



Study of Electrochemical Behaviour of ZK21 Alloy

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Abstract : This paper aims to show that the ZK21 and its alloy are not highly corrosive and can be used in many areas and thus to popularize the use of this alloy and project it as future materials¹. Magnesium alloys possess lucrative properties such as high strength to weight ratio, low machining cost, low thermal stress modules and superior hot forming properties. Because of these advantageous characteristics they are used in many areas such as in corrosion protection, aeronautics and automobiles sectors². Hence it has been recommended to make use of this alloy as one of the important material for most of the applications. In this present analysis, it has been attempted to investigate the electrochemical behaviour of ZK21 alloy, particularly its unusual behaviour in certain aqueous environments is studied by using galvano-gasometry. It is also intended to show that the magnesium alloy is not as corrosive as expected from the standard potential³. The general perception of magnesium and its alloys as highly corroding materials is derived from certain extreme environmental conditions prevailing only at high salt contents⁴, humid and wet conditions. This is not at all valid in many other conditions where magnesium and its alloy resist corrosive attack and serve the decide purpose most satisfactorily⁵.

Introduction:

Magnesium is one of the lightest metals available in plenty in sea water its density is about 1.67 gm/cm³ and its alloys with many metals such as Aluminium, Zinc, Manganese, Zirconium and rare earth metals. Magnesium is available on the earth surface as ores and in plenty in seawater and hence the importance of the metal lies in the in exhaustive nature of its availability as well as the high strength to weight low alloys⁶. Due to attractive properties magnesium alloys are used in varied application such as structural materials in automobile and industries, as anodes in power sources and sacrificial anodes in corrosion prevention systems, even though magnesium is assumed to the freely corroding metal. It is not so in many aqueous environments it has been observed from the practical study that ennoblement to an extent of 1.0V is resulted in aqueous solutions. This has been attributed to the formation of the protective film of Mg(OH)₂ on the surface of the electrode⁷. Hence this study aims to show that the magnesium and its alloys are not highly corrosive and can be used in many new areas and thus popularize the use of these alloys and project them as future materials. Alloying of magnesium has been used to obtained strength, ductility, workability, corrosion resistance, low density and cast ability. Magnesium alloys are used mainly in the form of casting. Magnesium casting finds usage in aircraft engines, landing wheels and accessories where lightweight, high strength and shock resistance are of prime importance. Cast magnesium alloys have been used for probable tools and manually handled equipment's of all kinds, such as vacuum cleaners, portable grinders and polishers, and also for boundary flasks. Owing to their low specific gravity, magnesium alloys have been widely used in their aircraft industry⁸. Magnesium alloys are used where lightweight, high strength and shock resistance are required. In high speed rotating and reciprocating parts, lightweight magnesium castings are used to affect smother and more efficient operation and to reduce inertia⁹.

Aim and Scope:

Magnesium and its alloys are envisaged to be suitable and competitive substitutes for Aluminium, steel and plastics. Magnesium alloys possess lucrative properties such as high strength to weight ratio, low machining cost, low thermal stress modules and superior hot forming properties. Because of these advantageous characteristics they are used in very many areas such as in corrosion protection, aeronautics and automobiles¹⁰. In the present study, the investigator has made an attempt to investigate the electrochemical behaviour of ZK 21 alloy, particularly its unusual behavior in certain aqueous environments is studied by using galvano- gasometry. It is also intended to show that the magnesium alloy is not as corrosive as expected from the standard potential. The general perception of magnesium and its alloys as highly corroding materials is derived from certain extreme environmental conditions prevailing only at high salt contents, humid and wet conditions. This is not at all valid in many other service conditions where magnesium and its alloys resist corrosive attack and serve the decide purpose most satisfactorily¹¹.

Experimental Techniques:

Preparation of solutions:

The water used for the preparation and the dilution of solutions was tripled distilled using quartz distillation apparatus. Acids used for digestion and dissolutions were of guaranteed reagent grade. Chemicals used for the preparation of electrolytic media were all guaranteed reagents. Magnesium sulphate, ammonium sulphate, magnesium nitrate, and ammonium nitrate were procured from sarabhai M.chemicals. The required quantities of these chemicals were dissolved in triple distilled water to prepare a solution 0.5M. Lower concentrations were made by dilution of strong solution with tripled distilled water¹².

Electrode preparation:

The ZK21 electrode has been turned into small rods with grooves and fitted into the electrode assembly with the help of Teflon and copper rods. The exposed active surface area of the working electrode was 1.0 cm². Rest of the area was masked by lacquer application. The refined magnesium electrode was polished with 1/0, 2/0, 3/0, 4/0 emery papers and degrease with trichloroethylene. The unexposed area of the test electrode was masked by lacquer application, fitted into the cell assembly and then introduced into the cell¹³.

Analysis of the metal:

The material used in this study was screened by atomic absorption spectrophotometer (AAS) model GBC, 904 Australia, using air- acetylene flames. AAS is a very versatile tool by which more than 60 metals can be estimated at microgram levels. It is a technique to measure the degree of absorption by atoms of incident energy at discrete wavelengths. Absorption is proportional it population of atoms in turn too analytic concentration. The main advantages of AAS are (1) all metals can be estimated at ppm level, (2) the time for each element is only few seconds (3). The amount of sample required for analysis is very small and (4) estimation can be done without any inter elemental interference. This has been elaborately employed by many researches for the determination of various elements¹⁴.

