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Application of a Platinum Electrode in the Study of Microbially Influenced Corrosion

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Abstract

A prepassivated platinum electrode was used in laboratory-based studies of microbially influenced corrosion of Type 439 stainless steel. The platinum electrode served as an indicator of changes in dissolved oxygen content at the platinum/bacteria interface. Results of electrochemical tests revealed that a double-electrode system (metal-under-study and platinum) can be used to investigate the time effects of bacterial processes on the corrosion of materials.

Introduction

The process of microbially influenced corrosion (MIC) involves a combination of the corrosion activities of materials and the metabolic activities of bacteria. It is generally understood that the same fundamental electrochemical reactions are involved with MIC as with classical localized corrosion, except that microbial action promotes the corrosion processes. In order to understand the MIC processes, it is important to evaluate the change of dissolved oxygen content at the metal/biofilm interface. Oxygen content not only is important to classical corrosion processes, but also is the preferred electron acceptor for microbial respiration [1]. In the present studies, a prepassivated platinum electrode was used to serve as an indicator of dissolved oxygen concentration at the platinum/biofilm interface. Measurements of open-circuit potential of both a platinum electrode and a metal specimen in the same test cell were conducted in batch solution with and without bacteria.

Experimental Procedures

The platinum electrode consisted of a thin platinum foil in size 3.8 x 3.8 cm. A platinum wire was spot welded onto the foil. The wire was inserted into a 3.2 mm glass tube sealed at

the tip close to the platinum foil. The electrode was prepassivated in 25% HNO_3 + 75% H_2O solution at 50°C for 20 minutes.

In order to evaluate the possiblility of using this platinum electrode as a dissolved oxygen content indicator, it was calibrated in a neutral solution containing 100 ppm chloride ions by aeration with pure oxygen and subsequent purging with pure nitrogen. The open-circuit potential changes of the platinum electrode was measured with a digital electrometer (Keithley Instruments, Model 615), and the changes of dissolved oxygen content of the solution was measured with a portable dissolved oxygen meter (Leeds & Northrup Model 7932).

The Type 439 stainless steel (SS) used in this investigation was in the as-received wrought-annealed condition. The compositions of the 439 SS, the single bacterial strain, and the growth medium have been reported previously [2]. Therefore, only a brief description will be presented here.

The 439 SS was mounted in Maraglass 655 epoxy (Allied Products Co.). The exposed surface was ground with 600 grit SiC paper, and as part of a procedure to avoid interface crevice corrosion [3], then prepassivated in 50% HNO_3 + 50% H_2O solution at 50°C for 30 minutes. The metal/epoxy interface was coated with Glyptal 1201 Red Enamel (General Electric Co.). Finally, the passive film at the exposed metal surface was removed with 600 grit SiC paper.

A 600 ml polyvinyl chloride (PVC) test cell was employed, which consisted of the platinum electrode, a saturated Ag-AgCl reference electrode, a gas bubbler, and air inlet and outlet glass tubes with in-line 0.2 µm filters. The specimen was mounted in the middle of the vertical side wall with silicone sealant. The entire test cell was ethylene oxide gas sterilized.

A single bacteria strain, designated as A6F and extracted from a known MIC failure site in an industrial fresh-water system, was used in the present studies. The A6F bacteria was characterized as a gram-negative, facultatively anaerobic, acid producing, rod shape bacteria. A synthetic fermenter enrichment medium containing dextrose and mineral salts was used in these experiments. The medium was sterilized by autoclaving at 121°C for minutes. In the present studies, the bacterial solution consisted of the sterilized medium inoculated with A6F bacteria; whereas the control solution consisted of the sterilized medium only. During all experiments, filter-sterilized air was continuously bubbled through the solutions. Consequently, dissolved oxygen was always available within the bulk solutions.

Measurements of the open-circuit potential of the platinum electrode, E_{pt}, and the open-circuit corrosion potential of 439 SS, E_{corr}, were conducted in batch growth medium with

and without the A6F bacteria for 72 hours. The data were collected at 10 minutes time intervals by a multichannel computer system. After the tests, the specimen surfaces were evaluated by light microscopy.

Results

The results of the measurements of E_{pt} versus dissolved oxygen content are shown in Figure 1. The results indicated that E_{pt} provides a useful semi-quantitative indication of dissolved oxygen concentration. As the oxygen content increased, the E_{pt} increased.

The variation of E_{corr} for 439 SS in the bacterial solution during 72 hours exposure is shown in Figure 2. It sequentially underwent a sharp increase, then remained relatively stable (designated as an "incubation" for bacterial attack), then underwent a large reduction, and finally underwent a slow increase. As shown in Figure 3, there was virtually no change in E_{corr} as a function of time for 439 SS in the sterile solution.

