Study of Electrochemical Behaviour of ZK21 Alloy

P.Kalpana, K.Kayalvizhi

Department of Chemistry, IFET College of Engineering Villupuram, India

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 materials[1]. 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 sectors [2]. 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 potential[3]. 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[4], 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 satisfactorily.[5].

Keywords: Electrochemical, of ZK21 Alloy.

Introduction:

Magnesium is one of the lightest metals available in plenty in sea water its density is about 1.67 gm/cm^3 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 alloys[6]. 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 electrode[7]. 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 industry[8]. 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 inertia[9].

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 automobiles[10]. 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 satisfactorily[11].

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 water[12].

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 cm^2. 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 cell[13].

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 elements[14].

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 magnesium[15]. The ZK21 was subjected to this study in 0.02M, 0.05M, 0.1M, 0.2M and 0.5M $MgSO_4$, $(NH_4)_2SO_4$, $Mg(NO_3)_2$ and NH_4NO_3 solutions. In this technique the volume of hydrogen liberated during dissolution of the metal was collected[16].

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 sealing[17].

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 cm^2. 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 cm^2) was masked by lacquer.

125ml of solution was taken into the reaction cell, covered with air-tight lid carrying the test electrode and platinum electrode[18]. 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 terminal[19]. 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 (V_0).

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} (V_t) 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.

Δ = Vo - (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 $mm^3cm^{-2}min^{-1}$. 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 latter[20].

Results and Discussion:

The data collected by carrying out experiments using ZK21 alloy specimens as working electrode in four different media namely $MgSO_4$, $(NH_4)_2SO_4$, $Mg(NO_3)_2$, and NH_4NO_3 solutions at concentrations of 0.02M, 0.05M, 0.1M, 0.2M and0.5M are presented in this chapter. The relationship between hydrogen evolution rate (Vt) and current density (I) for all the experimental conditions are given in the form of tables. Similarly the difference effect (Δ) calculated from the V0 and Vt are tabulated. The plot of Vt Vs I and Δ Vs I for all the systems are furnished in this chapter.

Table:2 Vt Vs I for ZK21 in $MgSO_4$ solution.

Current density mA/cm²	$Vt, mm^3cm^{-2}min^{-1}$				
	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
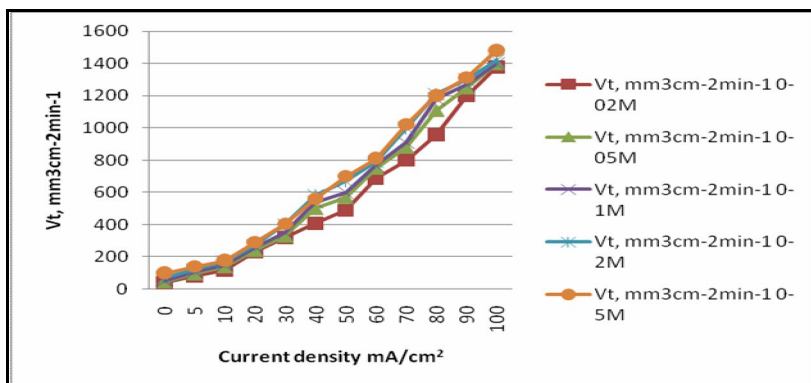
Table:3 Vt Vs I for ZK21 in $(NH_4)_2SO_4$ solution.

Current density mA/cm^2	Vt, mm^{3}cm^{-2}min^{-1}				
	0-02M	0-05M	0-1M	0-2M	0-5M
0	50	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
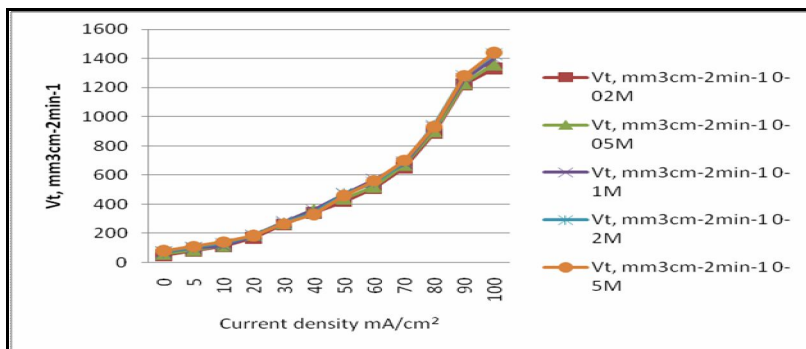
Table: 4 Vt Vs I for ZK21 in $Mg(NO_3)_2$ solution.

