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ELECTROCHEMICAL PARAMETERS FOR Mo ALLOYED STEEL IN CHLORIDE SOLUTIONS

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ABSTRACT

The electrochemical parameters for a type of Mo alloyed stainless steel (containing 3.15%) was studied in chloride solutions (0.1 - 5.0 M) at different pH values and 30°C. The results show that the electrochemical parameters were dependent on the concentration and pH of the test solution.

The Mo alloyed steel containing 3.15% Mo can be passivated in chloride solutions having molarity from 0.1 to 3.0 M at pH from 1.0 to 3.0 and the passive range become wide with increase of pH value. The alloys dissolve actively from their corrosion potentials, and can not passivated in 5.0 M chloride solution at all.

The scanning rate of which the potential of the alloy is varied, dV/dt has a considerable influence on the shape of the polarization curve. E_{corr} and E_c decrease and E_{pp}, I_{crit} and I_{pit} increase with increasing dV/dt.

INTRODUCTION

The electrochemical behaviour of Mo alloyed steel in sulphate and sodium chloride solutions were previously studied in this laboratory[1-6]. The literature contains contraversal results to pitting potentials and corrosion parameters[2,7,8-20]. Because of the well established usage of molybdenum alloying for increasing the resistance of steinless steel to pitting corrosion interest

was developed in extending potentiodynamic study of the 3.15% Mo steel containing 16.98% Cr and 11.29% Ni in sodium chloride solutions (0.1 - 5.0 M) at different pH values at 30°C. The effect of the rate of which the potential of the alloy is varied, dV/dt on the corrosion parameters of the alloy has been also studied. The chemical composition of the steel used is shown in Table 1.

Table 1. Composition of steel.

Element	C	S	Cr	Ni	Mo	Mn	Si	P	Cu
wt%	0.052	0.014	16.98	11.29	3.15	1.66	0.40	0.022	-

EXPERIMENTAL

The steel is produced by Avesta (Sweden) in the shape of rods with a diameter of 20 mm. It was heated for 20 min at 1050°C and then was quenched in water.

PRETREATMENT OF SPECIMEN

Circular specimens of 15 mm ϕ were embeded in a plastic resin ground with emery paper and polished with diamond paste (1 um). Finally the specimens were cleaned in bidistilled water and ethyl alcohol.

To avoid crevice corrosion Glyptal Protecting Lacque was applied directly after polishing around the edges of the specimens (1 mm around the edges).

The specimens were prepolarized in the actual NaCl solutions (from 0.1 to 5.0MNaCl)at different pH values (from 1.0 to 3.0) at -700 mV_{SCE} for 1 hr.

CONDITIONS AND PROCEDURE

Experiments were carried out at 30°C in sodium chloride solutions with concentration varying from 0.1 to 5.0 M. at different pH (from 1.0 to 3.0). The cell was continously

purged with purified nitrogen to get rid of oxygen. The reference electrode was a saturated calomel electrode, connected by a salt bridge and Haber Lyggin Capillary approximately 0.5 mm from the specimen surface. The specimens were placed in a specimen holder as shown in Fig. 1. The counter electrode was a sheet of Pt placed in a separate cell containing the same used electrolyte connected with the measuring cell by a salt bridge.

For potentiodynamic measurements, the potential was controlled by Tormatic Potentiostat P_2 and the diagrams were recorded by means of Sevogor RE 511 Recorder.

The experimental procedure consisted of :

(1) Bubbling with nitrogen gas at a potential of -700 mV_{SCE} (for 1 hr) in chloride solutions.

(2) Changing the potential in noble direction using a scanning rate of 5 mV/min in (0.1 - 5.0 M NaCl at pH from 1.0 to 3.0) or at different dV/dt (from 5 to 100 mV/min in 1M NaCl at pH 2). The potential was stopped when the total current through the system reached 160 uA, this means a current density of 85 uA/Cm^2.

DISCUSSION

Typical potentiodynamic curves for the steel used are shown in Fig. 2 and 3. The active region exhibited maxima in dilute sodium chloride solution (0.1 M) at different pH values. The active region exhibited two current maxima in concentrated solutions from 0.5 to 5 M-NaCl and especially at lower pH values (1 and 1.4). These data are shown in Figs. 4, 5, 6, 7 and 8 where a pronounced second current maximum is observed in most of the figures at different potentials. The amplitude of this

current maximum increases with the decrease of pH values.

It is clear from the Figs. (2-8), that this type of steel can be passivated in chloride solutions having molarily from 0.1 to 3 M at pH values 1-3.0 and the passive range become wide with increase of pH value. It dissolve actively from its corrosion potential and is not passivated in 5.0 M NaCl at all.

The electrochemical parameters for this type of Mo alloyed steel are given in tables (2-4).

Table 2. The electrochemical parameters for Mo alloyed steel containing 3.15% Mo in chloride solutions C_{Cl^-} from 0.1-5 M at pH 1-2.

M NaCl	pH	$E_{pp.}$ $mV_{SCE.}$	$I_{crit.}$ $\mu A/cm^2$	$I_{p.}$ $\mu A/cm^2$	I_{pit} $\mu A/cm^2$	$b_{cathode}$ mV/decade	$E_{corr.}$ $mV_{SCE.}$
0.1	2	-265	9.5	2.5	3.5	95	-405
0.1	1	-220	28	15	37	280	-275
0.5	2	-285	20	3,4	9,75	150	-415
0.5	1.4	-295	26.5	3,5	11	125	-410
0.5	1	-280	95	10.5	14	135	-345

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Table 3.

M NaCl	pH	$E_{pp.}$ $mV_{SCE.}$	$I_{crit.}$ $\mu A/cm^2$	$I_{p.}$ $\mu A/cm^2$	I_{pit} $\mu A/cm^2$	$b_{cathode}$ mV/decade	$E_{corr.}$ $mV_{SCE.}$
3	3	-370	5.5	1.8	5	150	-415
3	2	-330	17.5	3	10	105	-410
3	1	-315	16	33	20	115	-395

Table 4.

