Int. J. Electrochem. Sci., 7 **(2012)** 12254 - 12261

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Behavior of Magnesium Alloys as Biodegradable Materials in Phosphate Buffer Saline Solution

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Received: 9 October 2012 / *Accepted:* 21 October 2012 / *Published:* 1 December 2012

The electrochemical behavior of extruded AZ31E and AZ91E alloys was investigated in Phosphate Buffer Saline (PBS) Solution of pH 7.4 at 37 °C. The behavior of the two alloys was studied with immersion time by using electrochemical impedance spectroscopy (EIS). Polarization measurements are carried out to study the corrosion rate. It was found that the corrosion resistance of AZ91E alloy is higher than that of AZ31E using EIS tests and this is confirmed by polarization tests. Also, the effect of adding 10^{-3} M concentration of 2-thiouracil and L-tyrosine as inhibitor in PBS solution for AZ91E alloy was studied. The corrosion was inhibited by addition of L-tyrosine more than 2-thiouracil.

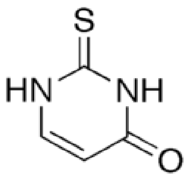
Keywords: AZ31E; AZ91E; EIS; PBS solution.

1. INTRODUCTION

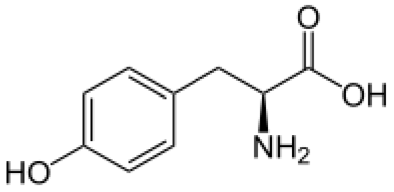
Magnesium and its alloys are used in different applications like computer parts, mobile phones, etc. [1-5]. The development of biodegradable implants is one of the most important research areas in medical science. Mg alloys can gradually be dissolved and absorbed after implanting, so it has been recently regarded as a potential biodegradable implant material due to its low density, high strength/weight ratio and its similar elastic modulus to that of human bone (40–57 GPa) [6-7]. Mg or its alloys are non-toxic to the human body. There is growing evidence that if the releasing of Mg^{2+} is acceptable by human body, it will help to stimulate the healing of bone tissue [8–10]. Magnesium has a high negative standard electrode potential (−2.37 V at 25 °C) and thus is corroded relatively faster than other metallic materials, especially in Cl^{-} containing media indicating that it can be corroded in a human body, so after the recovery or healing of the bone. The implant should be gradually dissolved, consumed or absorbed by the human body and doesn’t need another surgery to remove it.

Phosphate buffered saline (abbreviated PBS) is a buffer solution commonly used in biological research. It is a water-based salt solution containing sodium chloride, sodium phosphate, potassium chloride and potassium phosphate. The buffer's phosphate groups help to maintain a constant pH. The osmolarity and ion concentrations of the solution usually match those of the human body (isotonic). PBS has many uses because it is isotonic and non-toxic to cells.

The present study aims to investigate the influence of PBS solution on magnesium-based AZ91E and AZ31E alloys (biodegradable materials for temporary implant) with immersion time at 37°C. Furthermore, to decrease the corrosion rate of less corroded alloy AZ91E, the effect of adding 2-ThioUracil and L-Tyrosine to PBS solution is done.



2-ThioUracil
M.wt. = 128.2



L-Tyrosine
M.wt. = 181.2

2. EXPERIMENTAL

An extruded magnesium aluminum alloys (AZ31E, AZ91E) donated from Department of mining, Metallurgy and Materials Engineering, Laval University, Canada with chemical composition (wt%): 2.8 Al, 0.96 Zn, 0.28 Mn, 0.0017 Cu, 0.0111 Fe, 0.0007 Ni, 0.0001 Be and balance Mg for AZ31E and 9.0 Al, 0.7 Zn, 0.13 Mn, 0.03 Cu, 0.01 Si, 0.006 Fe, 0.004 Ni, 0.0007 Be and balance Mg for AZ91E. The sample was divided into small coupons. Each coupon was welded to an electrical wire and fixed with Araldite epoxy resin in a glass tube leaving cross-sectional area of the specimen 0.2 cm^2 for both AZ91E and AZ31E alloy. The solution used was Phosphate Buffer Saline with composition:

Composition of PBS		
Salt	Concentration (mmol/L)	Concentration (g/L)
NaCl	137	8.01
KCl	2.7	0.20
$Na_2HPO_4 \cdot 2\ H_2O$	10	1.78
KH_2PO_4	2.0	0.27
pH	7.4	7.4