Very fine turnings of the metals were taken and accurately weighed amount was dissolved in 1:1 hydrochloric acid and made up to 100 ml in a standard flask with triple distilled water. These solutions were nebulised into the flames and concentrations were read out. Impurities checked include aluminium, antimony, calcium, chromium, copper, iron, manganese, sodium, zinc and zirconium. The analysis of the Zk21 is given in the table.1.

Table-1 Analytical Report of ZK21

| Elements | % |
|-----------|------|
| Aluminium | 0.01 |
| Antimony | 0.01 |
| Calcium | 0.02 |
| Chromium | 0.01 |

| | |
|-------------------------|-------|
| Copper | 0.02 |
| Ion | 0.02 |
| Manganese | 0.02 |
| Sodium | 0.01 |
| Zinc | 1.80 |
| Zirconium | 0.95 |
| Magnesium by difference | 97.13 |

Galvano- gasometry:

Gasometric experiments, even though simple give excellent results at the cost of strict precautions. This has been particularly used to study the “negative difference effect” shown by magnesium¹⁵. The ZK21 was subjected to this study in 0.02M, 0.05M, 0.1M, 0.2M and 0.5M MgSO₄, (NH₄)₂SO₄, Mg(NO₃)₂ and NH₄NO₃ solutions. In this technique the volume of hydrogen liberated during dissolution of the metal was collected¹⁶.

The apparatus has been modified to collect the hydrogen gas evolved from the electrodes and polarised and non-polarised conditions. The experimental setup consists of double walled polarisation cell, air- tight ground glass lid with opening for gas, provision to introduce test electrode and platinum electrode to apply current. This gas was collected and measured with the help of vertical column tubes made of standard graduated burettes, surrounded by glass jackets for circulation of coloured liquid. The column was filled with 20% NaCl solution coloured by hydrochloric acid and methyl orange. All the ground glass joints and other flexible joints were made leak proof by araldite sealing¹⁷.

The metal was turned into small rods of 1.13 cm diameter fitted to Teflon and in turned to copper rod. The test specimen had an exposed area of 1 cm². They thoroughly polished with 1/0, 2/0, 3/0 and 4/0 emery papers and degreased with trichloroethylene. Area other than the exposed (1 cm²) was masked by lacquer.

125ml of solution was taken into the reaction cell, covered with air-tight lid carrying the test electrode and platinum electrode¹⁸. The assembly was placed on a magnetic stirrer and the connected the opening to the eudiometer by means of leak proof rubber tubing. Solutions were stirred and water was circulated from the thermostat (32 ± 1°C). The test electrode was connected to the positive terminal of the constant current regulator and counter electrode to the negative terminal¹⁹. The initial level in the column was noted after equalizing with reservoir bulb.

A stopwatch was instantly started and the reaction was allowed to proceed for 30 minutes. The gas was collected and the reading in the column was noted after equalizing the reservoir bulb. The difference between the two readings gives the volume of hydrogen gas liberated at zero current i.e., open circuit volume (V₀).

A current of 5mA.cm⁻² was applied (Mecon 603) with the help of a constant current generator, stirring was continued and the gas was collected. After 30 minutes the current was stopped, equalized the column levels and noted the reading. The difference between the initial and final readings gives the volumes of hydrogen produced for 30 minutes from the same electrode by passage of current at the rate of 5mA. cm⁻², collected the gas for 30 minutes and measured the volume of hydrogen collected. The average of these two values was taken as the volume of hydrogen collected from the electrode for 30 minutes at a constant current density of 5mA.cm⁻² (Vt) i.e. closed circuit volume.

The same procedure was repeated for other current density values and the volume of hydrogen collected for each current density was measured up to current density of 100 mA.cm⁻². The experiments had to be conducted in duplicate and even in triplicate, since there may be chance of slight error in the volume measurement or leakage from the system. From the volume of gas collected for each system without passing current (Voltage) and with passing known current for the same (Vt) the difference effect Δ was calculated using the relationship.

$$\Delta = V_0 - (Vt - 6.97 I),$$

Where the factor 6.97 converts milli amperes of current flowing through the test electrode for 1 minute into cubic millimeter of hydrogen at standard conditions and I is substituted in mA. The unit of Δ is mm³cm⁻³

min^{-1} . Relationship between rate of hydrogen evolution and current density was plotted. Likewise the difference effect and current density values were plotted to get the variation of the former with the latter²⁰.

Results and Discussion:

The data collected by carrying out experiments using ZK21 alloy specimens as working electrode in four different media namely MgSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$, and NH_4NO_3 solutions at concentrations of 0.02M, 0.05M, 0.1M, 0.2M and 0.5M are presented in this chapter. The relationship between hydrogen evolution rate (V_t) and current density (I) for all the experimental conditions are given in the form of tables. Similarly the difference effect (Δ) calculated from the V_0 and V_t are tabulated. The plot of V_t Vs I and Δ Vs I for all the systems are furnished in this chapter.