M NaCl	pH	$E_{pp.}$ $mV_{SCE.}$	$I_{crit.}$ $\mu A/cm^2$	$I_{p.}$ $\mu A/cm^2$	I_{pit} $\mu A/cm^2$	$b_{cathode}$ mV/decade	$E_{corr.}$ $mV_{SCE.}$
5	1	-290	240	110	70	105	-405
5	1.4	-340	77.5	5.5	19.0	100	-415
5	2	-320	215	65	30	115	-420

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It is clear from these tables how the critical current ($I_{crit.}$) varied with pH and chloride concentrations at 30°C. The results show an increase in $I_{Crit.}$ with decreasing pH due to the increase of corrosion rate with acidity and conductivity of the electrolyte. Similar observation was also found for the same type of steel in sulphate solutions[2]. The critical current increased by more than two orders of magnitude (From 9.5 to 215 $\mu A/cm^2$) as chloride concentration was increased from 0.1 to 5.0 M at pH 2. From the anodic diseolution parameters for this type of steel which are listed table (2-4), corrosion potentials ($E_{Corr.}$) increased with decreasing the pH of the solution and usually were more active the smaller the magnitude of $I_{Crit.}$

Samples with respectively increasing $I_{Crit.}$ required a correspondingly longer time to passivate, and in some cases never passivated at all as in concentrated chloride solutions in 5M at pH 1 and 2 (as in Fig. 8).

It is clear from tables (2-4) that I_{Pit} increases with increase of chloride ion concentration especially at lower pH values.

Tables (2-4) show that $b_{cathode}$ (Tafle slope) lies within the range 100 - 150 mV/log i for most specimens investigated, excluding the results in 0.1M NaCl at pH 1., which yield a higher value (280 mV/log i). This Tafel slope may suggest a slow discharge step (Volmer mechanism). The deviation from 118 mV/decade may be ascribed to changes in the symmetry of the energy barrier (a depart from 0.5).

It is clear that the current density I_p in the passive region of steel increases with increasing chloride

concentration (especially at lower pH values). The results indicate the progressive increase in the corrosion rate in higher concentrated chloride solutions (3 and 5 M NaCl at pH 1 and 1.4). We found all potentials decreased as would be expected with increasing chloride ion concentration.

The effect of the rate of which the potential of the specimen is varied dV/dt has a considerable influence on the shape of the polarization curve. On the other hand, investigations carried out by Greene and Leornard[22] indicate that it is of no importance whether the potential is varied in steps or continuously. The continuous potentiodynamic method is nowadays the most widely used and was preferred in this study. Fig. (9) illustrates some characteristic values of the polarization curve for the used steel in 1M NaCl solution at pH 2 against dV/dt. It is clear from Fig. 9 that E_{corr} and E_c (pitting potential) where as E_{pp} (protection potential from pitting), I_{Crit} and I_{Pit} increase with increasing dV/dt. Littlewood[23] reported that a low transverse rate of polarization give rise to an etching effect, whereas in the present study it was not the case. Probably the higher value of E_{Corr} at low dV/dt are due to enrichment of more noble alloying elements just below $E_{Corr.}$. Similar observation has been found by lars Troselius[27] on AISI 304 in 1M-H_2SO_4 solution.

The actual polarization curves obtained at the highest and lowest scanning rates indicate that the scanning rates affect several aspects of the measurements. The higher scanning rate gives rise to a higher active anodic dissolution peak, which is shifted toward more noble potentials. It has been reported that the faster scans give more noble pitting[25,26], but the opposite we found in this work on molybdenum containing alloy. This may be due to the increase of the passive film thickness

with time at a potential in the passive range. Thus the passive film would be thicker the lower the speed of the scanning. As the film thickness increases, a low fraction of the potential difference between metal and solution would be expected to occur within the film and thus not be available at the film - solution interface to assist in the entry of chloride ions into the film. A similar effect was reported by Bond and Lizlovs[27] for the 17.6% Cr 13.5% Ni 2.9% Mo in 1M NaCl solution.

The lower values of E_{Crit} at low dV/dt are attributable to a combination of these effects. Similar observation has been observed by Lars Troselius[24]. The polarization curve measured for a metal alloy is the resultant of the superimposed polarization curves for the alloying elements, E_{pp} does not have the same significance as the flade potential of a pure metal. The latter is the potential at which the entire metal surface is passivated because an oxide is thermodynamically stable or oxygen is chemisorbed. E_{pp}, on the other hand is a potential at which the resultant polarization curve has a maximum and its position is dependent upon the surface fractions of the included alloying elements.

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LEGEND :

Fig. 1. Specimen holder: 1- PVC, 2- Oring, 3- Resin, 4- Specimen, 5- Brass road, 6and7- PVC, 8- Copper road and 9- Electric connection.

Fig. 2. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 0.1M NaCl (pH 1).

Fig. 3. Potentiodynamic anodic Polarization for the 3.15% Mo alloyed steel in 0.1M-NaCl (pH 2).

Fig. 4. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 0.5M-NaCl (pH 1).

