Asian Journal of Chemistry Vol. 5, No. 2 (1993), 445–451

Effect of Acid Medium on Lead-Steel Couple

GAMAL K. GOMMA
Faculty of Education
Chemistry Department, Kafr El-Sheikh, Egypt

The effects of oxalic acid and perchloric acid have been studied on the Pb-Fe couple by means of the open circuit potential and the galvanic current of the couple electrodes. The potential of the coupled as well as galvanic current were followed as a function of time till the steady state was attained. In all cases of oxalic acid and perchloric acid in the pH range 1.5–6.5, lead is the more noble electrode of the couple. This is due to the weak complexing of lead in these solutions. Lead is initially anodic to steel. However, reversal of polarity takes place after some time and steel becomes the anode of the couple.

INTRODUCTION

Marine constructions may be protected by lead sheets. The present study was initiated in order to assess the corrosion of lead when it is coupled with steel in acid medium. Lead coupled to steel may be either the anode or the cathode depending upon the type of the medium.

EXPERIMENTAL

The lead used was of commercial grade; steel metal contained 0.05% C and will be designated usually as Fe. The two electrodes had the same dimensions, 1 cm^2. The distance between lead and steel electrodes was fixed at 2 cm. Before each experiment Pb and Fe were cleaned and connected to the ammeter. There was no time lag between contact with the solution and the flow of current.

During potential measurements, the potentials of the separate or coupled lead and steel electrodes immersed in the test solutions were measured against a saturated calomel electrode (SCE) till steady-state potential and were plotted as a function of time. A manual potentiometer was used. Chemicals used were of AR-grade and the pH of the tested solutions was adjusted by small amounts of NaOH and $HClO_4$. The experiments were conducted at 30°C. All the values reported were carried out at a triplicate experiment.

RESULTS AND DISCUSSION

Potential-time measurements

Potentials of lead-steel couple in stagnant oxalic acid and perchloric acid were measured till steady-state values were obtained. Typical potential-time curves for the coupled electrodes in stagnant solution of oxalic acid and perchloric acid were presented in Figs. 1, 2 at different pH values. The potential-time relationship for separate lead or steel electrodes are included in the Figs. for comparison. It can be seen from these Figs. in all tested solutions that the behaviour of lead-steel

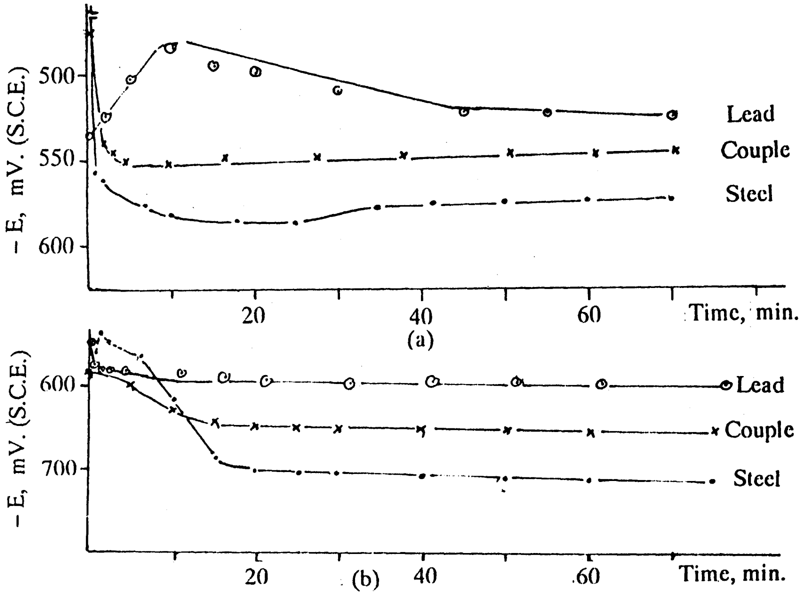

Fig. 1 Potential/time curve for separated and coupled Pb & Fe electrode in 0.1 M oxalic at (a) pH 2.5 and (b) pH 6.5.