Table:2 V_t Vs I for ZK21 in MgSO_4 solution.

| Current density mA/cm^2 | $V_t, \text{mm}^3 \text{cm}^{-2} \text{min}^{-1}$ | | | | |
|---|---|-------|------|------|------|
| | 0-02M | 0-05M | 0-1M | 0-2M | 0-5M |
| 0 | 40 | 45 | 50 | 70 | 100 |
| 5 | 80 | 95 | 105 | 120 | 140 |
| 10 | 120 | 140 | 150 | 170 | 180 |
| 20 | 230 | 240 | 260 | 270 | 290 |
| 30 | 320 | 330 | 350 | 400 | 405 |
| 40 | 410 | 500 | 540 | 580 | 560 |
| 50 | 490 | 570 | 600 | 670 | 700 |
| 60 | 690 | 750 | 770 | 790 | 810 |
| 70 | 800 | 880 | 910 | 1000 | 1020 |
| 80 | 960 | 1110 | 1180 | 1210 | 1200 |
| 90 | 1200 | 1250 | 1270 | 1300 | 1310 |
| 100 | 1380 | 1400 | 1400 | 1420 | 1480 |

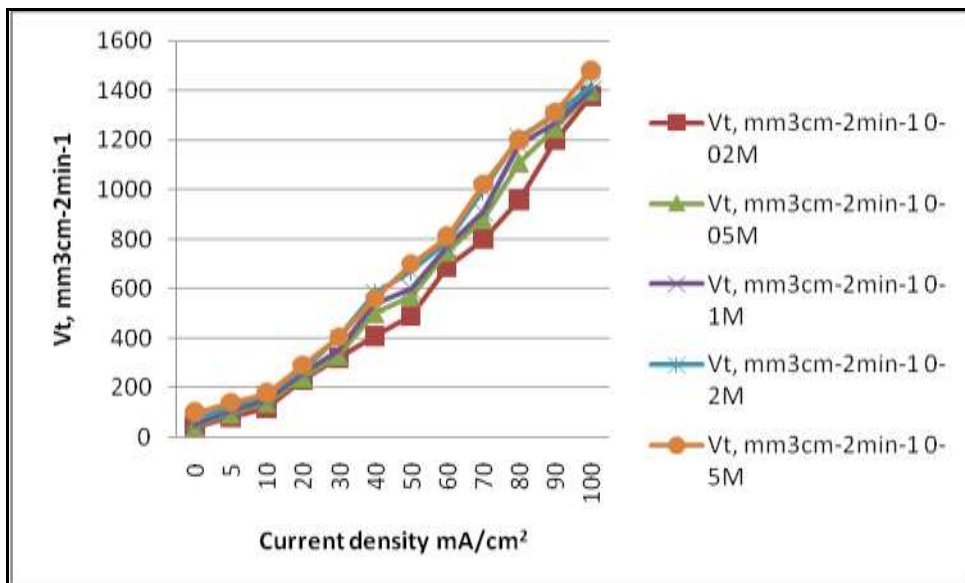
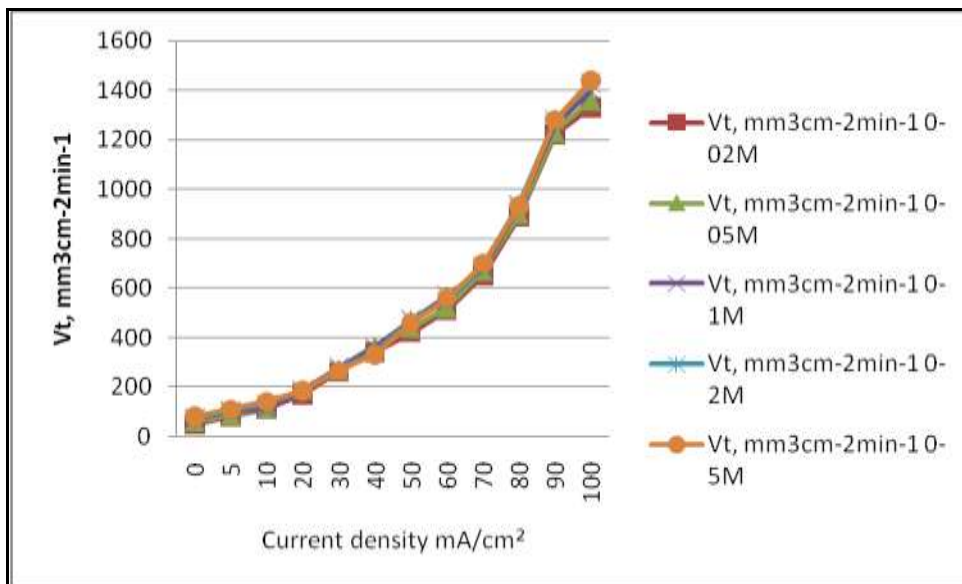


Table:3 V_t Vs I for ZK21 in $(NH_4)_2SO_4$ solution.

| Current density mA/cm^2 | $V_t, mm^3 cm^{-2} min^{-1}$ | | | | |
|---------------------------|------------------------------|-------|------|------|------|
| | 0-02M | 0-05M | 0-1M | 0-2M | 0-5M |
| 0 | 50 | 60 | 70 | 70 | 80 |
| 5 | 80 | 85 | 100 | 105 | 110 |
| 10 | 110 | 115 | 110 | 130 | 140 |
| 20 | 170 | 190 | 185 | 185 | 185 |
| 30 | 260 | 270 | 280 | 270 | 265 |
| 40 | 340 | 365 | 360 | 340 | 330 |
| 50 | 420 | 440 | 470 | 470 | 460 |
| 60 | 510 | 520 | 570 | 550 | 560 |
| 70 | 650 | 670 | 680 | 690 | 700 |
| 80 | 890 | 900 | 930 | 940 | 930 |
| 90 | 1220 | 1230 | 1260 | 1280 | 1280 |
| 100 | 1330 | 1360 | 1400 | 1430 | 1440 |



