CORROSION OF ROTATING MAGNESIUM ELECTRODE IN NEUTRAL ELECTROLYTES

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ABSTRACT

Rotating disc electrode technique is a versatile method to study the electrochemical aspects of solid electrodes. Moreso for the investigation of corrosion of magnesium, on which a bubble effect is usually experienced in static environments. The metal and its alloys are readily recyclable, comparatively cheaper than aluminium, environmentally clean and hence are used in many strategic areas. To popularize further and enhance the application of the magnesium, an understanding of the corrosion aspects is mandatory. The objective of the study was to investigate the corrosion behaviour of primary magnesium(99.8%) under rotation of 100, 250, 500, 1000 and 2000 rpm in NaCl, $MgCl_2$ and $Mg(ClO_4)_2$ electrolytes at various concentrations ranging from 0.1 to 1.0 M. Different data namely E_{corr}, I_{corr} , Tafel slopes and i_k show a shift in corrosion potential towards negative direction with rotation and concentration. Similarly the I_{corr} is found to increase with the rate of rotation of the electrode and increasing the concentration of the electrolytes. Moreover a synergistic influence of concentration and rotation is observed in the study. The plots of i^{-1} Vs $\omega^{-1/2}$ indicate the relationship between disc current and rate

of rotation. The mechanism of electrochemical dissolution has been discussed on the basis of i_k computed from i^{-1} Vs $\omega^{-1/2}$ graphs.

INTRODUCTION

An added awareness in magnesium applications potentiality in newer areas has evinced fresh interest in investigating of its electrochemical behaviour. The corrosion aspects of magnesium and its alloys have been studied by galvanostatic, potentiostatic, impedance, gasometric and rotating disc methods [1- 7]. The behaviour of magnesium under normal conditions has been found to be transient in nature with ennoblement in potential to an extent of 1.0 V in comparison to its emf of –2.37 V Vs SHE [8-9]. This study has been undertaken to investigate the special behaviour of rotating magnesium electrode in solutions containing, sodium chloride,magnesium chloride and magnesium perchlorate at different concentrations. The effect of various anodic and cathodic environments on the mechanism of dissolution of rotating electrode has been studied during this investigation [10-13]. The mass transport of the solution has been improved by rotation of the electrode, rather than moving the solution by magnetic stirrer. The important feature of this method is that the electrode surface is highly and uniformly accessible with uniform rate of mass transport. The turbulent flow at very high rotation is achieved through laminar flow patterns of the solution at low electrode rotations. The corrosion current($I_{corr,}$) corrosion potential($E_{corr,}$) kinetic current(i_K), and such Tafel constants have been calculated for the system and interpreted.

EXPERIMENTAL

A three electrode polarization set up was used to collect various data under rotating condition of the electrode [6]. The working electrode of the assembly was electrolytic grade magnesium containing Si 380, Al 340, Fe 320, Cr 30, Zn 30 and Mn 20 ppm. The specimen was turned in to a small knobs with an active surface area $0.3cm^2$ and connected to the shaft of a rotating setup (pine MSRX). The specimens were polished with 1/0 to 4/0 emery sheets and degreased with acetone. Saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode of the experimental cell. The test solution of concentrations 0.10, 0.20, 0.50 and 1.0 M were prepared from analytical grade NaCl, $MgCl_2$ and $Mg(ClO_4)_2$ salts and triple distilled water. The test solution was taken in the cell and the open circuit potential (OCP) was recorded after the system attained equilibrium conditions [14,15]. A constant potential at a sweep rate of $1.0 \ mV.Sec^{-1}$ was applied from an electrochemical analyzer BAS –1000 model. The measurements were carried out at electrode rotations of 100, 250, 500, 1000 and 2000 rpm from –200 to +200 mV at thermoset conditions of $32\pm 1°C$. Various data were calculated and presented in table 1 –3. The $\omega^{-1/2}$ Vs i^{-1} graphs were drawn for all the systems Figs. 1-3. The kinetic current values were calculated by the extrapolation of the lines to the current coordinate for the three systems and are given in the table 4. From the Tafel plots, the corrosion parameter I_{corr}, E_{corr}, b_a and b_c were evaluated. The layer of liquid immediately adjacent to the surface is stagnant with respect to movement towards disc and rotates with it, at the same angular velocity.

