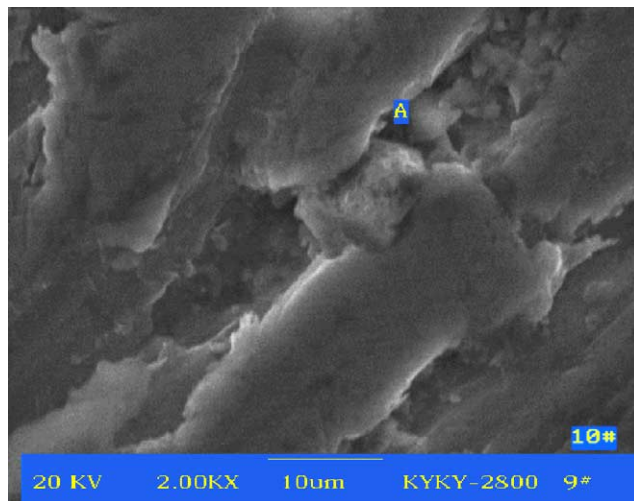


Fig. 2. SEM photo of Al–In–Zn alloy.

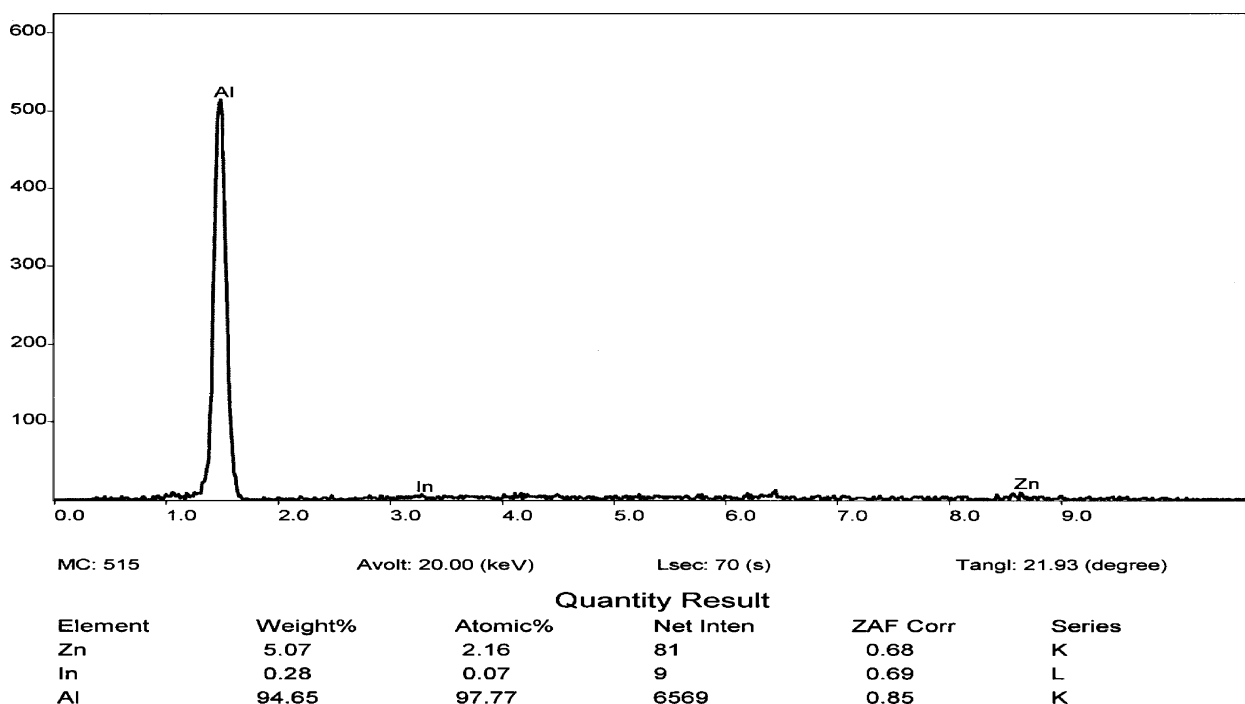


Fig. 3. EDAX diagram of point A on Al-In-Zn alloy.