Current density mA/cm^2	Vt, 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

P.Kalpana *et al* /International Journal of ChemTech Research, 2016,9(6),pp 635-646.

640
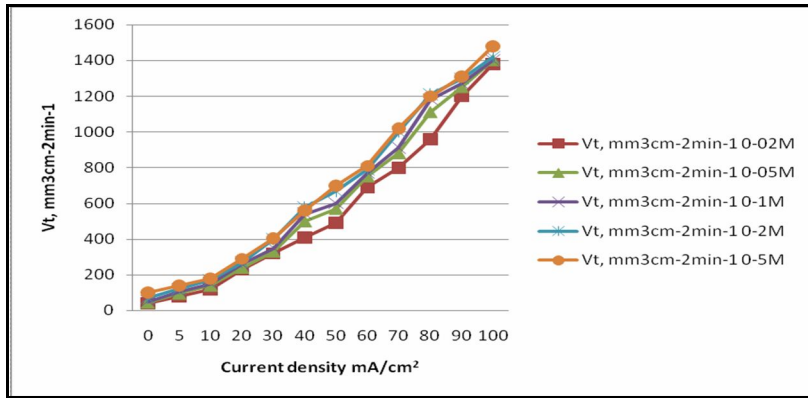
Table:5 Vt Vs I for ZK21 in NH$_4$NO$_3$ solution.

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
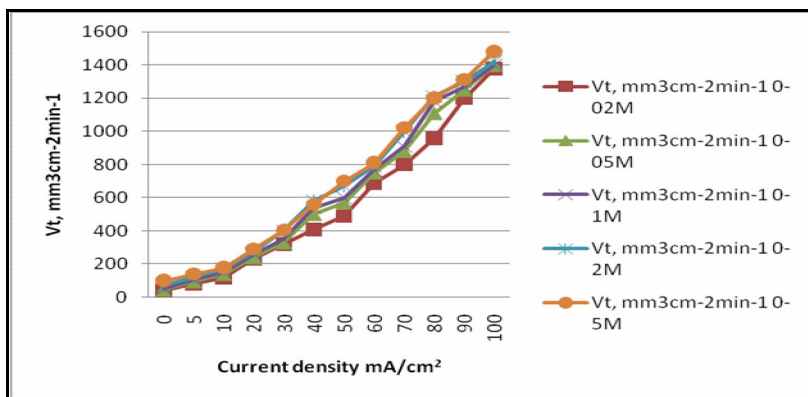
Table 6. Δ Vs I for ZK21 in MgSO$_4$ solution

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
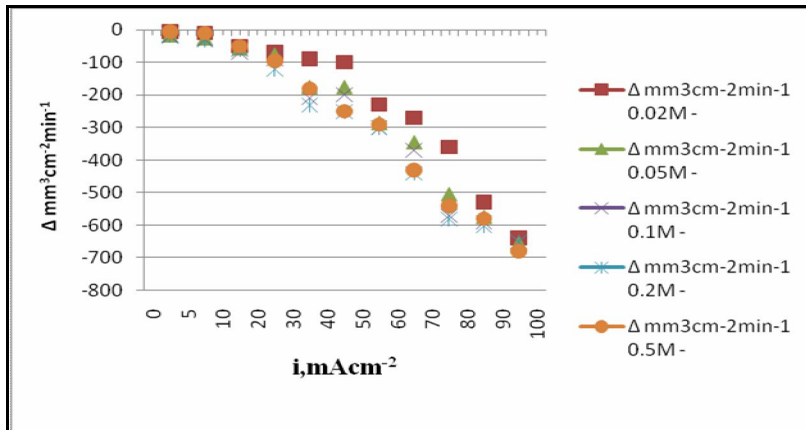
Table 7. Δ Vs I for ZK21 in $(NH_4)_2SO_4$ solution

| 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
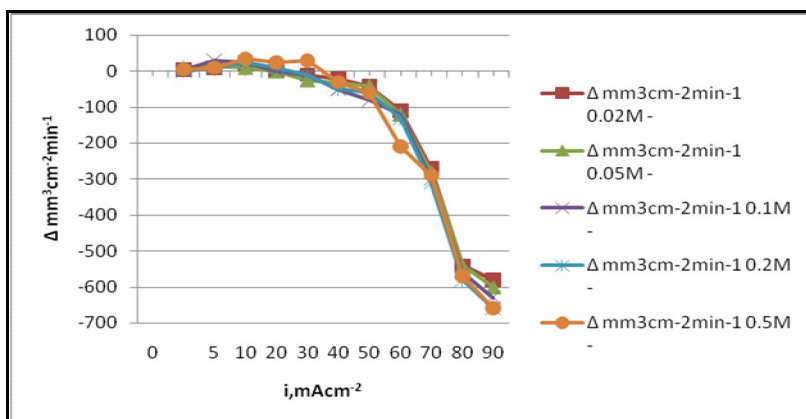
P.Kalpana *et al* /International Journal of ChemTech Research, 2016,9(6),pp 635-646.