2-ThioUracil and L-Tyrosine are Analar and solutions are prepared using triply distilled water. The surface of the test electrode was mechanically polished by emery papers with 400 up to 1000 grit to ensure the same surface roughness, degreasing in acetone, rinsing with ethanol and drying in air. The cell used was a typical three-electrode one fitted with a large platinum sheet of size 15×20×2mm as a counter electrode (CE), saturated calomel (SCE) as a reference electrode (RE) and the alloy as the working electrode (WE). The impedance diagrams were recorded at the free immersion potential (OCP) by applying a 10 mV sinusoidal potential through a frequency domain from 100 kHz down to 100 mHz. The instrument used is the electrochemical workstation IM6e Zahner-elektrik, GmbH, (Kronach, Germany).The electrochemical experiments were always carried inside an air thermostat which was kept at 37°C.

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance measurements in PBS solution

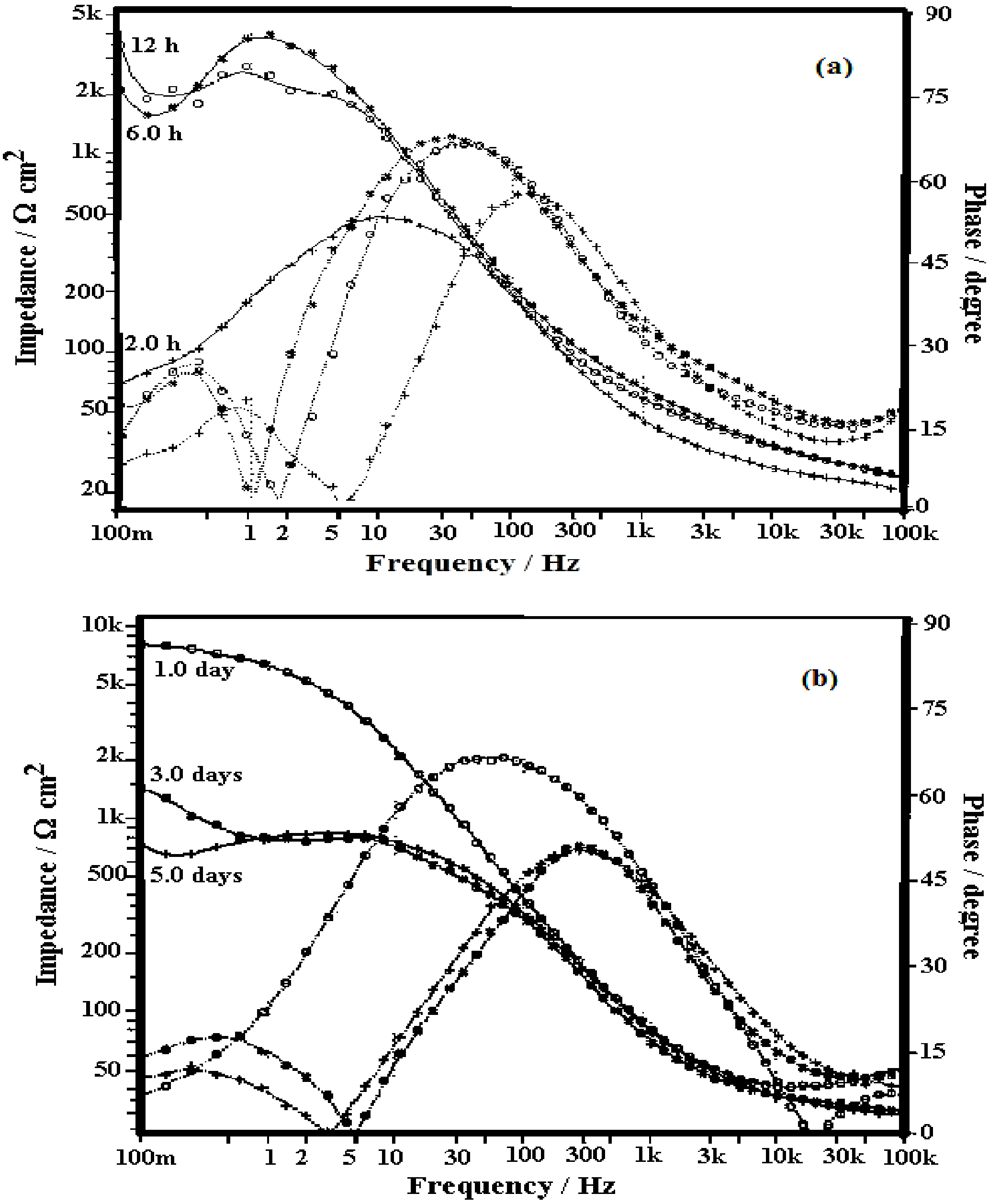


Figure 1. Bode Plots of AZ31E alloy in PBS solution at 37°C.