of the reasons that the current efficiency drops. Moreover the aluminum will form a new galvanic couple with the Al_2O_3 film. Its potential difference is large, and the driving force for dissolving aluminum is very strong. Therefore aluminum will be activated and largely dissolved. However the indium-enriched phase turns cathodic and In^{3+} sediments are formed on the surface of the alloy. This is supported by the fact that the dissolving of indium in the aqueous phase is stopped.

Obviously the addition of zinc to the aluminum alloy decreases the number of the indium-enriched segregative phases. The existence of zinc promotes indium alloying with aluminum. The elements In, Zn, Bi, Pb, and Al give a low temperature melting alloy that forms a clear melt in the liquid phase. However in the solid state it forms low temperature melting crystals, which have an In-Zn enriched composition. This is also shown in the SEM photograph of the Al-In-Zn alloy.

3.2. The electrochemical character of Al-In-Zn alloys in alkaline solution

3.2.1. Tafel polarizing curve, cyclic voltammetry curve, and hydrogen evolution curve of aluminum anode in NaOH

The Tafel polarizing curves of pure aluminum and the first Al-In-Zn alloy in NaOH (4 mol L^{-1}) are shown in Fig. 4. The corrosive potential of this alloy is at -1.64 V (versus SCE) and about 70 mV lower than that of pure aluminum. Additionally there is a flat line at about -1.4 V . An oxidative peak of this alloy appears at about -1.4 V as shown in Fig. 5. As the potential of $Zn/Zn(OH)_2$ is -1.216 V (versus SCE),

the peak may be due to the Zn oxidative peak when compared with the Tafel polarizing curve of aluminum.

In the polarizing process a layer of $Zn(OH)_2$ can be observed covering the surface of the aluminum electrode. This $Zn(OH)_2$ film obstructs the contact between aluminum and the electrolyte, and thus weakens the hydrogen evolution. Moreover with the increase of zinc and indium the rate of hydrogen evolution becomes slower. This is demonstrated in Fig. 6.

3.2.2. Ac impedance spectrum of the aluminum anode

Through analyzing the frequency and shape of the ac impedance spectrum, which vary with the conditions of

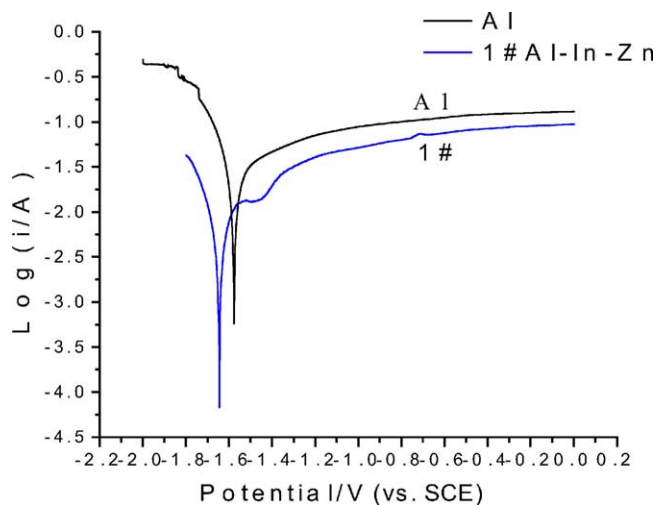


Fig. 4. Tafel polarizing curve of Al and Al-In-Zn alloy anode.