642

Table 8. Δ Vs I for ZK21 in Mg(NO₃)₂ solution

Current Density mA/cm²	Δ $mm^3cm^{-2}min^{-1}$				
	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
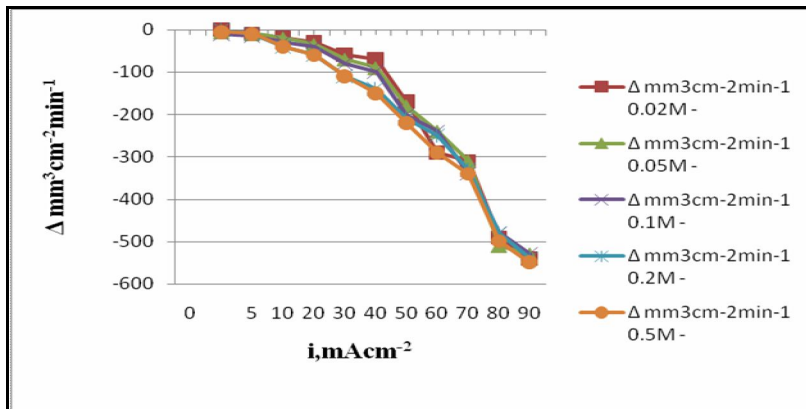
Table 9. Δ Vs I for ZK21 in NH₄NO₃ solution

Current Density mA/cm²	Δ $mm^3cm^{-2}min^{-1}$				
	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
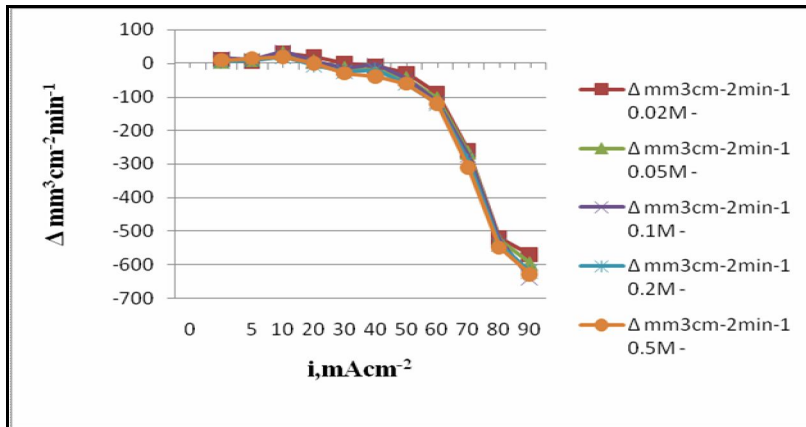
Experimental Discussion

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 Vo. Tables 2 to 9 give the galvano- gasometry data for $MgSO_4$, $(NH_4)_2SO_4$, $Mg(NO_3)_2$, and NH_4NO_3 respectively. From table 2 the Vo 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 $100mm^3$ cm^{-2} min^{-1}. Similar observations of increased V0 values are noted for the anode in, $(NH_4)_2SO_4$, Mg $(NO_3)_2$, 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 V0 values between 40 and $100mm^3$ cm^{-2} 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 Vo 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 $MgSO_4 > (NH_4)_2SO_4 > NH_4NO_3 > Mg(NO_3)_2$.

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 mm^3 $cm^{-2}min^{-1}$ 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 Vt*Vs* 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 mm^3 $cm^{-2}min^{-1}$ 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 mm^3 $cm^{-2}min^{-1}$ at 5mAcm-2 in 0.5M. Whereas overall highest Vt value in $MgSO_4$ is 1480 mm^3 $cm^{-2}min^{-1}$ 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 $(NH_4)_2SO_4$, $Mg(NO_3)_2$ 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 $(NH_4)_2SO_4$ than $Mg(NO_3)_2$.

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 $Mg(NO_3)_2$ 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 $(NH_4)_2SO_4$ 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

$\Delta = (Vo + 6.97 \, I) - Vt$
Where
Vo = Volume of hydrogen at no current
Vt = Volume of hydrogen with known current density
I = Applied current density
6.97 = Volume of hydrogen in $mm^3 cm^{-2} min^{-1}$ for milli amphere

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 Vo and Vt. 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

P.Kalpana *et al* /International Journal of ChemTech Research, 2016,9(6),pp 635-646.