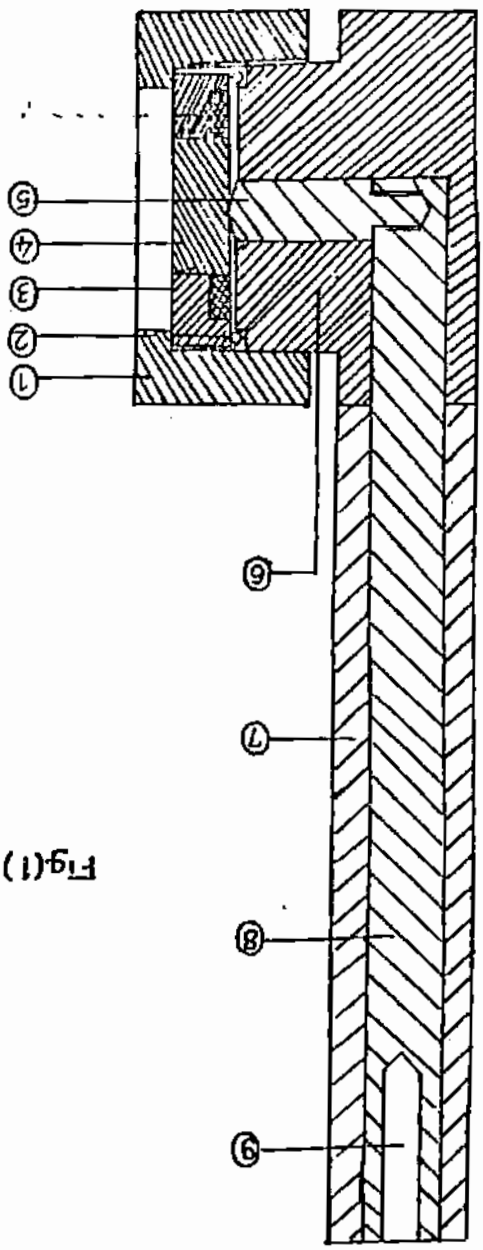
Fig. 5. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 0.5M NaCl (pH 1.4).

Fig. 6. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 3M NaCl (pH 1).

Fig. 7. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 3M NaCl (pH 3).

Fig. 8. Potentiodynamic anodic polarization for the 3.15% Mo alloyed steel in 5M NaCl (pH 1).

Fig. 9. Electrochemical parameters for 3.15% Mo alloyed steel in 1M NaCl (pH 2) using different dV/dt.



Fig(1)

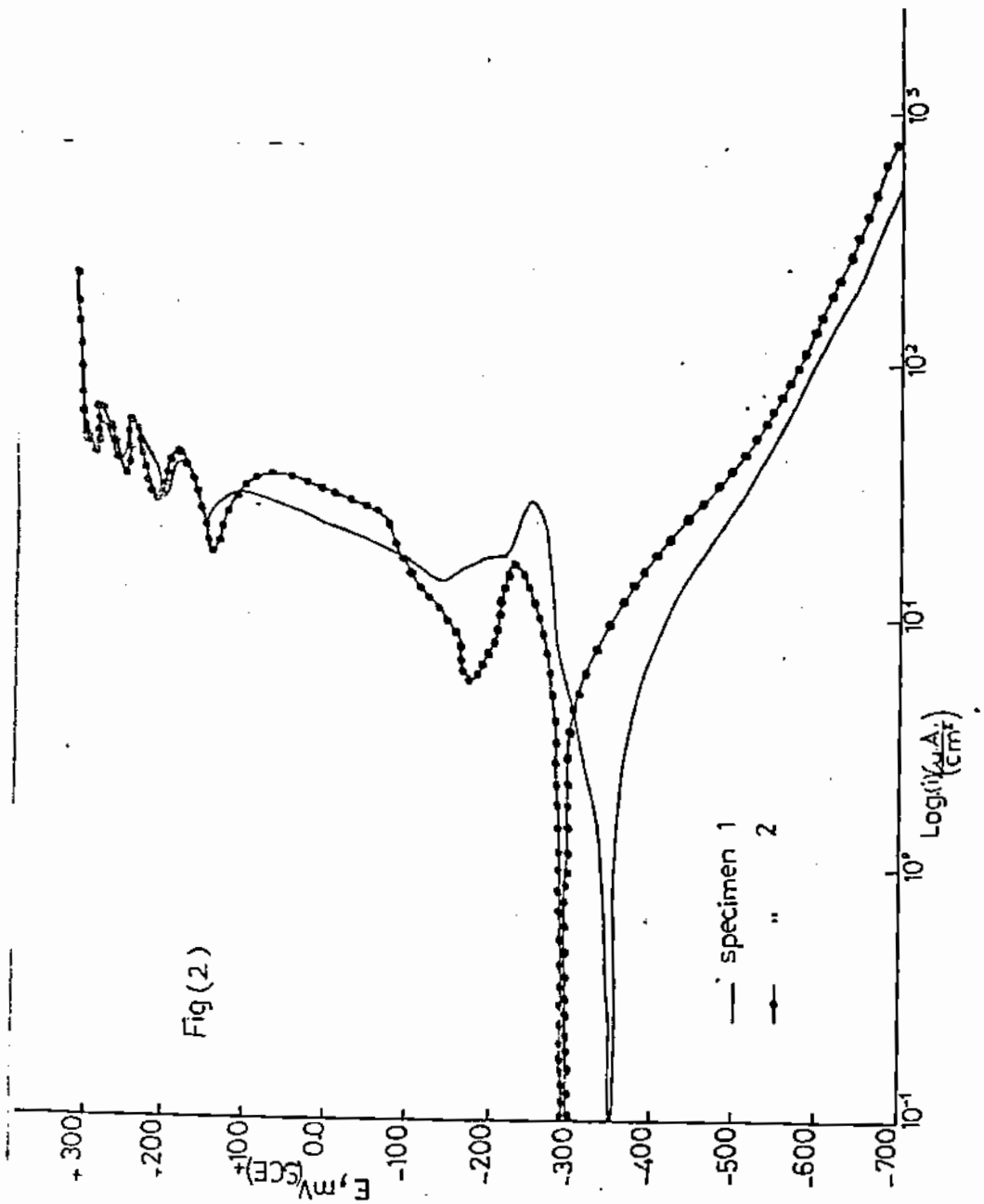

+300
+200
+100
0.0
-100
-200
-300
-400
-500
-600
-700
E, mV (SCE)
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
Log i (μA/cm²)
specimen 1
" 2