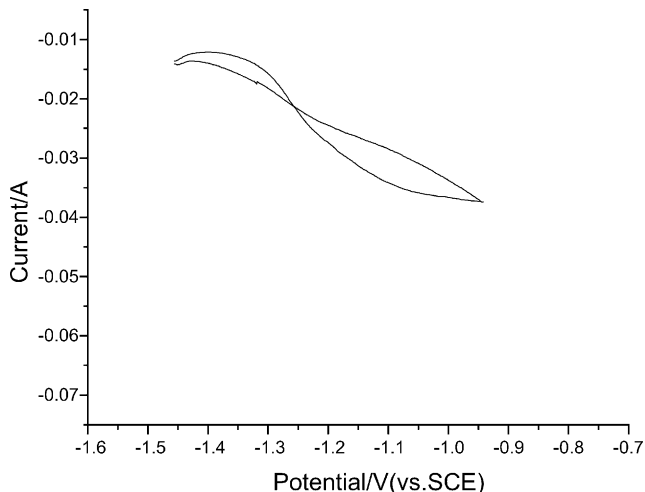


Fig. 5. Cyclic voltammery curve of Al-In-Zn alloy anode.

preparation and reaction of the electrode system, important information about the electrode process can be obtained. In this paper we adopted a big surface counter electrode, thereby only the interface resistance of the operational electrode and the resistance of the solution have been considered.

Fig. 7 shows the ac impedance spectrum of the Al-In-Zn alloy electrode. It can be seen that the ac impedance spectrum of Al-In-Zn alloy is composed of three parts: (1) an inductive impedance part in the high frequency region, (2) a capacitive impedance one in the middle frequency region, (3) a capacitive impedance part in the low frequency region. In the diagram, the inductive impedance spectrum in the high frequency region might be due to the adsorption of H_2 produced by the hydrogen evolution reaction. The capacitive impedance part of the spectrum in the middle frequency region might result from the interfacial electrochemical reactions. The capacitive impedance spectrum in the low frequency region might be due to thickening of the oxide film on the surface of the electrode. The surface film of the Al-In-Zn alloy electrode differs from that of pure aluminum and the Al-In alloy. The formed $Zn(OH)_2$ precipitate that

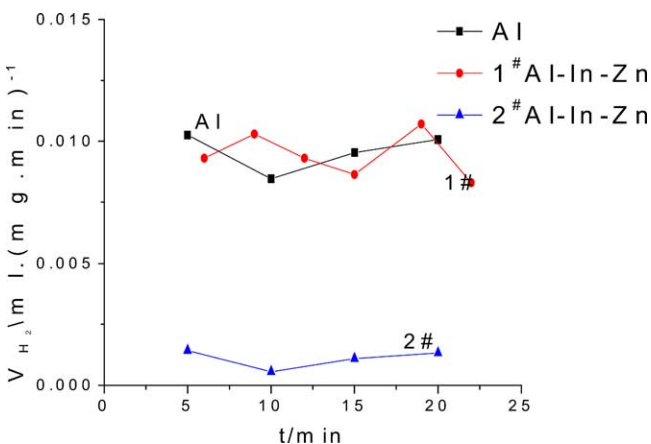


Fig. 6. Hydrogen evolution curve of pure Al, first and second alloy.

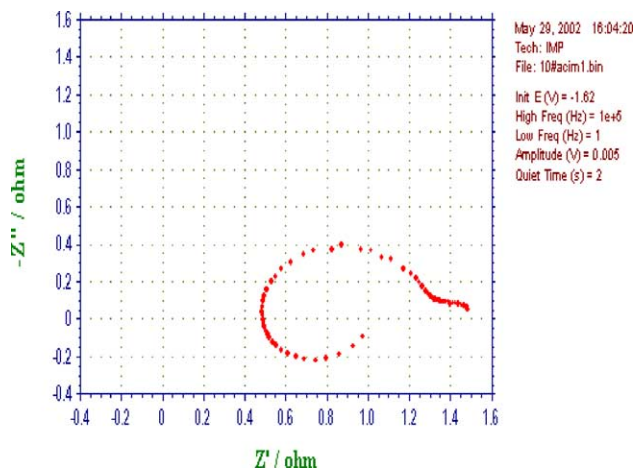


Fig. 7. ac impedance spectrum of the Al-In-Zn alloy at the electrode potential.

has been adsorbed on the surface destroyed the original aluminum oxide film. Therefore an inductive impedance could not be formed in the low frequency region.