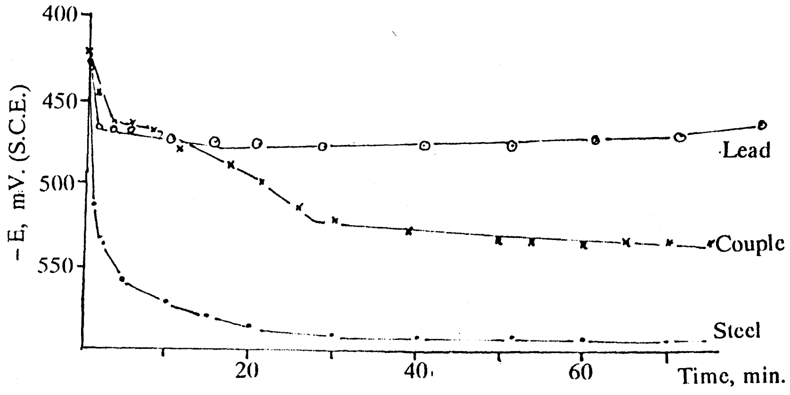

Fig. 2 (a) Potential/time curve for separated and coupled Pb & Fe electrode in 0.1 M perchloric acid at pH 1.5.

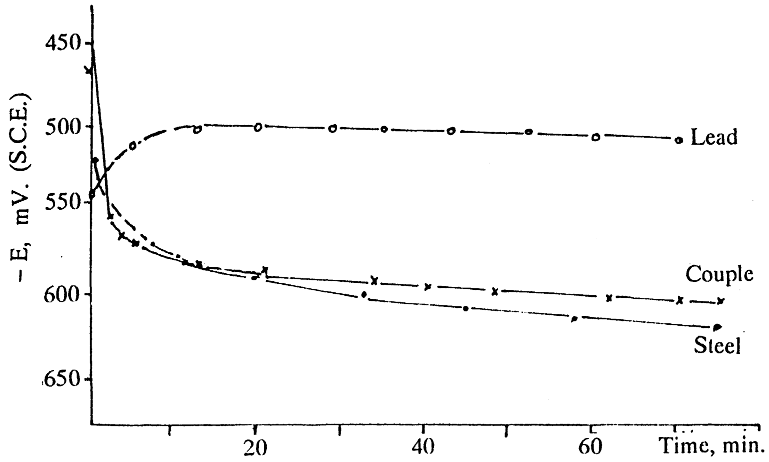

Fig. 2 (b) Potential/time curve for separated and coupled Pb & Fe electrode in 0.1 M perchloric acid at pH 4.5.

couple was generally have the same trend. The potential shifts with time to the active direction till the steady-state values was attained, and the time required to reach steady state values varies from 40–70 min. It was found that the initial and steady state potential values of the couple were lying between these of the uncoupled lead and steel electrodes. The initial and final potential values of lead-steel couple are given in Table 1.

The relation between potential-time curves was obtained for lead-steel couple in 10^{-2} M of the same tested solutions, the behaviour was similar to that obtained in 10^{-1} M of the same tested solutions (curves are not shown). The potential of the couple electrodes shifted with time towards more negative direction till the steady-state potential was attained. However, in all cases of pH 1.5–6.5 for oxalic acid and perchloric acid, the lead electrode was cathodic to steel after the reversal of polarity.

Galvanic current-time measurements for coupled electrode

Fig. 3 shows current-time curves for a Pb-Fe couple immersed in 10^{-1} M oxalic acid solution in the pH range 1.5–6.5 as an example of galvanic current-time relationships.

From this figure it is clear that the galvanic current diminishes rapidly, changing its sign after 1–15 min. according to the pH (the current is positive when Pb is the anode) and finally decreases, whereby a steady state is approached. The initial positive and the steady-state currents are higher and the time taken by current to reverse its sign is higher, the lower the pH values. The galvanic current obtained having initially positive values, changes its sign and then increases in the negative direction till the steady-state is reached.