Fig (2)

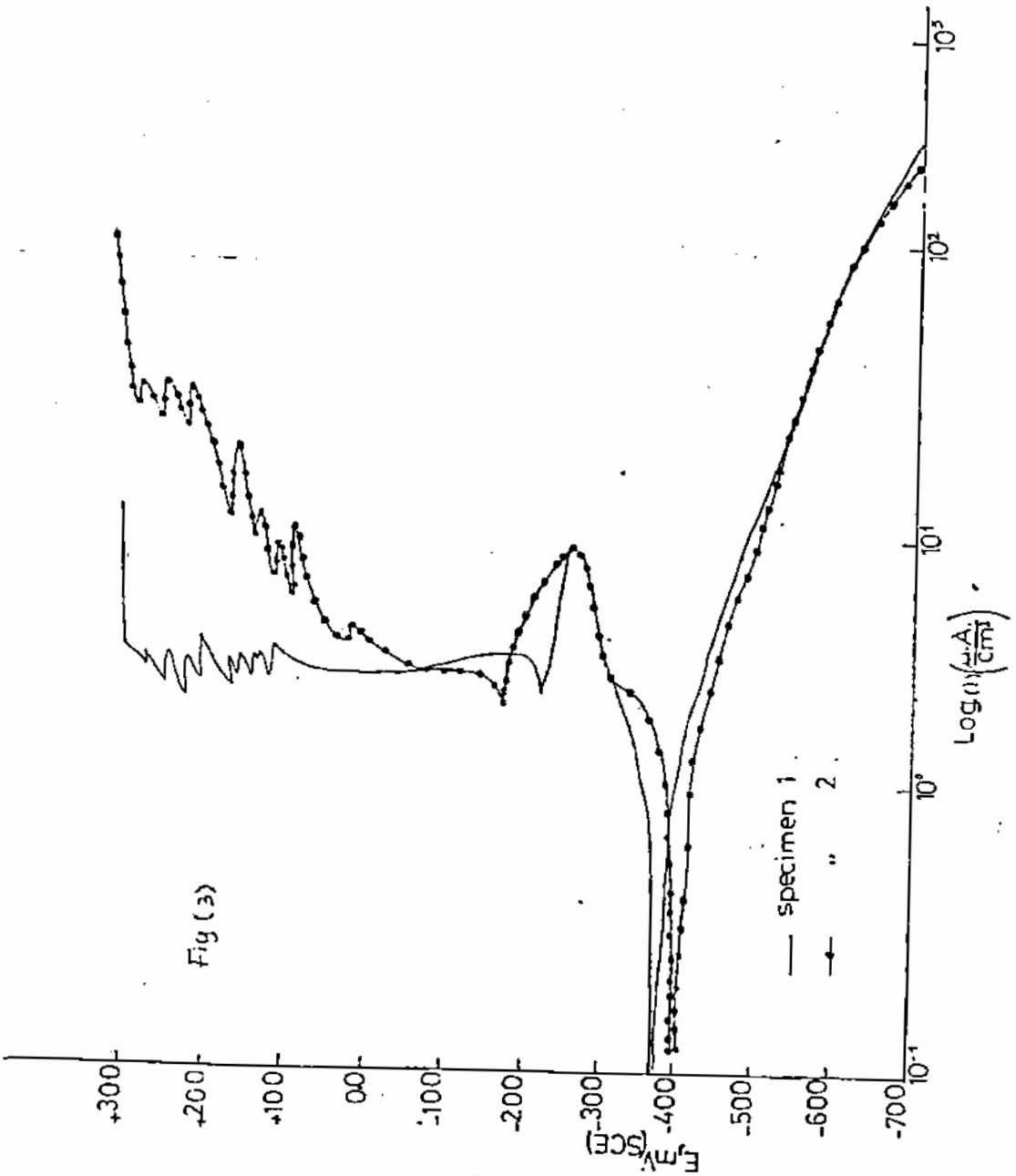