3.3. Effects of $ZnCl_2$ additive on the electrochemical characters of aluminum alloy in neutral electrolyte

3.3.1. Effects of $ZnCl_2$ additive on polarizing curve of aluminum alloy

Fig. 8 shows the polarizing curves of Al-In alloy in NaCl (0.5 mol L^{-1}) with various concentrations of $ZnCl_2$. As it can be seen from the diagram, in aqueous NaCl, the addition of Zn^{2+} can largely improve the polarization of the Al-In alloy anode and shifts the activation potential of the electrode to more negative values. The degree of polarization is different with different concentrations of $ZnCl_2$. As shown in Fig. 8, when the concentration of Zn^{2+} was $2.0 \times 10^{-3} \text{ mol L}^{-1}$, the activation potential shifts 60 mV to the negative side. It is interesting to note that when the concentration of Zn^{2+} increases to $5.8 \times 10^{-3} \text{ mol L}^{-1}$, the activation potential shifts to negative nearly by 300 mV! However, when the concentration of Zn^{2+} continuously increases to $7.7 \times 10^{-3} \text{ mol L}^{-1}$, the activation potential shifts to negative only by 70 mV. The following steps for the activation might be possible [5]: when Zn^{2+} is reduced to the metal by aluminum and deposited on the surface of the electrode, zinc exerts the cooperative function on activation of the aluminum alloy electrode with indium. While indium is enriched between the aluminum and the oxide film, it could separate from the oxide film. The enriched zinc in the oxide film could destroy the tightness of the oxide film and consequently the surface of the aluminum alloy could be activated and dissolved.

3.3.2. Effect of $ZnCl_2$ as an additive on the hydrogen evolution curve of the Al-In alloy

Fig. 9 demonstrates the hydrogen evolution curves of the Al-In alloy in NaCl (0.5 mol L^{-1}) with various concentra-

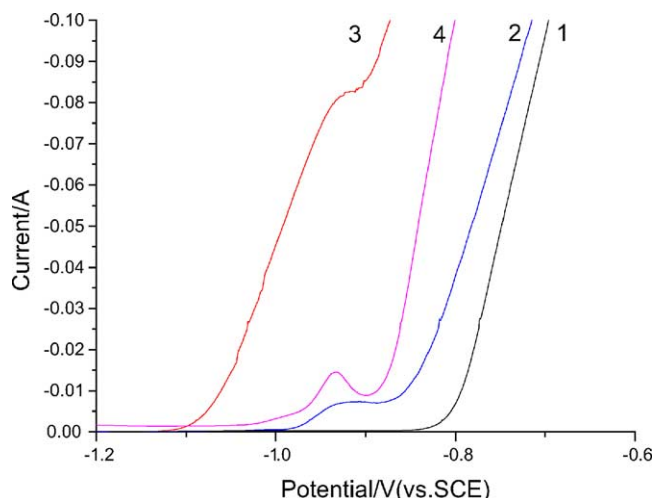


Fig. 8. The polarizing curves of Al–In alloy in the electrolyte of NaCl with ZnCl₂. (1) NaCl (0.5 mol L⁻¹); (2) NaCl (0.5 mol L⁻¹) and ZnCl₂ (2.0 × 10⁻³ mol L⁻¹); (3) NaCl (0.5 mol L⁻¹) and ZnCl₂ (5.8 × 10⁻³ mol L⁻¹); (4) NaCl (0.5 mol L⁻¹) and ZnCl₂ (7.7 × 10⁻³ mol L⁻¹).