TABLE 1

INITIAL (E_1) AND STEADY-STATE POTENTIAL (E_2) VALUES AND COUPLED Pb AND Fe ELECTRODES IN OXALIC ACID AND PERCHLORIC ACID AT DIFFERENT pH VALUES

Acid	pH	1.5		2.5		3.5		4.5		5.5		6.5	
		E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
Perchloric 0.1 M	Un-coupled Pb	430	460	437	480	482	492	452	515	519	532	574	556
	Pb-Fe	425	539	428	575	430	595	460	600	484	508	348	615
	Un-coupled Fe	432	592	422	605	430	612	450	617	479	622	299	635
10^{-2} M	Un-coupled Pb	411	434	422	444	455	456	530	500	553	512	542	520
	Pb-Fe	417	481	445	490	452	510	513	557	446	555	486	578
	Un-coupled Fe	382	532	395	582	445	592	382	597	459	605	318	620
Oxalic 0.1 M	Un-coupled Pb	504	464	537	524	548	550	597	560	587	580	575	595
	Pb-Fe	409	478	482	555	539	570	562	580	570	622	582	650
	Un-coupled Fe	529	543	539	580	545	600	583	605	508	620	582	680
10^{-2} M	Un-coupled Pb	451	405	523	417	542	460	563	485	576	495	509	510
	Pb-Fe	422	460	488	473	520	535	540	560	468	572	530	595
	Un-coupled Fe	396	535	517	552	525	600	529	615	421	625	376	640

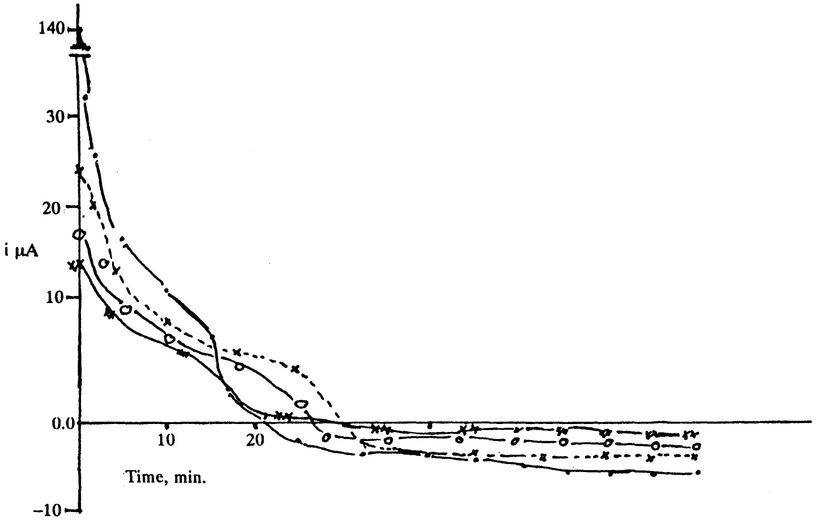

Fig. 3 Galvanic current/time for Pb-Fe couple in 0.1 M oxalec acid at pH (o) 1.5 (x) 2.5 (o) 3.5 and (xx) 4.5.

The initial and the final values of galvanic currents are given in Table 2. Since all the electrodes of the corrosion couple had almost the same area, the corrosion current density is considered in the broader sense of current-time electrode area.

TABLE 2

INITIAL (i_1) AND FINAL (i_2) VALUES OF GAVANIC CURRENT μA, FOR Pb-Fe COUPLE IN 0.1 M OF OXALIC AND PERCHLORIC ACID SOLUTIONS

Medium	Conc. (M)	1.5		2.5		3.5		4.5		5.5		6.5	
		i_1	i_2	i_1	i_2	i_1	i_2	i_1	i_2	i_1	i_2	i_1	i_2
Oxalic	0.1	128	−7	29	−4.2	22	−3.9	18	−2.1	16	−1.5	14	−1.2
$HClO_4$	0.1	14	−13.6	13	−9.5	8	−4.2	12	−3.9	28	−3.4	36	−2.2

When lead is coupled with steel and immersed in oxalic acid and perchloric acid, lead is initially anodic to steel; lead will be polarised anodically and Fe cathodi- cally[1-5]. As a result, the corrosion of lead will be enchanced. The continuous negative drift of the potential of steel will lead to reversal of polarity; consequently lead will be polarised cathodically and the cathodic process may partially consist in the discharge of Pb ions already formed before reversal of polarity.