| Current density mA/cm^2 | $V_t, mm^3 cm^{-2} min^{-1}$ | | | | |
|---------------------------|------------------------------|-------|------|------|------|
| | 0-02M | 0-05M | 0-1M | 0-2M | 0-5M |
| 0 | 40 | 50 | 50 | 60 | 60 |
| 5 | 75 | 90 | 95 | 95 | 100 |
| 10 | 120 | 130 | 135 | 140 | 140 |
| 20 | 200 | 210 | 220 | 240 | 240 |
| 30 | 280 | 295 | 300 | 330 | 330 |
| 40 | 380 | 400 | 410 | 450 | 450 |
| 50 | 460 | 490 | 500 | 550 | 560 |
| 60 | 630 | 650 | 670 | 690 | 700 |
| 70 | 750 | 780 | 780 | 800 | 840 |
| 80 | 910 | 920 | 950 | 950 | 960 |
| 90 | 1160 | 1190 | 1160 | 1170 | 1190 |
| 100 | 1280 | 1280 | 1280 | 1300 | 1310 |

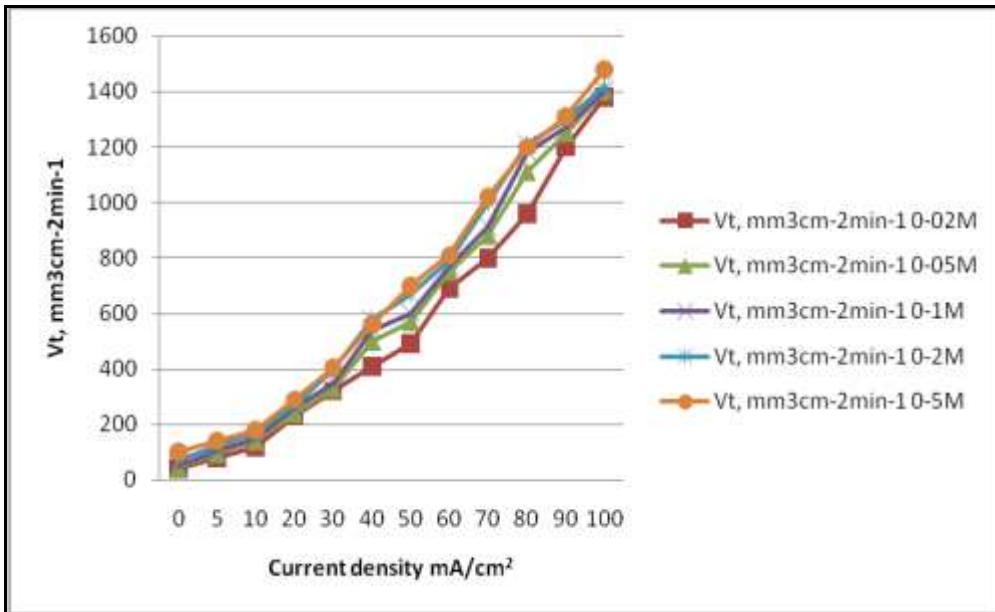


Table:5 Vt Vs I for ZK21 in NH₄NO₃ solution.

| Current density mA/cm ² | Vt, mm ³ cm ⁻² min ⁻¹ | | | | |
|------------------------------------|--|-------|------|------|------|
| | 0-02M | 0-05M | 0-1M | 0-2M | 0-5M |
| 0 | 50 | 55 | 65 | 60 | 70 |
| 5 | 75 | 85 | 85 | 90 | 95 |
| 10 | 115 | 120 | 125 | 120 | 125 |
| 20 | 160 | 165 | 170 | 180 | 190 |
| 30 | 240 | 260 | 270 | 275 | 280 |
| 40 | 330 | 350 | 360 | 365 | 380 |
| 50 | 410 | 425 | 420 | 430 | 460 |
| 60 | 500 | 520 | 530 | 540 | 550 |
| 70 | 630 | 650 | 670 | 670 | 680 |
| 80 | 870 | 880 | 900 | 910 | 940 |
| 90 | 1200 | 1220 | 1230 | 1230 | 1250 |
| 100 | 1320 | 1350 | 1380 | 1380 | 1400 |