645

density in $MgSO_4$ solution. At a low current density of $5 mAcm^{-2}$ difference effect has a value -5 in 0.02M concentration which goes on increasing and attains -640 at $100 mAcm^{-2}$. 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 *Vs* current density in $(NH_4)_2SO_4$, $Mg(NO_3)_2$ and NH_4NO_3 solution respectively $Mg(NO_3)_2$ solution shows almost identical behavior of exhibiting negative difference effect values only at all concentration and current density up to $100 mAcm^{-2}$. Therefore both $MgSO4$ and $Mg (NO_3)_2$ are similar in behavior towards ZK21. Tables 7 and 9 show the variation of Δ with current density and concentration in $(NH_4)_2SO_4$ and NH_4NO_3 it is seen that at $5 mAcm^{-2}$,a +5 value is obtained which goes on increasing up to $20 mAcm^{-2}$ 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 $100 mAcm^{-2}$. 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 $(NH_4)_2SO_4$, $Mg (NO_3)_2$ 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 Vo becomes greater than Vt. 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 $Mg(NO_3)_2$ solutions where as positive , zero and negative difference effect in $(NH_4)_2SO_4$ 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.

References:

1. Song G. Recent progress in corrosion and protection of magnesium alloys. *Advance Engineering Materials*. 2005; 7:563-586.
2. Song G, Atrens A.Corrosion mechanisms of magnesium alloys. *Advance Engineering Materials*. 1999; 1:11-33.
3. J. L Robinson and P F King, Electrochemical Behavior of the Magnesium Anode *J. Electrochem.soc*.1961, 108,36

4. G Song, A Atrens, S St John, X Wu and J Nairn, Corrosion Prevention of Magnesium Alloys *Corros. Sc*i, 1997, 39, 1981.
5. T Przyluski, E palka, Electrochemical Synthesis of Inorganic Compounds, *Electrochim.Acta* 1970, 15,853.
6. G GPerrault,J. The negative-difference effect during the localized corrosion of magnesium and of the AZ91HP alloy, *Electroanal.chem*.1970, 27,47.
7. G Song, Corrosion of Magnesium Alloys, *Corros.Sci*.1997, 39, 855.
8. Weber C, Knörschild G, Dick L. The negative-difference effect during the localized corrosion of magnesium and of the AZ91HP alloy. *Journal Brazilian Chemical Society*. 2003; 14:584-593.
9. M N Hull, J. Electrochemical Measurements of Isopolyoxomolybdates: *Electroanal.chem*.1972, 3.143.
10. T H Nguyen and R T Foley: J. Surface Oxide Films, *Electrochem.Soc*.1979, 126, 1855.
11. A S Fouda, Bull. Pyrazole Derivatives as Corrosion Inhibitor for C- Steel in Hydrochloric Acid Medium *Electrochem*.1995, 11,522.
12. N Sato, Corrosion Behaviour of a Highly Alloyed Austenitic Alloy UB6 in Contaminated Phosphoric Acid, *Corros.Sci* 1995, 37, 947.
13. B W Samuels, K Sotoudehand and R T Foley: Pitting Corrosion Inhibition of Some Copper Alloys in Neutral Solutions by Straight Chain Carboxylates, *Corrosion* 1981, 37, 92.
14. S P Lynch and P Trevena: Characterisation of stress corrosion cracking (SCC) of Mg–Al alloys *Corrosion* 1988, 136, 563.
15. G L Makar and J Kruger, Corrosion and Corrosion Control J. *Electrochem.Soc*.1990, 137,414.
16. C A Nunezlopez, P Skeleton, G E Thompson, P lyon, H Karimzadeh and T E Wilks, Corrosion Behavior of Mg-Al/TiC Composites in NaCl Solution, *Corros.Sci*.1995, 37, 689.
17. R Udayan, P Bhatt, Ionic Liquid Electrolytes for Li–Air Batteries: Lithium Metal Cycling *J.Power sources* 1996, 63,103.
18. Li L, Gao J, Wang Y. Evaluation of cyto-toxicity and corrosion behavior of alkali-heat-treated magnesium in simulated body fluid. *Surface Coating*. 2006; 185:9-98.
19. Song G, Atrens A., Stjohn D, Nairn J, Li Y. Electrochemical corrosion of pure magnesium in 1 N NaCl.*Corrosion Science*. 1997; 39:855-875.
20. Song G, Atrens A, Wu X, Zhang B. Corrosion behaviour of AZ21, AZ501 and AZ91 in sodium chloride.*Corrosion Science*. 1998; 40:1769-1791.

✱✱✱✱✱