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RESULTS AND DISCUSSION

The potentiodynamic polarisation data for magnesium in NaCl, MgCl$_2$ and Mg(ClO$_4$)$_2$ solutions at different conditions given in tables 1-3,   bring out the following observations. The corrosion potential E$_{corr}$ is noticed to be in the vicinity of -1.52 V in MgCl$_2$(Table-2) which is found to increase with   concentration of the medium and rate of rotation of the working electrode . Thus the highest E$_{corr}$ for the magnesium is exhibited in 1.0 M MgCl$_2$ at 2000 rpm rotation. Corrosion current I$_{corr}$ also increases quite expectedly with both rotation and concentration. As is evident from the table the lowest I$_{corr}$ of 1.4 mA cm^{-2} is observed in 0.1 M MgCl$_2$ at 100 rpm rotation, and the highest I$_{corr}$ of 11.6 mAcm^{-2} in 1.0 M MgCl$_2$ at 2000 rpm rotations. These observations substantiate the combined effect of concentration and rotation on the corrosion of magnesium electrode.   The Tafel constant readily confirms the cathodically controlled mechanistic behaviour of the dynamic electrode as b$_c$ is found to be greater than b$_a$, irrespective of the rate of rotation of the electrode or concentration of the MgCl$_2$ solutions.

A similar behaviour of enhancement of E$_{coor}$ and I$_{corr}$ with increasing in concentration of Mg(ClO$_4$)$_2$ and NaCl solution is also observed. However the E$_{corr}$ values are noticed to be slightly positive in Mg(ClO$_4$)$_2$ than in NaCl medium.   Again the I$_{corr}$ values are also found to be lowest in Mg(ClO$_4$)$_2$ than in other solutions but NaCl solutions exhibit an aggressive behaviour towards the electrode as evident from the highest I $_{corr}$ value   (18.5 mAcm^{-2}) at 2000 rpm rotation in 1.0 M concentration.

Table – 1

Potentiodynamic polarisation data for Magnesium in NaCl solution

Conc. (M)	ω (rpm)	E_{Corr} (-V)	I_{corr} (mA.cm^{-2})	b_a (mv/dec)	b_c (mv/dec)	R_p (Ω cm^2)
0.10	100	1.57	1.7	150	156	8.8
	250	1.57	2.2	147	150	7.0
	500	1.58	2.8	144	147	5.2
	1000	1.58	3.5	140	144	4.3
	2000	1.58	3.8	146	140	3.1
0.20	100	1.58	3.6	143	153	4.3
	250	1.57	4.0	140	150	3.7
	500	1.57	4.6	137	147	3.3
	1000	1.58	5.2	136	146	3.1
	2000	1.57	5.6	133	144	2.7
0.50	100	1.62	7.6	144	--	3.9
	250	1.62	8.0	141	--	3.6
	500	1.63	9.0	137	--	3.2
	1000	1.62	10.1	135	--	2.8
	2000	1.63	10.7	132	--	2.5
1.0	100	1.65	15.5	139	--	3.4
	250	1.66	16.1	137	--	3.2
	500	1.65	17.0	135	--	3.0
	1000	1.66	17.6	131	--	2.8
	2000	1.67	18.5	129	--	2.4

Table – 2

Potentiodynamic polarisation data for Magnesium in MgCl₂ solution

Conc (M)	ω (rpm)	E_{Corr} (-V)	I_{corr} (mA.cm^{-2})	b_a (mv/dec)	b_c (mv/dec)	R_p (Ω cm^2)
0.10	100	1.52	1.4	147	151	10.2
	250	1.52	1.9	144	148	8.4
	500	1.53	2.5	141	145	6.8
	1000	1.53	3.0	140	144	5.6
	2000	1.53	3.5	137	142	5.0
0.20	100	1.53	2.7	132	149	6.8
	250	1.54	3.3	127	146	5.6
	500	1.54	3.8	123	142	4.5
	1000	1.55	4.6	120	137	3.8
	2000	1.55	5.5	118	135	3.1
0.50	100	1.57	5.0	105	--	4.5
	250	1.57	5.8	102	--	4.0
	500	1.58	6.6	99	--	3.4
	1000	1.58	7.5	98	--	3.1
	2000	1.59	8.8	95	--	2.9
1.0	100	1.61	8.1	65	--	3.5
	250	1.61	8.8	61	--	3.3
	500	1.62	9.5	57	--	3.1
	1000	1.63	10.7	53	--	2.9
	2000	1.63	11.6	50	--	2.8