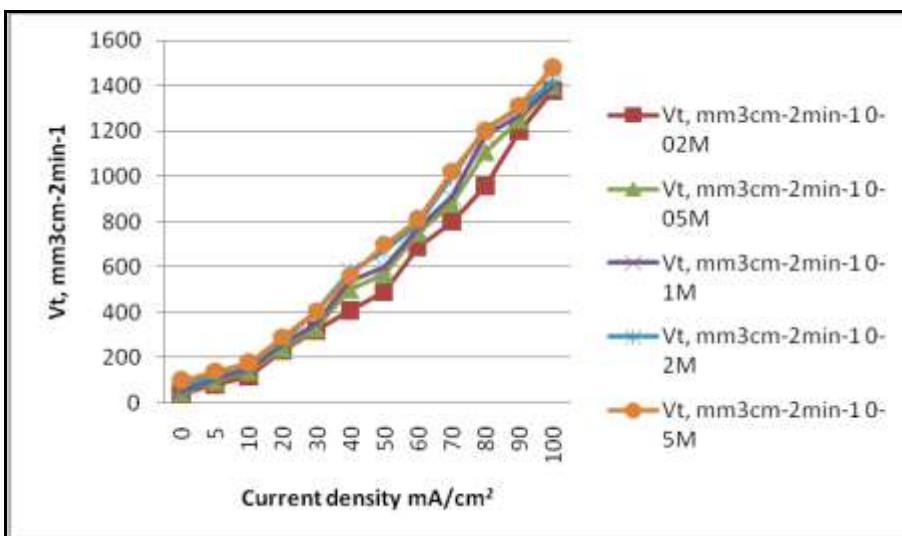


Table 6. Δ Vs I for ZK21 in MgSO₄ solution

| Current Density mA/cm ² | Δ mm ³ cm ⁻² min ⁻¹ | | | | |
|---------------------------------------|---|-------|------|------|------|
| | 0.02M | 0.05M | 0.1M | 0.2M | 0.5M |
| 0 | - | - | - | - | - |
| 5 | -5 | -15 | -20 | -15 | -5 |
| 10 | -10 | -25 | -30 | -30 | -10 |
| 20 | -50 | -55 | -70 | -60 | -50 |
| 30 | -70 | -75 | -90 | -120 | -95 |
| 40 | -90 | -175 | -210 | -230 | -180 |
| 50 | -100 | -175 | -200 | -250 | -250 |
| 60 | -230 | -285 | -300 | -300 | -290 |
| 70 | -270 | -345 | -370 | -440 | -430 |
| 80 | -360 | -505 | -570 | -580 | -540 |
| 90 | -530 | -575 | -590 | -600 | -580 |
| 100 | -640 | -655 | -650 | -650 | -680 |

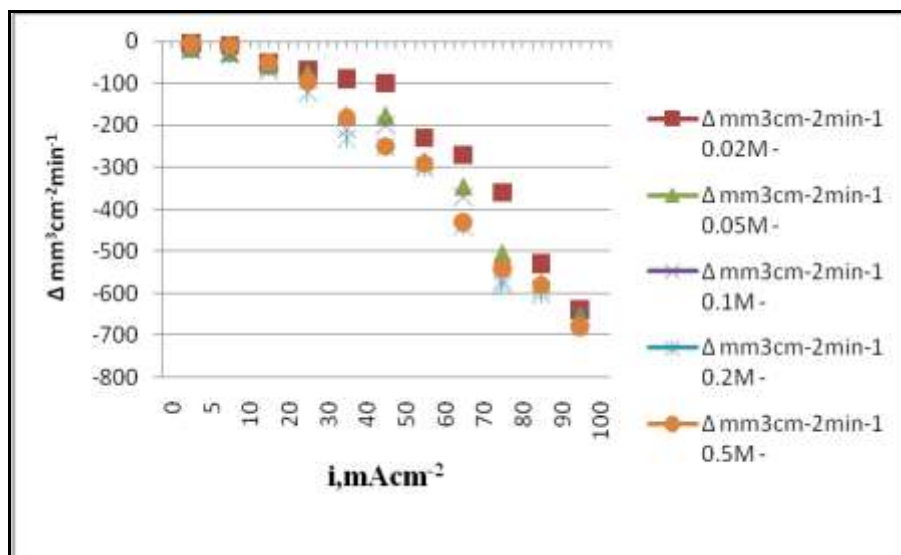


Table 7. Δ Vs I for ZK21 in (NH₄)₂SO₄ solution

| Current Density mA/cm ² | Δ mm ³ cm ⁻² min ⁻¹ | | | | |
|---------------------------------------|---|-------|------|------|------|
| | 0.02M | 0.05M | 0.1M | 0.2M | 0.5M |
| 0 | - | - | - | - | - |
| 5 | 5 | 10 | 5 | 0 | 5 |
| 10 | 10 | 15 | 30 | 10 | 10 |
| 20 | 20 | 10 | 25 | 25 | 35 |
| 30 | 0 | 0 | 0 | 10 | 25 |
| 40 | -10 | -25 | -10 | -10 | 30 |
| 50 | -20 | -30 | -50 | -50 | -30 |
| 60 | -40 | -40 | -80 | -60 | -60 |
| 70 | -110 | -120 | -120 | -130 | -210 |
| 80 | -270 | -280 | -300 | -310 | -290 |
| 90 | -540 | -540 | -560 | -580 | -570 |
| 100 | -580 | -600 | -630 | -660 | -660 |