Fig. 1(a,b) and Fig. 2(a,b) show EIS scans as Bode plots at different immersion times (5 days = 120 hr) for AZ31E and AZ91E, respectively, in PBS solution at 37°C. It can be seen that these diagrams for both alloys show resistive regions at high and low frequencies. For AZ31E alloy as shown in Fig.1a the impedance (|*Z*|) as well as the phase shift θ for both alloys is found to increase with time till reaching 24h (1 day) and this may be due to incorporation of Cl^- ions through defect sites and formation of resistive transitory compounds in the film with time [11] and also due to adsorption of phosphate ions. The same behavior occurs for AZ91E alloy as shown in Fig.2a till reaching 3 days. And then impedance values for both tested alloys decrease sharply after 1 day for AZ31E and 3 days for AZ91E. This trend is most likely due to a decrease in the adsorbed amount of anions forming PBS solution as Cl^-, H_2PO^{4-} or HPO_4^{2-} on the electrode surface [12].

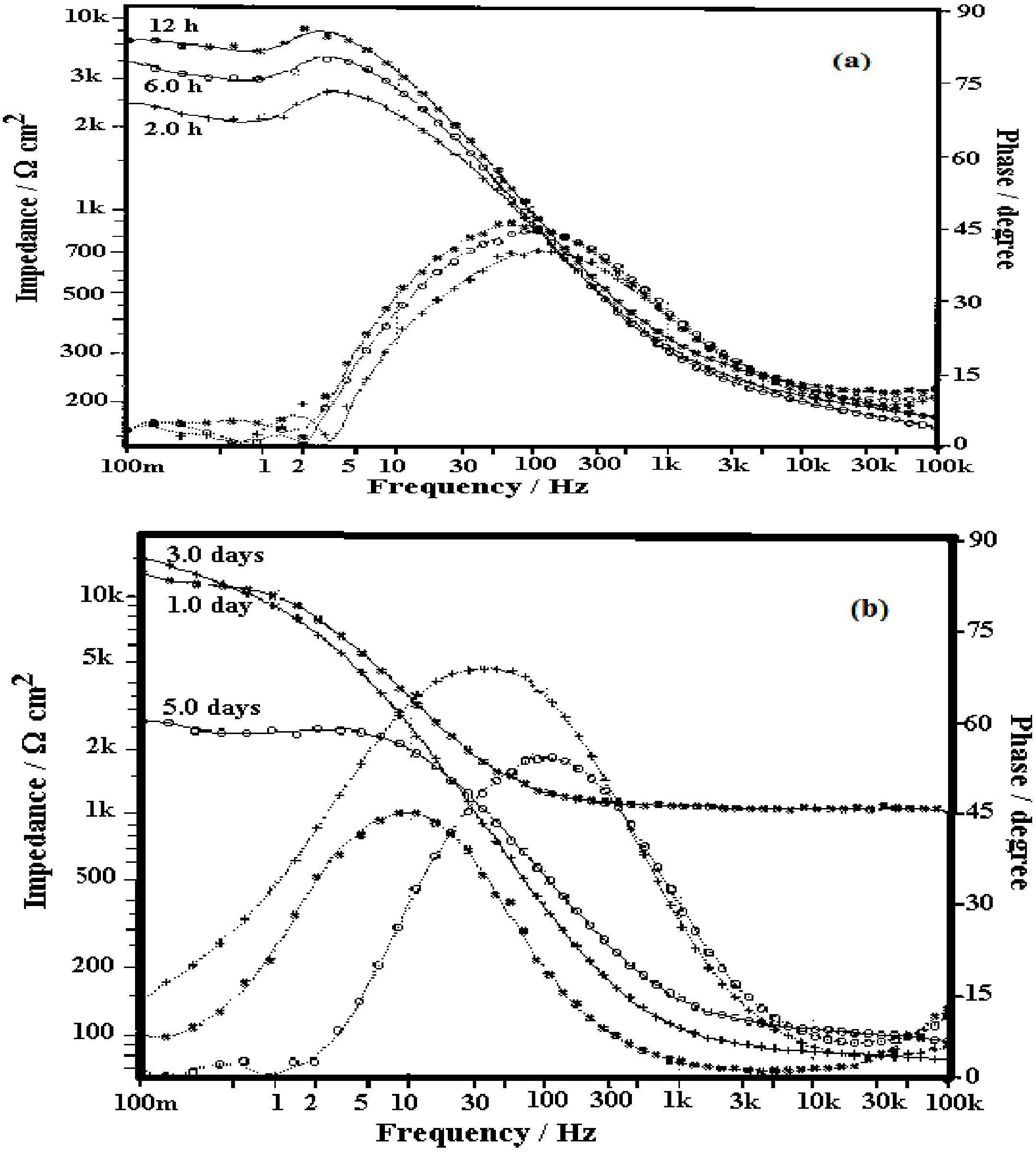


Figure 2. Bode Plots of AZ91E alloy in PBS solution at 37°C.

The results in general show that Bode plots display one time constant for AZ31E and AZ91E alloys. Analysis of the experimental spectra was made by best fitting to the corresponding equivalent circuit using Thales software provided with the workstation where the dispersion formula suitable to each model was used [13,14]. In this complex formula an empirical exponent (α) varying between 0 and 1, is introduced to account for the deviation from the ideal capacitive behavior due to surface inhomogeneties, roughness factors and adsorption effects [14]. In all cases, good conformity between theoretical and experimental was obtained for the whole frequency range. The impedance data were thus simulated to the appropriate equivalent circuit for the case with one time constant (Fig. 3).

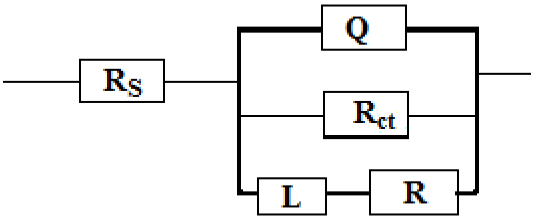


Figure 3. Equivalent circuit for one time constant.