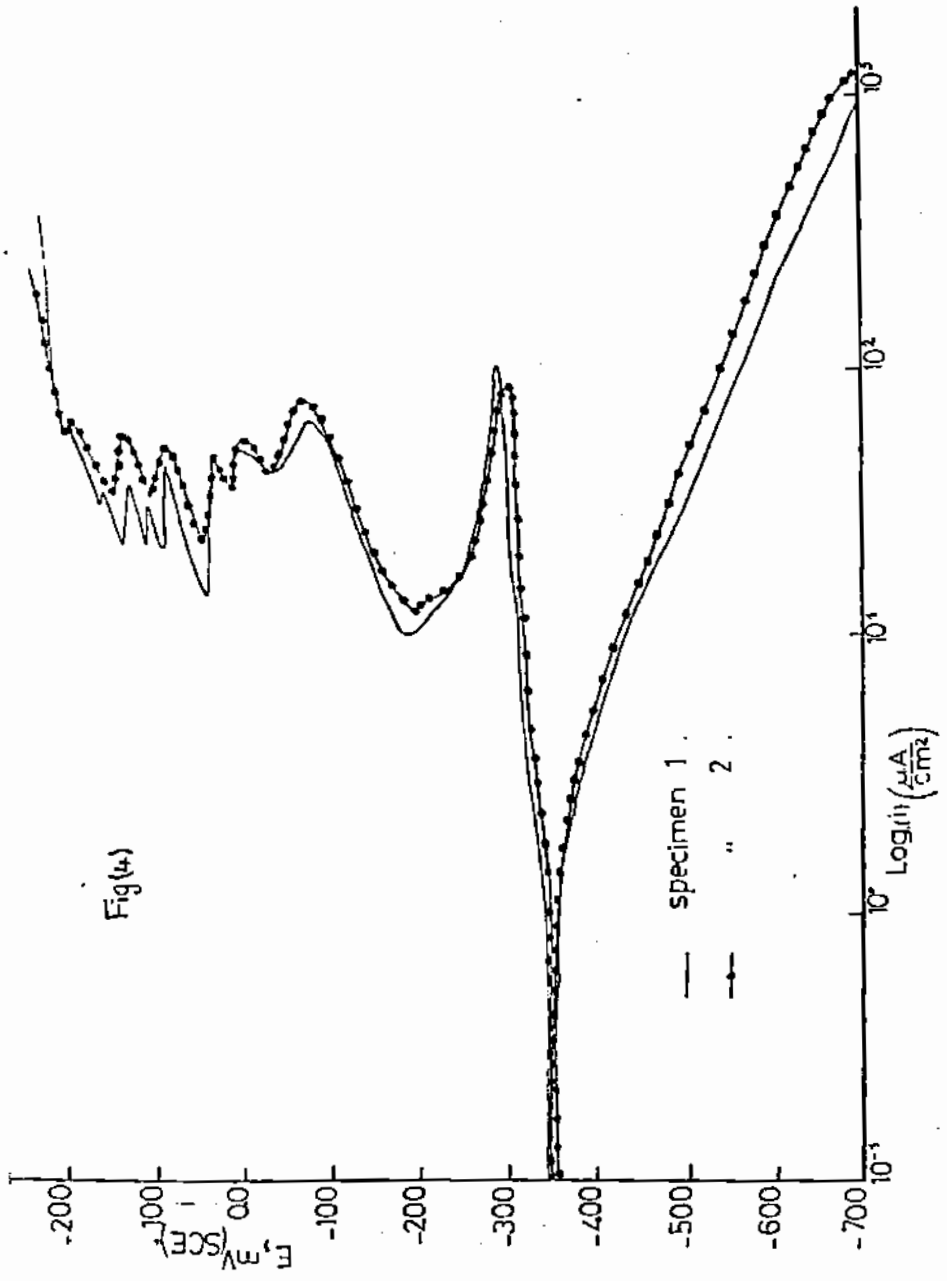
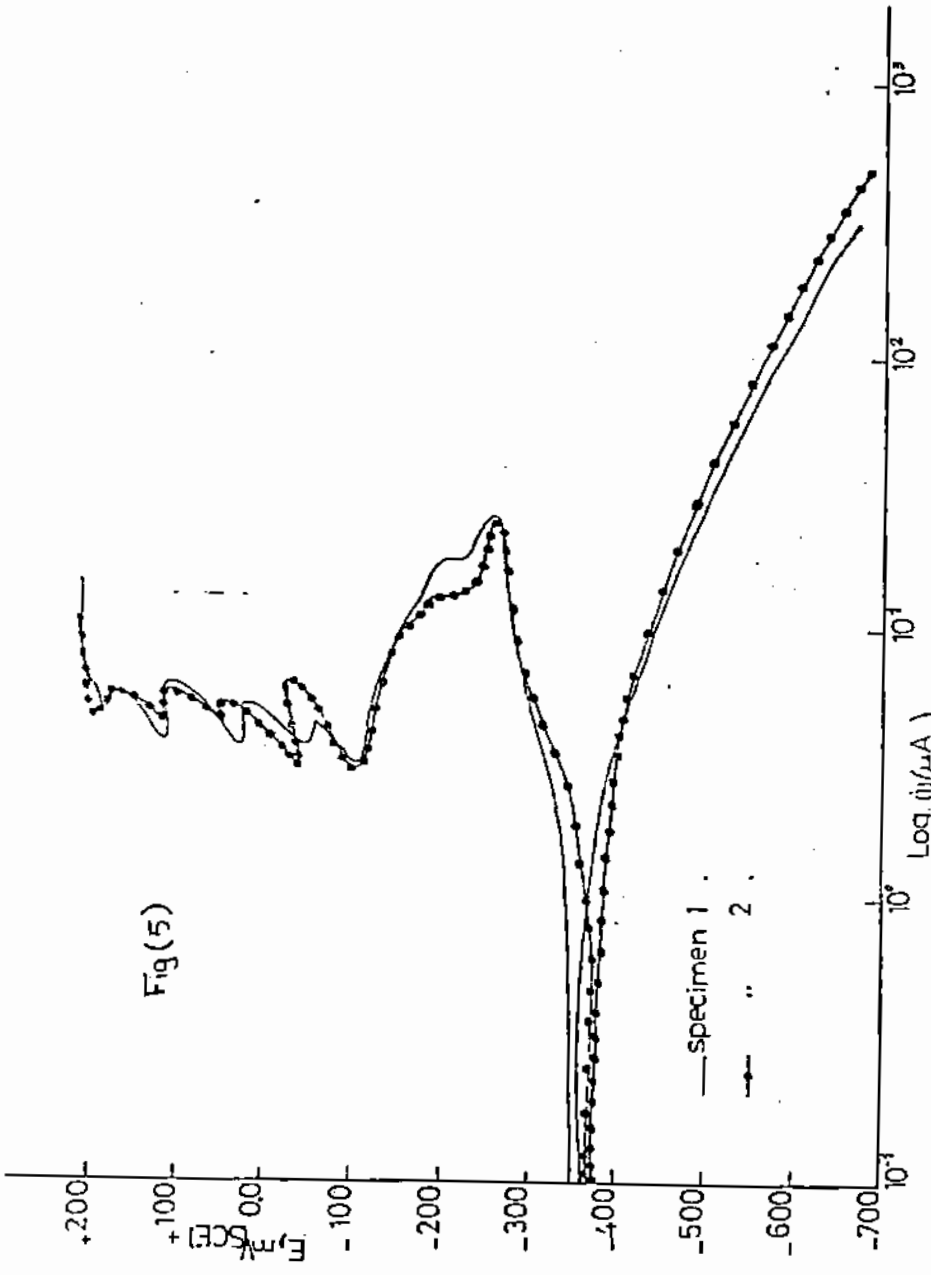