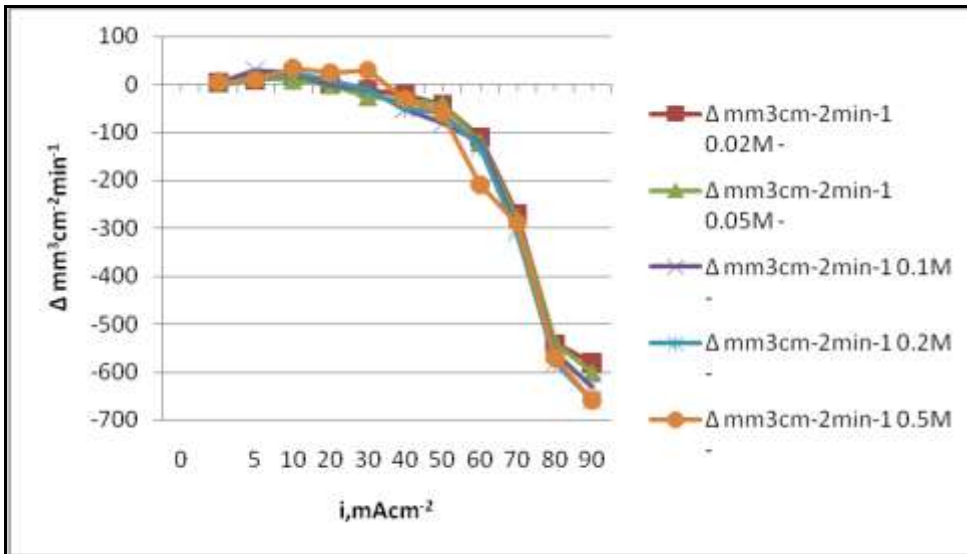


Table 8. Δ Vs I for ZK21 in $Mg(NO_3)_2$ solution

| Current Density mA/cm^2 | $\Delta \text{ mm}^3 \text{ cm}^{-2} \text{ min}^{-1}$ | | | | |
|------------------------------|--|-------|------|------|------|
| | 0.02M | 0.05M | 0.1M | 0.2M | 0.5M |
| 0 | - | - | - | - | - |
| 5 | 0 | -5 | -10 | 0 | -5 |
| 10 | -10 | -10 | -15 | -10 | -10 |
| 20 | -20 | -20 | -30 | -40 | -40 |
| 30 | -30 | -35 | -40 | -60 | -60 |
| 40 | -60 | -70 | -80 | -110 | -110 |
| 50 | -70 | -90 | -100 | -140 | -150 |
| 60 | -170 | -180 | -200 | -210 | -220 |
| 70 | -290 | -240 | -240 | -250 | -290 |
| 80 | -310 | -310 | -340 | -330 | -340 |
| 90 | -490 | -510 | -480 | -480 | -500 |
| 100 | -540 | -530 | -530 | -540 | -550 |

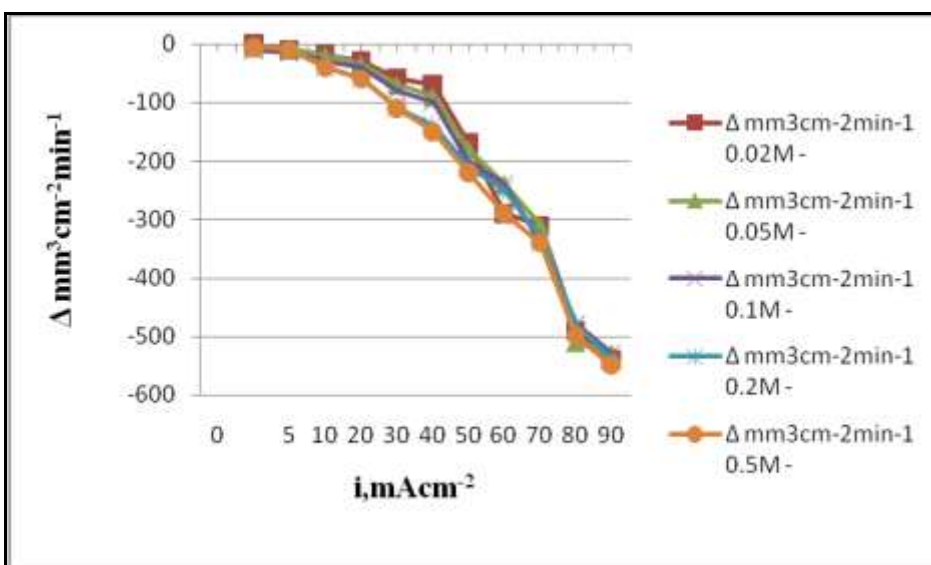
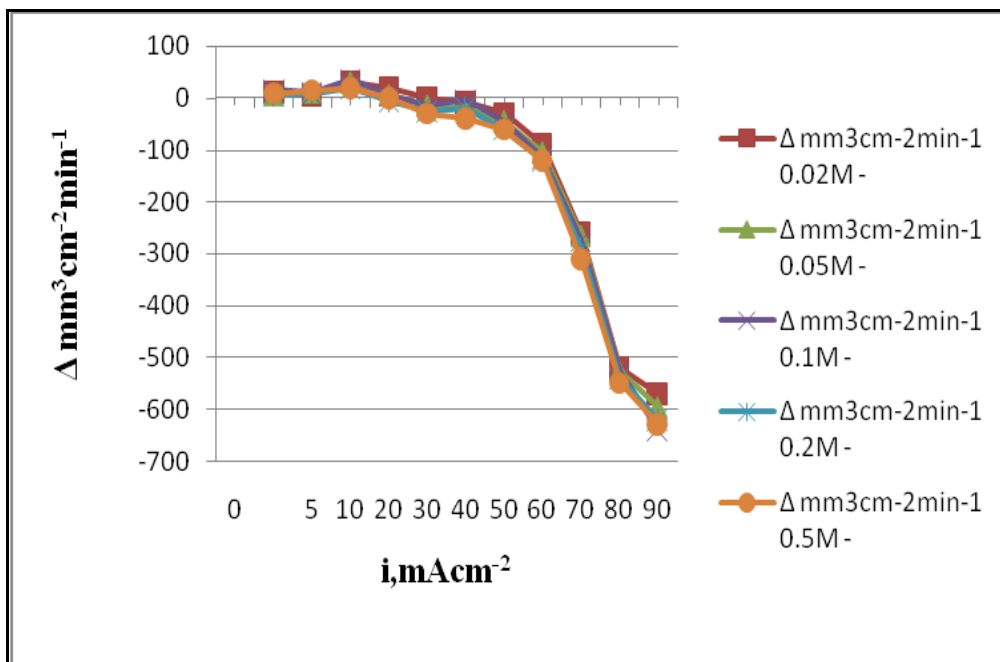