It consists of Q, which is the Constant phase element of double layer capacitance that is used instead of pure capacitance to account for inhomogenity and roughness of electrode surface [13,15-16]. R_{ct} is charge transfer resistance. R (inductance resistance) and L (inductance) are in series to each other [13] which may be due to chloride ion adsorption [16,17] and R_s is the solution resistance. All these parameters indicated a series of complicated corrosion reactions occurring on tested electrode surface in PBS solution. Generally, good conformity between theoretical and experimental results were obtained with an average error of 3%. The fit results are given in Table 1.

Table 1. Impedance parameters of tested electrodes in PBS solution with time, at 37°C.

Material	t/ h	R_s / $\Omega\ cm^2$	R_{ct}/ $k\Omega\ cm^2$	Q/ $\mu F\ cm^{-2}$	α	R_L / Ωcm^2	L/ kH
AZ31E	2.0	19.6	0.05	6.50	0.68	2.3	1.7
	6.0	22.4	3.21	4.31	0.76	3.4	1.9
	12	25.3	4.50	3.56	0.84	5.8	2.0
	24	36.6	8.14	2.53	0.87	8.4	6.4
	72	45.1	1.53	9.44	0.60	6.9	3.5
	120	48.2	0.90	11.13	0.61	7.0	2.9
AZ91E	2.0	50.1	2.50	1.05	0.82	13	5.1
	6.0	40.5	6.00	0.89	0.87	24	8.7
	12	41.3	8.43	0.43	0.85	45	9.5
	24	1455	21.7	0.23	0.87	60	9.9
	72	39.8	18.6	0.19	0.88	78	15.2
	120	46.1	2.95	1.92	0.87	56	11.7

As given in Table 1, it was found that film healing and thickening becomes effective by increasing time of immersion in PBS solution leading to a quasi-steady state thickness at longer times. This is caused by the formation of adherent corrosion products on the sample surface including, magnesium hydroxide, as well as phosphates [14]. They are precipitated from the solution during the corrosion of magnesium alloys due to saturation and localized alkalization [14]. In a saline environment, magnesium-based alloys would be degraded to magnesium chloride, oxide or phosphate [14] and this occurs in PBS solution. For chloride ions, in poorly buffered chloride solutions, they reveal low corrosion rates due to the formation of a partially protective $Mg(OH)_2$ layer. Also, phosphates inhibit dissolution of the oxide film and formed on it with increasing immersion time [14]. Generally, PBS solution improves slightly the corrosion resistance of both AZ91E and AZ31E alloys with time.