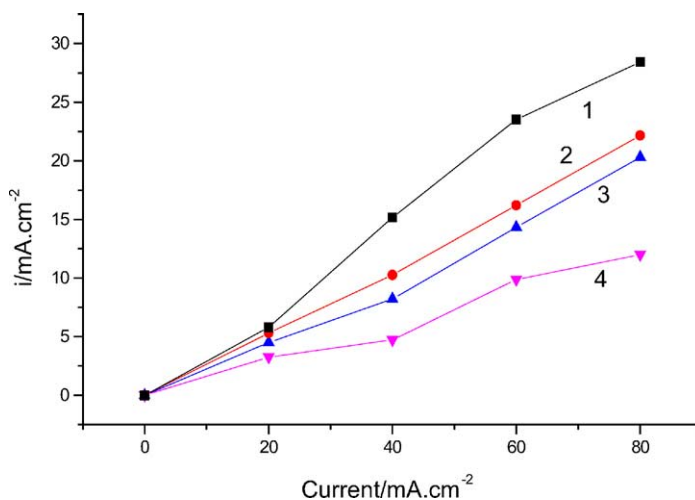


Fig. 9. The hydrogen evolution curves of the Al–In alloy in the electrolyte of NaCl with ZnCl₂. (1) NaCl (0.5 mol L⁻¹); (2) NaCl (0.5 mol L⁻¹) and ZnCl₂ (2.0 × 10⁻³ mol L⁻¹); (3) NaCl (0.5 mol L⁻¹) and ZnCl₂ (5.8 × 10⁻³ mol L⁻¹); (4) NaCl (0.5 mol L⁻¹) and ZnCl₂ (7.7 × 10⁻³ mol L⁻¹).

tions of ZnCl₂. From the diagram it can be seen that along with increasing Zn²⁺ in the electrolyte, the effect on repressing the hydrogen evolution is more and more obvious, although the aluminum negative difference effect cannot be changed in the aqueous NaCl solution. The reason for this might be that along with increasing concentration of the Zn²⁺, more zinc is accumulated on the surface of the alu-

minum alloy. Due to the electrode potential of zinc that is more negative than the potential of indium, but more positive than that of aluminum, there are three tiny batteries on the superficial aluminum alloy: In–Zn, In–Al and Zn–Al. Zinc and indium exist as the cathode, and the hydrogen evolution occurs on their surface. As they are metals with higher over-potential for hydrogen evolution, zinc and indium can restrain the hydrogen evolution at aluminum alloy electrodes.

Table 1
Electrochemical parameters of the Al–In Alloy in NaCl (0.5 mol L⁻¹) solution

ZnCl ₂ (mol L ⁻¹)	Electrode potential (V)	Self-corrosion potential (V)
0	-0.79	-0.95
2.0 × 10 ⁻³	-1.06	-1.15
5.8 × 10 ⁻³	-1.07	-1.28
7.7 × 10 ⁻³	-1.00	-1.42

3.3.3. Other electrochemical parameters of the Al–In alloy

As shown in Table 1, with the increase of Zn²⁺, the electrode potential shifted to the negative direction. The self-corrosion potential also became more negative.

4. Conclusions

In summary, the addition of zinc can lower the anodic polarization, decrease the hydrogen evolution and shift the electrode potential to negative values.

In aqueous alkaline solution, the corrosion potential of the Al–In–Zn alloy electrode is about 70 mV more negative than that of pure aluminum, therefore zinc helps to lower the aluminum anodic polarization. Moreover $\text{Zn}(\text{OH})_2$ covers the surface of the electrode in the process of polarization and consequently decreases the hydrogen evolution.

In the neutral electrolyte of NaCl (0.5 mol L^{-1}) and ZnCl_2 ($5.8 \times 10^{-3} \text{ mol L}^{-1}$), the activation potential shifts to negative nearly by 300 mV and the effect of eliminating the polarization is the best. Furthermore, hydrogen evolution decreases and the self-corrosion potential shifts to more negative values with increasing concentrations of Zn^{2+} .

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