Table 9. ΔV vs i for ZK21 in NH_4NO_3 solution

| Current Density mA/cm^2 | $\Delta mm^3 cm^{-2} min^{-1}$ | | | | |
|------------------------------|--------------------------------|-------|------|------|------|
| | 0.02M | 0.05M | 0.1M | 0.2M | 0.5M |
| 0 | - | - | - | - | - |
| 5 | 10 | 5 | 15 | 5 | 10 |
| 10 | 5 | 10 | 10 | 10 | 15 |
| 20 | 30 | 30 | 35 | 20 | 20 |
| 30 | 20 | 5 | 5 | -5 | 0 |
| 40 | 0 | -15 | -15 | -25 | -30 |
| 50 | -10 | -20 | -5 | -20 | -40 |
| 60 | -30 | -45 | -45 | -60 | -60 |
| 70 | -90 | -105 | -115 | -120 | -120 |
| 80 | -260 | -265 | -275 | -290 | -310 |
| 90 | -520 | -525 | -525 | -540 | -550 |
| 100 | -570 | -595 | -640 | -620 | -630 |



Experimental Discussion

This chapter provides a thorough discussion of the tables and figures presented in the previous chapter in order to bring out the effects of various parameters. The relationship between self-corrosion of the specimen, hydrogen evolution rate and difference effect, with different media, concentration and current density are discussed. In general the electrochemical behavior of Mg is primarily by the evolution of hydrogen gas from aqueous solutions. Hence all the factors influencing the evolution of hydrogen gas will alter the dissolution and corrosion of the test anode the magnesium, zinc, zirconium alloy. Moreover the current density which is the driving force for the electrochemical dissolution of the anode and subsequent liberation of hydrogen will also have marked effect on the overall performance of the anode.

Self-corrosion of the anode:

The self corrosion of the anode can be assessed from the nature and extent of hydrogen evolved from the anode at zero current. That is from the value of V_o . Tables 2 to 9 give the galvanogassometry data for $MgSO_4$, $(NH_4)_2SO_4$, $Mg(NO_3)_2$, and NH_4NO_3 respectively. From table 2 the V_o values in $MgSO_4$ at concentrations 0.02M, 0.05M, 0.1M, 0.2M and 0.5M can be obtained. It shows that the value increases from 40

to $100\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$. Similar observations of increased V_0 values are noted for the anode in, $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$, and NH_4NO_3 as evident from tables 3, 4, 5,6,7,8 and 9. So an overall scrutiny of all the tables indicates the V_0 values between 40 and $100\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ the highest values is resulted in 0.5M MgSO_4 which shows that the medium causes highest self-dissolution of the alloy. Further considering the V_0 value in all these solution at 0.5M , the self corrosion phenomenon of the alloy can be predicted which is observed to be in the decreasing order as $\text{MgSO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{NO}_3 > \text{Mg}(\text{NO}_3)_2$.

Rate of hydrogen evolution (Vt):

The electrochemical behaviour of the ZK21 alloy in aqueous solution is assumed to takes place by the anodic dissolution of the alloy and cathodic evolution of hydrogen gas. The hydrogen evolved was measured in $\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ which is the hydrogen evolution rate from the alloy anode. Based on the reactivity and rate of corrosion of the medium there may be variation in the hydrogen evolution rate (Vt). Tables 2 to 5 tabulate the Vt values for all the systems. Table 2 gives the VtVs current density in MgSO_4 at concentrations 0.02M , 0.05M , 0.1M , 0.2M and 0.5M . It can be observed that as current density increases the Vt value is increased and the value of $1380\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ is obtained for 100mAcm^{-2} . Similarly the Vt value is increased with increasing concentration of MgSO_4 from 0.02M to 0.5M and the highest Vt value of $140\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ at 5mAcm^{-2} in 0.5M . Whereas overall highest Vt value in MgSO_4 is $1480\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ in 0.5M at 100mAcm^{-2} . This value indicates the effects of both current density and concentration. Similar trend of increased Vt value both with concentration and current density are observed for other media such as $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$ and NH_4NO_3 as can be seen from tables 3 to 5. Comparing all the tables it is noticed that the rate of change of Vt is not uniform with the applied current density. So to say initially at low current density only a study increase and at highest current density a higher rate of Vt. Further it is also observed that a 100mAcm^{-2} almost similar Vt values are resulted at all concentrations. That is to say at lower current densities the Vt value is found to depend upon both current density and concentration. Whereas at the highest applied current density and concentration the Vt value depend only on current density and hence Vt value is independent of concentration at highest applied current density.

Comparison of the tables indicates that the resulted hydrogen evolution rate are higher than the theoretical value to extend of 2 to 2.5 times. The excess of hydrogen evolution rate can be explained by a combination of chemical and an electrochemical reaction that is to say with the effect of higher current density some of the peripheral particles may be disintegrated which chemically react independently liberating hydrogen. It is also observed that the Vt is greater in NH_4^+ than Mg^{2+} as well as greater in SO_4^{2-} than NO_3^- thereby indicating the higher corrosivity of the $(\text{NH}_4)_2\text{SO}_4$ than $\text{Mg}(\text{NO}_3)_2$.

Effect of current density:

The data furnished in the tables 2 to 9 indicate the effect of current density on the hydrogen evolution rate and difference effect values. It shows the variation of these parameters from zero to 100mAcm^{-2} applied current density. It can be seen from table-2 that with increasing current density the hydrogen evolution rate increases. It has also been observed that a uniform increase in Vt is not always realized and it has been noted to be higher than the theoretical volume of hydrogen to be in line with this observation in other solutions at all concentrations.