It should be noted that the alloying elements Al and Zn tend to have a stabilizing effect on the protective film formed on an Mg alloy. AZ91E shows lower corrosion rate than AZ31E due to more aluminum content. This is also associated with the following mechanism: β-phase acts as an electrochemical barrier, Al_2O_3 and $Al(OH)_3$ compounds may be formed as passive film [13], indicating that the Mg matrix dissolution accompanies aluminium reaction on the metallic surface improving AZ91 alloy corrosion resistance. Song et al. [18] stated that the β-phase played a dual role in NaCl solutions and served as a galvanic cathode and accelerated the corrosion process of the α-matrix if the volume fraction of β-phase was small which may act as an anodic barrier to inhibit the overall corrosion of the alloy for its high volume fraction.

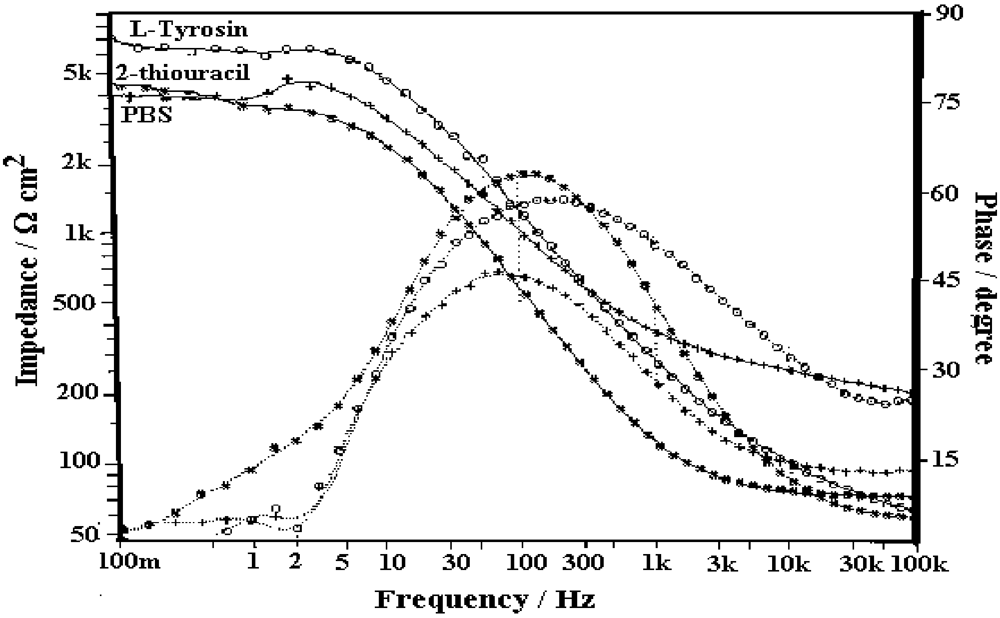


Figure 4. Bode plots of AZ91E alloy in PBS solution containing either 10^{-3} M L-Tyrosine or 10^{-3} M 2-Thiouracil after 6 h of immersion at 37°C.

On adding 10^{-3} M of L-Tyrosine or 10^{-3} M of 2-Thiouracil as inhibitors for lowest corroded alloy (AZ91E) in PBS solution at 37°C, it was found that L-tyrosine is more effective than 2-Thiouracil as shown in Fig.4. This may be due to higher molecular weight and more bulky structure of L-Tyrosine. This is also attributed to the electron rich environment on L-Tyrosine containing 4 active centers and 6-membered ring. Such action could be explained through the lone pair of non-bonding electrons on N and O atoms and the resonance of benzene ring. However, for 2-Thiouracil compound, it contains 4 active centers and 6-membered ring but the electrons on N atoms are restricted to be liberated due to they are involved into the aromatization of the ring.