The correspondent changes in E_{pt} in the bacterial solution, also shown in Figure 2, gave hints that when E_{corr} of the 439 SS increased sharply, the interfacial oxygen content underwent a large reduction, which in turn indicated a large increase in bacterial growth [2]. The subsequent stable regions of these two curves were followed by a large reduction in E_{corr} of the 439 SS and an increase in E_{pt}. In no case did E_{pt} change substantially in control solutions, as shown in Figure 3; which indicated that the variation of E_{pt} in bacterial solutions (Figure 2) were indeed due to bacterial action.

Discussion

Platinum is not inert to the uptake of oxygen as might be thought [4]. In an oxygen-enriched aqueous solution, platinum adsorbs oxygen and, at a given temperature, oxidizes [5]. Platinum adsorbs oxygen in the form of an electronically conducting film about a monolayer thick [6,7]. When this monolayer of oxygen is completed, it is ideally expected that the platinum electrode can reach the theoretical oxygen potential. This would be entirely dependent on the degree of completeness of the oxygen layer on the platinum surface, which is difficult to achieve at ambient temperature [7]. However, the theoretical reversible oxygen-electrode potential has rarely been established on platinum [8]. Factors contribuing to this include incomplete adsorption of oxygen to the surface, the slow kinetics of the oxygen reaction, and the presence of any oxidizable species in the solution.

The prepassivation treatment of the platinum electrode in the present study (25% HNO_3, 50°C, 30 minutes) is thought to have created a complete platinum oxide layer covering the entire surface. Therefore, the prepassivated platinum electrode is rather a platinum-oxide electrode. In oxygen-containing aqueous solutions, the oxygen reaction such as the one

below or others, must occur to some degree:

$$O_2 + 4H^+ + 4e = 2H_2O$$

The equilibrium potential for the above oxygen reaction as given by the Nernst equation is:

$$E = 1.229 + 0.015 \log a_{O_2} - 0.059\,pH$$

where E is in volts relative to the standard hydrogen electrode (SHE) and a_{O_2} is the activity of the dissolved oxygen. Furthermore, the platinum/platinum-oxide reaction may also take place to some degree. Therefore, a mixed potential might be expected. On the other hand, oxygen reduction can be profoundly affected when the level of some organic impurities is extremely small, on the order of 10^{-7} mole/liter [9]. At potentials in the range of 0.1 to 0.6 V (SHE), residual impurities from the solution, mostly organic, readily adsorb at the platinum surface [10]. This effect is especially relevant to the present study since the bacterial and control solutions contained organic species. For this possible reason, and others including imcomplete platinum-oxide coverage, slow kinetics of oxygen reactions, and oxidizable species in the solution, the potential of the prepassivated platinum in the sterile-medium (control) solution and the calibration solution could not be explained in terms of a single oxygen reaction. Nevertheless, results from the present research, as shown in Figure 1, indicated that changes in E_{pt} in the calibration solution were large enough to provide a useful semi-quantitative indication of the sensitivity of E_{pt} to oxygen concentration. Similar results have been reported in the literature [11]. Based on the theoretical oxygen reaction, E_{pt} should also increase as the pH decreases. A linear relation between E_{pt} and the pH in aqueous solution at constant dissolved-oxygen concentration has been demonstrated [12]. Therefore, it can be expected that the prepassivated platinum electrode can serve as an indicator of changes in either dissolved oxygen concentration or pH changes.

When a metal is immersed in a bacterial solution, two reactions must be considered: first, the corrosion process starts immediately after exposure of the surface; and second, the bacteria quickly adhere to the metal surface due to the enriched nutrition condition. It is believed that the metabolic activities of the bacteria employed in the present study resulted in local depletion of oxygen and local acidification at the interface, which in turn led to changes in the corrosion behavior of 439 SS. These reaction effects were reflected in the results of the electrochemical measurements.

The E_{corr} values of 439 SS shown in Figures 2 and 3 indicated that the bacterial activities promoted the corrosion processes of the stainless steel. The large reduction in E_{corr} after the

incubation time is belived to have been due to passive film breakdown caused by local differential aeration cells and local acidification [12]. Pits were found on the surface of the 439 SS after 72 hours exposure in the bacterial solution (Figure 4). It was also found that the bulk bacterial solution had undergone a large reduction in pH (from 7.0 to 4.2). The rapid increase in E_{pt} after the incubation period is believed to be an indication of this pH change at the interface where the pH would be lower than in the bulk solution.