+300
+200
+100
0.0
-100
-200
-300
-400
-500
-600
-700
E, mV (SCE)
10⁻¹
10⁰
10¹
10²
10³
Log (i) (μA/cm²)
specimen 1
" 2

Fig (3)


Fig(4)
E, mV (SCE)
-200
-100
0
-100
-200
-300
-400
-500
-600
-700
specimen 1
" 2
Log i (μA/cm²)
10⁻¹
10⁰
10¹
10²
10³


+200
+100
0.0
-100
-200
-300
-400
-500
-600
-700
E_{rest} (SCE)
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
Log. (i) $(\frac{\mu A}{cm^2})$
—Specimen 1 .
— " 2 .

Fig(5)

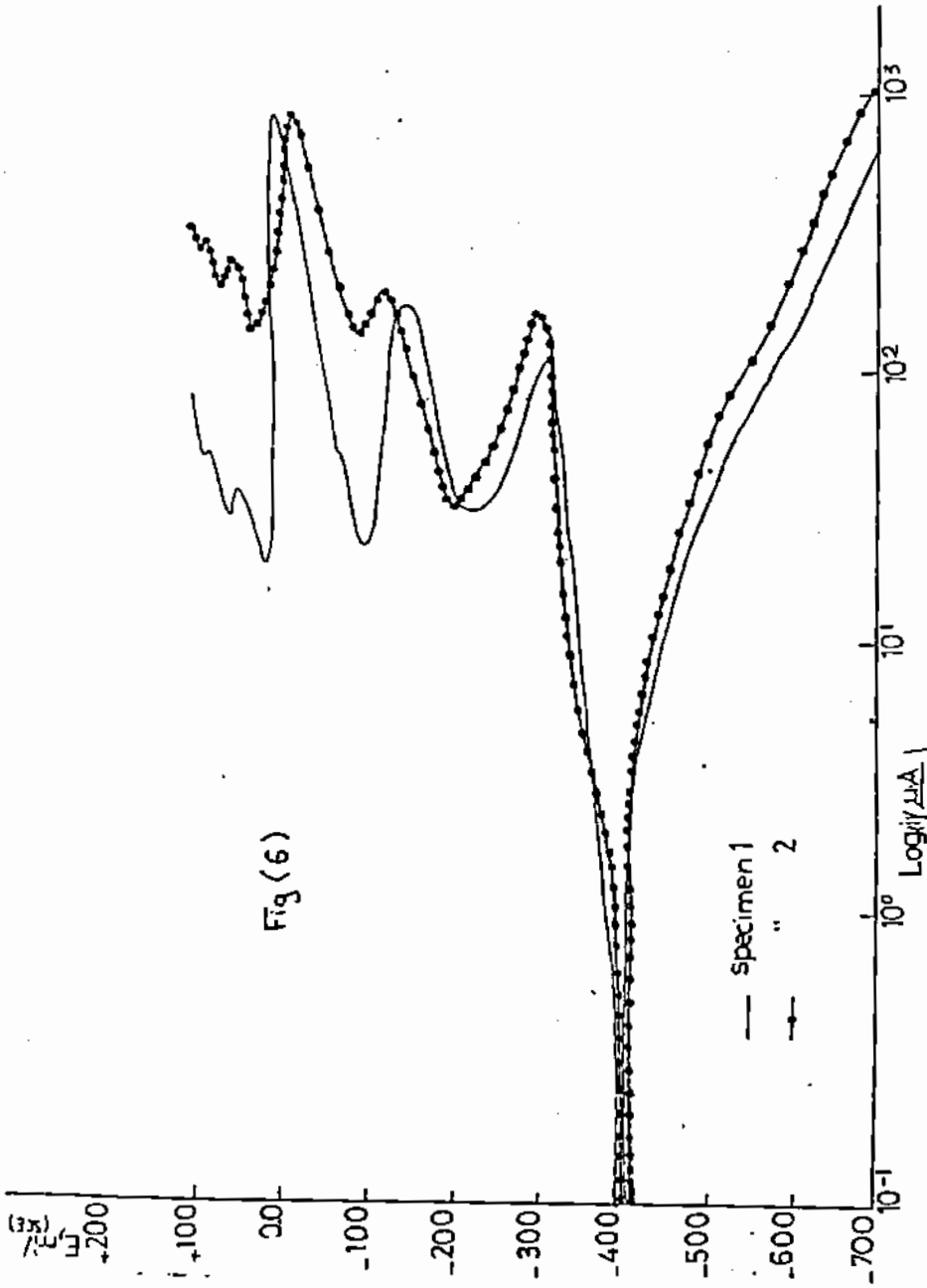
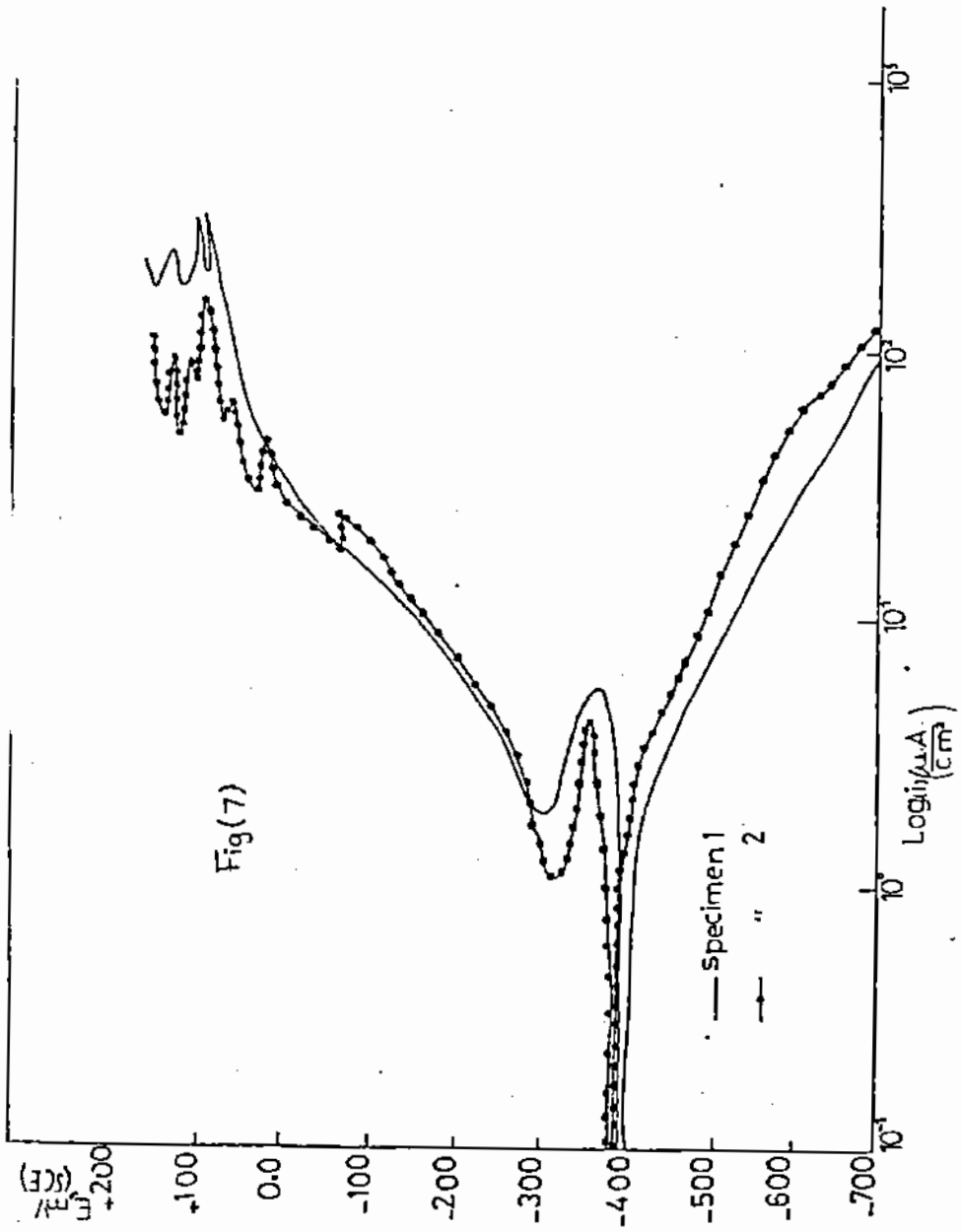