Table –3

Potentiodynamic polarisation data for Magnesium in Mg(ClO$_4$)$_2$ solution

Conc (M)	ω (rpm)	E_{Corr} (-V)	I_{corr} (mA.cm^{-2})	b_a (mv/dec)	b_c (mv/dec)	R_p (Ω cm^2)
	100	1.46	1.2	94	154	12.5
	250	1.46	1.5	93	153	10.0
0.10	500	1.46	2.0	91	150	8.6
	1000	1.47	2.4	89	148	7.7
	2000	1.47	3.0	87	145	7.0
	100	1.49	1.9	74	144	8.4
	250	1.49	2.8	71	141	7.1
0.20	500	1.50	3.4	69	137	5.8
	1000	1.50	4.0	66	133	4.9
	2000	1.51	4.7	63	131	3.5
	100	1.53	3.1	55	144	5.4
	250	1.53	4.0	54	141	4.3
0.50	500	1.54	4.8	53	139	3.5
	1000	1.54	5.1	52	137	3.4
	2000	1.54	5.5	51	134	3.0
	100	1.58	4.0	36	138	3.6
	250	1.58	4.8	34	137	3.5
1.0	500	1.59	5.3	33	135	3.2
	1000	1.59	5.6	30	132	3.1
	2000	1.60	6.0	28	130	3.0

The electrochemical behaviour of magnesium in NaCl and $Mg(ClO_4)_2$ is observed to be decisively under cathodic control as $b_c \gg b_a$. It is also observed that both the Tafel slope in NaCl are much higher than other solutions. A rationale of the experimental values available in table 1 unanimously confirms the predictable behaviour of gain in E_{corr} and I_{corr} with concentration and rotation. The contribution from the concentration of the solutions is noticed to be predominant in the enhancement of I_{corr} as a ten – fold increase in NaCl concentration results 14.0 $mAcm^{-2}$ increase in I_{corr}, where as for the same 10 fold increase in rotation enhances only 2.4 $mA\ cm^{-2}$. It is also understandable from the I_{corr} that the effect of rotation is more pronounced at high concentrations. Based on the corrosion current, the chloride ion is assessed to be more corrosive than perchlorate ion likewise sodium ion than magensium ion in line with the earlier observation [16]. Based on the observations the electrolytes may be graded in the decreasing order of aggressiveness as NaCl > $MgCl_2$ > $Mg(ClO_4)_2$.

The relationship between the rate of rotation of the working electrode and the corrosion current in NaCl, $MgCl_2$, and $Mg(ClO)_2$ are given Figs. 1- 3 respectively. The straight line graphs clearly indicate the phenomenon of increasing current with rate of rotation whereby the system is noticed to obey Levich equation. Hence the electrochemical behaviour of the magnesium in the media under dynamic conditions is well within the prescription of the equation. The slope of the line is decreasing with increasing concentration, which is a proof for the disc current becoming

progressively independent of rotation. Ultimately a concentration may be reached at which the disc current is entirely freed from the rotational barriers.

R_P values given table-1, show the polarization resistance of the magnesium anode in NaCl solution, at different concentrations and rotations. It can be seen that as rotation of the electrode increases, the R_P value decreases, thereby indicating enhanced corrosion and vulnerability of attack by violent rotation of the electrode. Similarly for a particular rotation, as concentration increases, the R_P value is found to decrease, inferring high corrosion at high concentration. From the table, it is also seen that the lowest R_P value of 2.4 Ωcm^2 is observed in 1.0M concentration at 2000 rpm rotation showing the most aggressive environment for rotating magnesium electrode. Similarly, the R_P values for the rotating magnesium electrode in $MgCl_2$ and $Mg(ClO_4)_2$ are given in the tables 2and3 respectively. Similar observations of decreasing trend in R_P values with increasing rotation and concentration are observed in these solutions also. Considering the three tables, maximum R_P of 12.5 Ωcm^2 is resulted at 100 rpm rotation in 0.1M concentration as against the lowest of 2.4 Ωcm^2 at 2000 rpm in 1.0M NaCl solution which are reckoned to be the two extremes of the corrosion environment. Accordingly the corrosivity of the electrolytes is found to be in the decreasing order as $NaCl > MgCl_2 > Mg(ClO_4)_2$.

Table – 4

Kinetic current   (i_k)   values for magnesium

Electrolyte	Concen (M)	OCP (-V)	i_k (mA cm^{-2})			
			Over potential (mV)			
			+20	+50	+100	+120
NaCl	0.10	1.57	8.2	10.9	24.6	32.8
	0.20	1.58	9.8	24.4	29.7	32.7
	0.50	1.62	14.1	32.8	39.5	49.1
	1.0	1.65	18.0	43.1	50.1	62.2
MgCl$_2$	0.10	1.60	5.1	16.4	32.7	49.5
	0.20	1.62	6.0	12.2	49.2	65.1
	0.50	1.64	8.1	24.8	65.7	99.6
	1.0	1.67	10.4	33.5	84.1	136.2
Mg(ClO$_4$)$_2$	0.10	1.46	3.8	6.5	13.8	24.7
	0.20	1.49	7.5	14.8	24.8	32.5
	0.50	1.53	10.5	29.7	49.5	99.8
	1.0	1.58	14.4	46.2	78.4	139.4