Under this condition, steel will be (after reversal) anodically polarised so that its corrosion rate will be much higher in the coupled than in the un-coupled.

By constructing an Evans diagram as shown in Fig. 4, we illustrate the galvanic behaviour. It is noteworthy that this diagram is constructed from the steady-state potential and current values obtained in 10^{-1} M of oxalic acid and perchloric acid solutions.

TABLE 3
GALVANIC CURRENT OF LEAD-STEEL COUPLE, THE POTENTIAL DIFFERNECE BETWEEN THE STEADY-STATE POTENTIAL VALUES OF THE SEPARATE ELECTRODES (ΔE) AND THE MIXED POTENTIAL IN 10^{-1} M OF OXALIC ACID AND PERCHLORIC ACID SOLUTIONS

Acid	pH	–E, mV	Galvanic current (μA)	Mixed potential, –mV
Oxalic	1.5	79	-7	478
	2.5	56	-4.2	500
	3.5	50	-3.9	550
	4.5	45	-2.1	580
	5.5	40	-1.5	622
	6.5	30	-1.2	650
Perchloric	1.5	132	-13.6	539
	2.5	125	-9.5	575
	3.5	120	-4.2	595
	4.5	102	-3.9	600
	5.5	90	-3.4	608
	6.5	70	-2.2	615

From Fig. 4 it is clear that the cathodic reaction in the case of perchloric acid is more polarised than in oxalic acid, while the anodic reaction in both cases is almost the same. Thus the increase of the galvanic current is due to the enhancement of the cathodic reaction in the former rather than of oxalic acid.

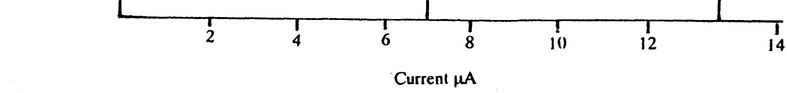

Fig. 4 Evans diagram representing the galvanic coupling in 0.1 M solutions of (a) perchloric and (b) oxalic acid

It was found that under certain thermodynamic conditions, the rate of corrosion is determined by the total kinetic retardation of the corrosion system and not by the EMF[6–8].

It was found that the resistance of the corrosive medium plays an important role when the corrosion couple consists of micro cells on the same metal. Thus when the two metals comprising the corrosion couple are situated opposite to one another, then the current path is affected and will depend in this case on the resistance of the medium.

Tomashov[2] discussed the contribution of the specific resistivity of the electrolyte to galvanic corrosion. Thus galvanic current in perchloric acid is much more than in case of oxalic acid.

REFERENCES

1. U.R. Evans, The Corrosion and Oxidation of Metals, Edward Arnold Ltd., London (1960).
2. N.D. Tomashov, Theory of Corrosion and Protection of Metals, McMillan, New York (1966) .
3. K.J. Vetter, Electrochemische Kinetic Spring-Verlag, Berlin (1961).
4. I.O'M. Bockris and A.K.N. Redy, Modern Electrochemistry, Vol **11**, Plenum, New York Press (1970).
5. G. Wranglen and I. Khokhar, *Corros. Sci.*, **9**, 439 (1969).
6. N.D. Tomashov, Theory of Corrosion and Protection of Metals, McMillan, N.Y. (1967).
7. H.P. Goddard, *Corrosion*, **11**, 542t (1955).
8. V.K. Gouda and H.M. Mourad, *Corrosion Sci*,. **14**, 681 (1979).

(*Received*: 15 June 1992; *Accepted*: 1 August 1992) AJC–461