3.2. Potentiodynamic Polarization Measurements

Potentiodynamic polarization behavior of AZ31E and AZ91E alloys were studied in PBS solution. The potential was scanned from -1.0 to 0.0 V vs. SCE at a rate of 1 mV s^{-1}, prior to the potential scan the electrode was left under open circuit conditions in the respective solution for 2 h until a steady free corrosion potential (E_{st}) value was recorded. Fig. 5 shows polarization scans for AZ31E and AZ91E alloys after immersion in PBS solution for 2 hours. The active dissolution parameters were estimated and the results indicate clearly that these parameters are dependent on the the alloy composition. The corrosion current (I_{corr}), which is proportional to the corrosion rate, is given by the intersection of the cathodic and anodic Tafel lines extrapolation. Because of the presence of some degree of nonlinearity in the Tafel slope region of the obtained polarization curves, the Tafel constants were calculated as the slope of the points after E_{corr} by ±50 mV using a computer least-square analysis [7]. The corrosion currents were then determined by the intersection of the cathodic Tafel line with the open circuit potential (i.e. the free steady E_{corr} value). Corrosion potential values shift toward more positive potential for AZ91E alloy (E_{corr} = -1.366 V vs SCE) indicating that AZ91E alloy is more passive than AZ31E alloy (E_{corr} = -1.456 V vs. SCE).

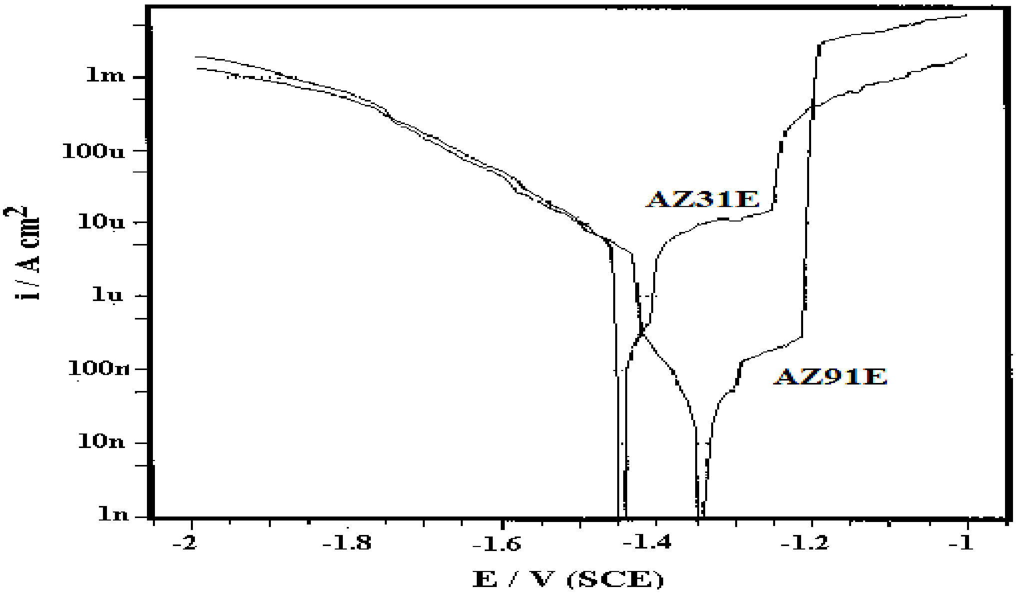


Figure 5. Polarization scans of AZ31E and AZ91E alloys in PBS solution at 37°C.

Obviously, from Fig.5, it is clear that i_{corr} for AZ91E is 61.5 nA cm^2 and for AZ31E is 5.11 μA cm^2. This indicates that AZ91E is lowest corroded one with lower corrosion rate than AZ31E alloy. This may be due to the percentage of Al and Zn in the alloy is higher that give it more stability. Indeed, without these alloying elements, pure magnesium experiences a much faster biodegradation under similar testing conditions. The results may be caused by the different distribution of alloying elements in microscopic scale and the microstructure of alloys, which are the fundamental reasons for the metal corrosion morphology and corrosion resistance. Generally, impedance and polarization results confirm each other.

4. CONCLUSIONS

- The corrosion resistance of AZ31E alloy increases with immersion time in PBS solution till 24 hour then decreases sharply till 5 days.

The corrosion resistance of AZ91E alloy increases with immersion time in PBS solution till 3 days then decreases sharply till 5 days.

- The corrosion resistance of AZ91E alloy is much better than AZ31E alloy in PBS solution.

- The corrosion of AZ91E alloy in the blank can be effectively inhibited by addition of 1 mM 2-ThioUracil or 1 mM L-Tyrosine. However, L-Tyrosine is much more effective than 2-ThioUracil as inhibitor.

- Polarization results confirm well impedance data.

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