Kinetic current (i_k) values furnished in table- 4 show their increase with concentration.   For a particular concentration, the quantity is highest in NaCl followed by MgCl$_2$ and lowest in Mg(ClO$_4$)$_2$. The extent of i_k , further ascertains the enhanced corrosivity of the media, giving a reaffirmation of higher activity of NaCl than other solutions. Moreover the very nature of the i_k , being low at the infinite rotation conditions certifies that it is independent   of concentration and hence controlled by charged transfer mechanisms only. Higher the value means less and less diffusion control. The quantity helps to identify the change of the mechanism from mass transfer to charge transfer. The highest i_k of 18 mAcm^{-2} resulted in 1.0 M NaCl within the linear polarization range, indicates the electrochemical reaction of magnesium electrode at infinite rotation is governed by charge transfer criteria.

Contrarily owing to the lowest i_k of 3.8 mAcm^{-2} in 0.1 M Mg(ClO$_4$)$_2$, the behaviour is assumed to be controlled by mass transfer mechanism.

CONCLUSIONS

Both concentration of the medium and rotation of the electrode influence the corrosion potential of the magnesium, which was noticed to be ranging between –1.46 and - 1.67 V.   Highest I$_{corr}$ of 18.5 mAcm^{-2} has been resulted in 1.0M NaCl at 2000 rpm rotation and lowest 1.2 mAcm^{-2} in 0.1M Mg(ClO$_4$)$_2$ at 100 rpm rotation. The kinetic current(i_k) is observed to be increased with nature and concentration of the electrolytes.   Effect of electrolyte concentration is found to be predominating than the effect of electrode rotation in the corrosion of the magnesium.   The corrosion behaviour of the rotating magnesium electrode is observed to obey Levich equation and the mechanism of electrochemical dissolution of the magnesium in these electrolytes at infinite rotation is controlled by charge transfer processes.

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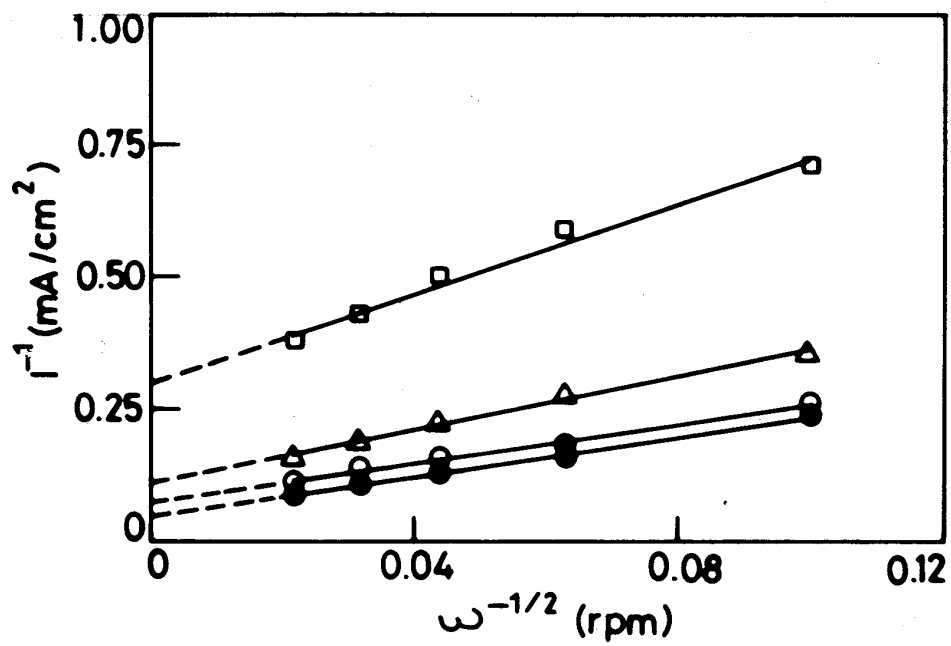16. C.O.Augustin, A.Antonyraj and S.V.K.Iyer, *Port Electrochim Acta*, 13, P.11, (1995)