+200
+100
0.0
-100
-200
-300
-400
-500
-600
-700
10³
10²
10¹
10⁰
10⁻¹
Log₁₀(μA/cm²)
Specimen 1
" 2

Fig (6)


Fig(7)
Specimen 1
" 2
Log10(μA/cm²)
(SCE)
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+100
0.0
-100
-200
-300
-400
-500
-600
-700

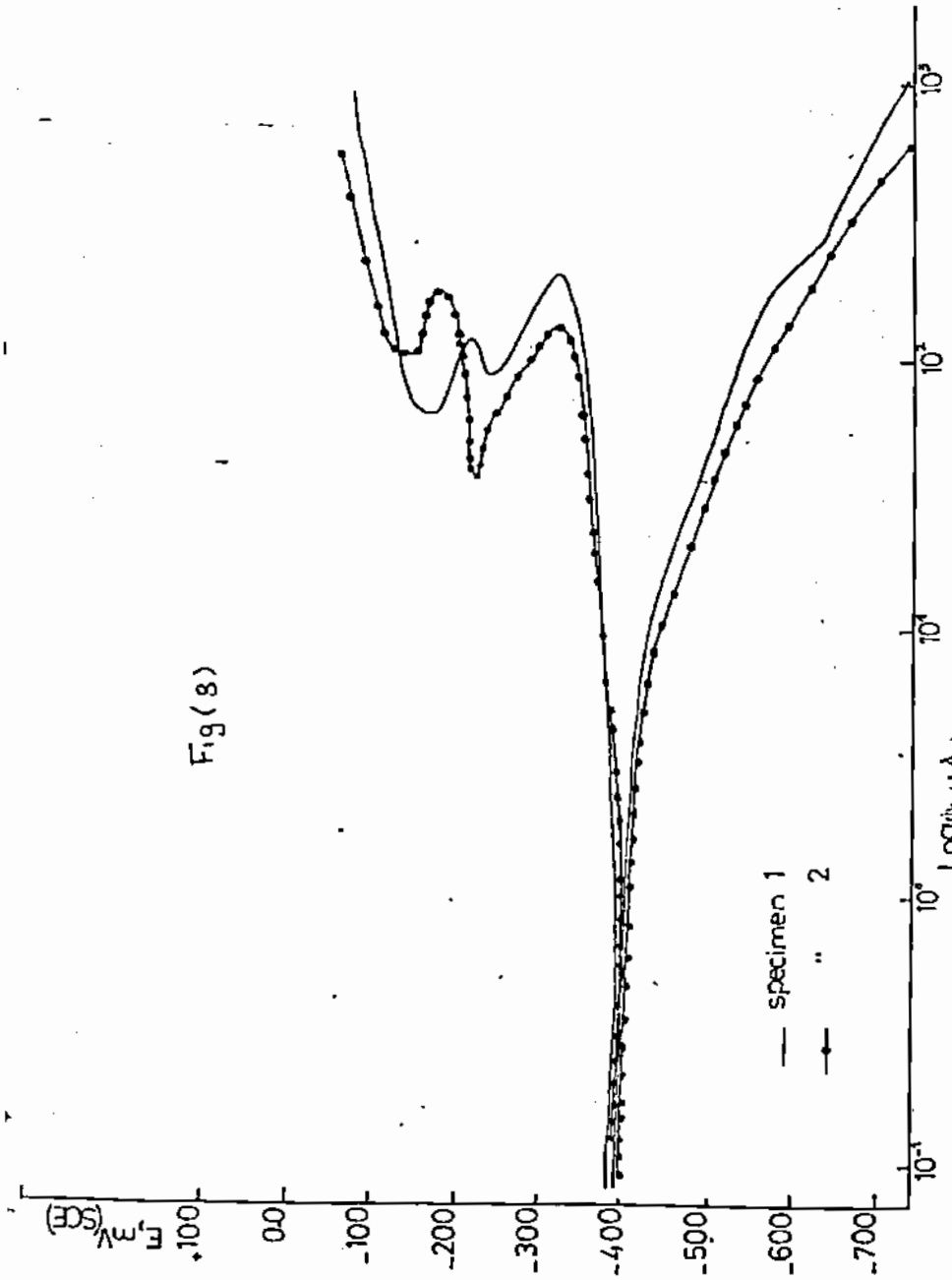
E, mV (SCE)
+100
0.0
-100
-200
-300
-400
-500
-600
-700
Log i (μA/cm²)
10⁻¹
10⁰
10¹
10²
10³
specimen 1
" 2