The effect of current density is also very much reflected in the difference effect value. It is understandable from table-2 that it is with increasing current density. The negative difference effect value is increased up to higher current density of 100mAcm^{-2} same is the case in $\text{Mg}(\text{NO}_3)_2$ solution as evident from table-4. Whereas the effect of current density is entirely different towards the magnesium alloy anode in other two solutions namely $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in these solutions at a low current density a positive difference effect and high current density a negative difference effect have been observed.

Influence of concentration:

The evolution of hydrogen from the anode is influenced by the concentration of the medium. In this study also the influence of concentration on the hydrogen evolution rate with passing and without passing are clear from the tables. It is noticed from the table that at low concentration, the hydrogen evolved is minimal which increased with concentration irrespective of self corrosion or polarized corrosion. Thus the highest rate of hydrogen evolution was noticed in 0.5M concentration solution whether it is sulphate or nitrate and magnesium

or ammonium. The increased rate of hydrogen evolution with increased concentration may be due to the presence of higher ionic environment at higher concentration.

Difference effect:

Difference effect (Δ) may be defined as the difference in hydrogen evolution rate with and without anodic polarization from an electrode. The electrochemical behavior of magnesium is associated with the difference effect phenomenon. This can be calculated from the volume of hydrogen liberated. This also indicated the nature and extent of unusual behavior exhibited by different anodes in different solutions. The difference effect (Δ) is calculated using the relationship

$$\Delta = (V_0 + 6.97 I) - V_t$$

Where

V_0 = Volume of hydrogen at no current

V_t = Volume of hydrogen with known current density

I = Applied current density

6.97 = Volume of hydrogen in $\text{mm}^3\text{cm}^{-2}\text{min}^{-1}$ for milli ampere

Therefore difference effect can assume any value from negative to positive and zero that is to say difference effect can have a negative difference effect, zero difference effect and positive difference effect. These three phenomena are exhibited based on the values of V_0 and V_t . Moreover these values are obtained when the self-dissolution of the anode is altered on anodic polarization. During the self-dissolution of the electrode at zero current, the hydrogen is liberated from the anode only due to the chemical reaction with the ionic environment. But on polarization with anodic current the hydrogen liberation comes from both anode and cathode. The difference effect values tabulated in tables-2 show the variation of these parameters with current density in MgSO_4 solution. At a low current density of 5mAcm^{-2} difference effect has a value -5 in 0.02M concentration which goes on increasing and attains -640 at 100mAcm^{-2} . This indicates that the difference effect values are all negative in MgSO_4 solution at all concentrations. It is also understandable that difference effect has a less negative value at low current density and high negative value at high current density. This further indicates that the hydrogen evolution rate is much higher at higher current density over and above the theoretical values.

Tables 6 to 9 show the Δ values V_s current density in $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$ and NH_4NO_3 solution respectively $\text{Mg}(\text{NO}_3)_2$ solution shows almost identical behavior of exhibiting negative difference effect values only at all concentration and current density up to 100mAcm^{-2} . Therefore both MgSO_4 and $\text{Mg}(\text{NO}_3)_2$ are similar in behavior towards ZK21. Tables 7 and 9 show the variation of Δ with current density and concentration in $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 it is seen that at 5mAcm^{-2} , a +5 value is obtained which goes on increasing up to 20mAcm^{-2} and after that difference effect becomes zero and further changes to a negative value. This negative value goes on increasing with further increasing current density and reaches the highest value of -580 at 100mAcm^{-2} . Same is the case with all other concentrations also. Similarly the ZK21 electrode in NH_4NO_3 solution exhibits an initial positive difference effect, zero difference effect and a negative difference effect at high current density values thereby showing an identical behavior for both of these solutions. In comparing all the tables two type of behaviors are noticed in Mg salt solutions and NH_4 salt solutions. Taking the solutions in pairs as MgSO_4 and $(\text{NH}_4)_2\text{SO}_4$, $\text{Mg}(\text{NO}_3)_2$ and NH_4NO_3 the effect of cations can be understood. Since anions are same any difference in difference effect will eventually reflects on the cations. It has been noticed that negative difference effect only in exhibited in Mg salt solutions. Whether in sulphate or nitrate where as all three difference effects are exhibited in NH_4 salt solutions. From the observations the effect of cations are clearly established, that is NH_4 ions behaves differently than Mg ion towards ZK21 alloys. Normally anions are considered to be predominant in electrochemical mechanism whereas this study clearly demonstrates the effect of cation on electrochemical dissolution of the ZK21 alloy.

The reasons for the prevalence of positive difference effect at low current density are the instant decrease in self dissolution of the anode on initial polarization whereby the V_0 becomes greater than V_t . At higher current density the disintegration of the electrode and excess evolution of hydrogen causes negative difference effect. At zero difference effect the system behaves as an ideal one at which faraday's law is completely obeyed. When the amount of the alloy dissolved through anode, hydrogen evolved and current passed are in agreement no difference effect is exhibited. Therefore the cations play an important role in the

electrochemical behavior of ZK21 alloy along with anions, applied current density and concentration of the environment.

Conclusion

The result of the present investigations is summarized below:

- The hydrogen evolution rate at lower current density is observed to be dependent on both concentration and current density while at highest value depends only on current density.
- ZK21 alloy exhibits negative difference effect only in MgSO_4 and $\text{Mg}(\text{NO}_3)_2$ solutions where as positive, zero and negative difference effect in $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 solutions.
- Galvano-gasometry experiments carried out have shown the dependence of hydrogen evolution rate on applied current density, nature and concentration of the solutions.
- This study has endorsed the fact that cations are also responsible along with anions for the electrochemical behavior of Mg alloys.

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