Fig.1. Plot of i^{-1} Vs $\omega^{-1/2}$ for Mg in NaCl at (0.1 (□ M, (Δ) 0.2M (O) 0.5M and (●) 1.0 M.
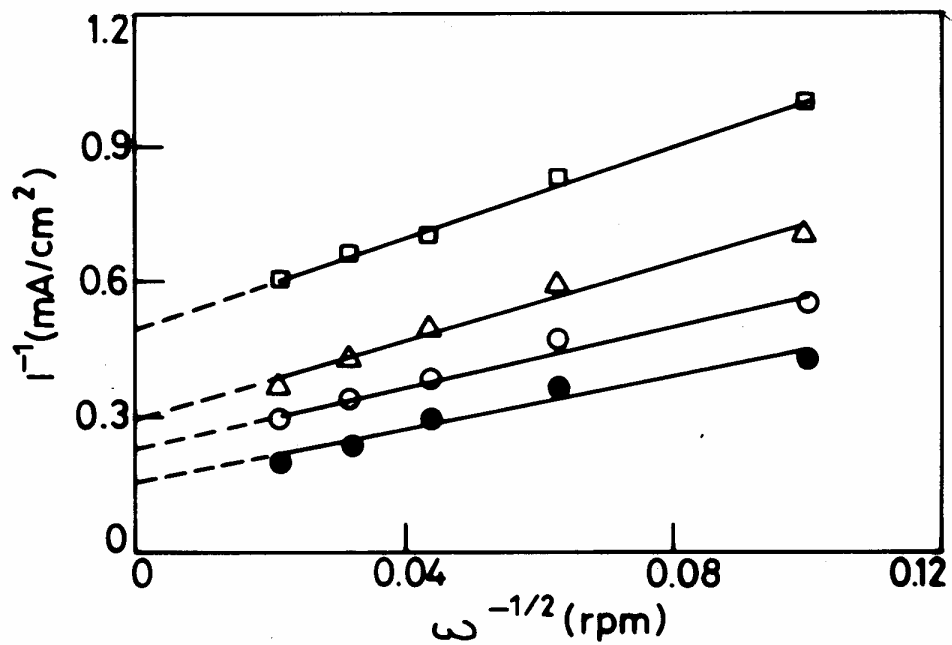

Fig.2. Plot of i^{-1} Vs $\omega^{-1/2}$ for Mg in MgCl$_2$ at (0.1 (□ M, (Δ) 0.2M (O) 0.5 M and (●) 1.0M.
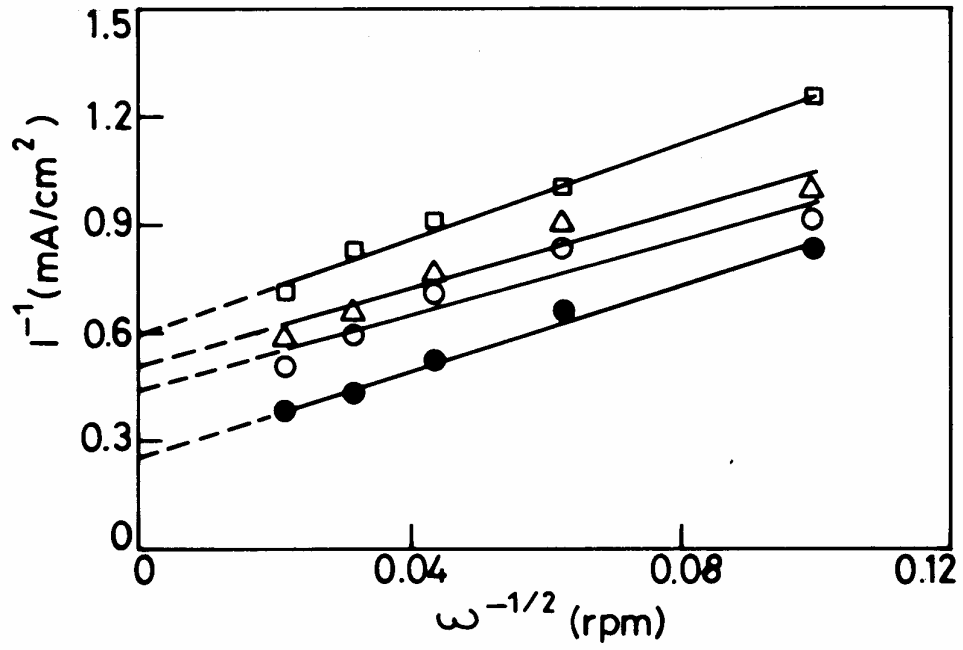
Fig.3. Plot of i^{-1} Vs $\omega^{-1/2}$ for Mg in $Mg(ClO_4)_2$ at (0.1 (□ M, (Δ) 0.2M (O) 0.5M and (●) 1.0 M.