Although it would have been at risk during the course of the study to have assumed a priori that the bacterial action on the platinum surface would be similar to that on the 439 SS surface, the fact that the potential changes were correspondent in time for both E_{pt} and E_{corr} in both solutions (with and without bacteria) led the authors to believe that the assumption was reasonable. Therefore, it is believed that the platinum electrode can be used as an indicator for changes in oxygen content and pH at the metal/bacteria interface of another material exposed to the same solution. Consequently, it should be useful in conjunction with other electrochemical measurements (and in particular, E_{corr} of the metal or alloy of concern) for monitoring and understanding MIC processes. A useful extension of these principles could involve measurements of the potential difference between the alloy under study and the platinum electrode.

Summary and Conclusions

1. Experimental results indicated that the open-circuit potential of a prepassivated platinum electrode, E_{pt}, can serve as an indicator of the changes in dissolved oxygen concentration due to bacterial metabolic processes at the platinum/biofilm interface.
2. Changes correspondent in time for E_{pt} and the open-circuit corrosion potential, E_{corr}, of Type 439 stainless steel in bacterial solutions indicated that E_{pt} could be used to reasonably follow the biofilm metabolic processes on the stainless steel.
3. Virtually no changes in E_{pt} or E_{corr} were observed in sterile (control) solutions.
4. The open-circuit corrosion potential of Type 439 stainless steel in bacterial solution during 72 hour immmersion tests underwent several large changes. These changes corresponded to the processes of bacterial growth, changes of local environment induced by the bacterial action, and the corrosion effects at the metal surface.
5. By use of a double electrode system (metal electrode and platinum electrode), one can study the time effects of bacteria on the corrosion behavior of materials by simulataneously measuring E_{corr} and E_{pt}. This approach would appear to be a useful procedure in monitoring MIC attack at industrial sites.

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Fig. 1

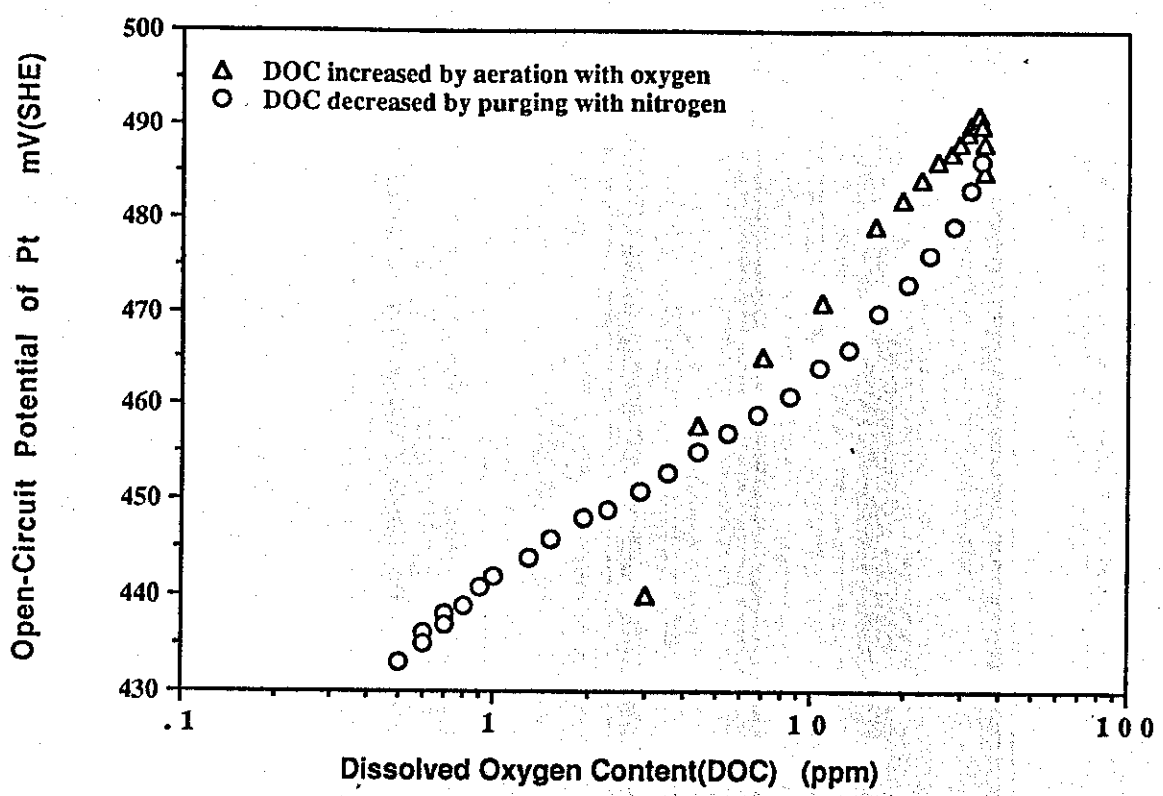

Open-Circuit Potential of Pt mV(SHE)
500
490
480
470
460
450
440
430
DOC increased by aeration with oxygen
DOC decreased by purging with nitrogen
.1
1
10
100
Dissolved Oxygen Content(DOC) (ppm)