Fig (8)

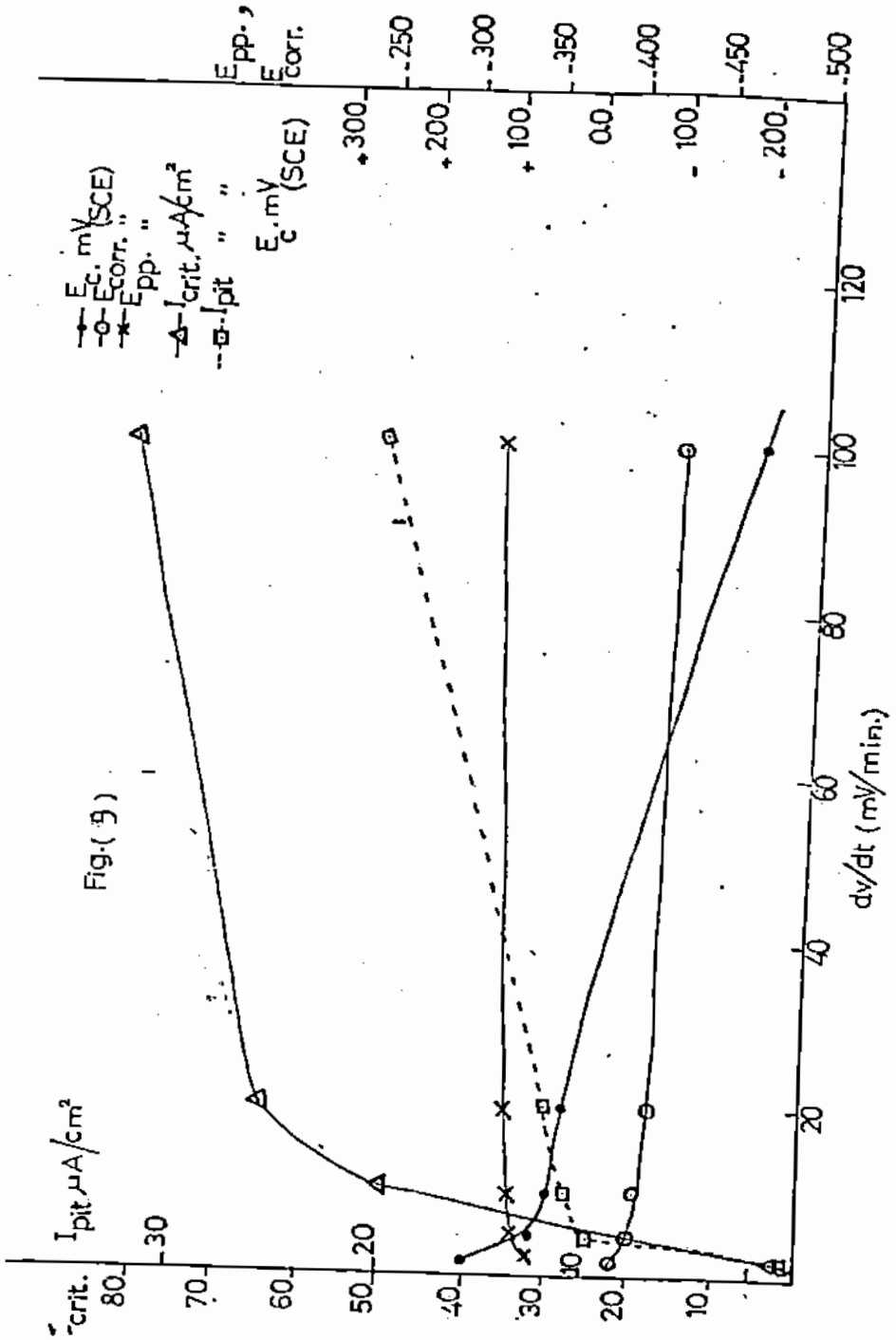
E_c. mV (SCE)
E_corr. "
E_pp. "
I_crit. μA/cm²
I_pit " "
E_c. mV (SCE)
E_pp., E_corr.
+300
+200
+100
0.0
-100
-200
-250
-300
-350
-400
-450
-500
I_crit. I_pit μA/cm²
80
70
60
50
40
30
20
10
30
20
10
dv/dt (mV/min.)
120
100
80
60
40
20

Fig.(9)