Fig. 2

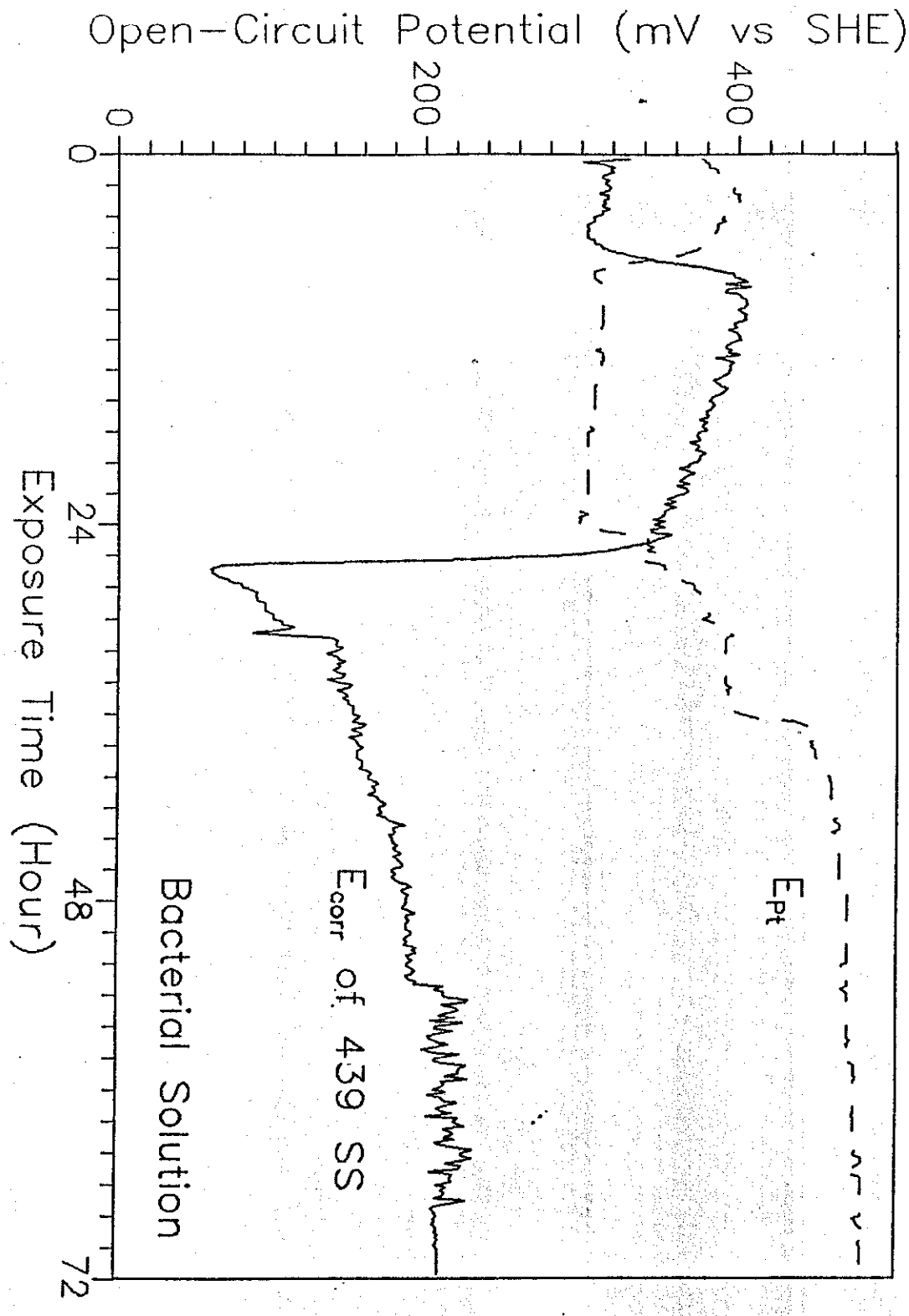
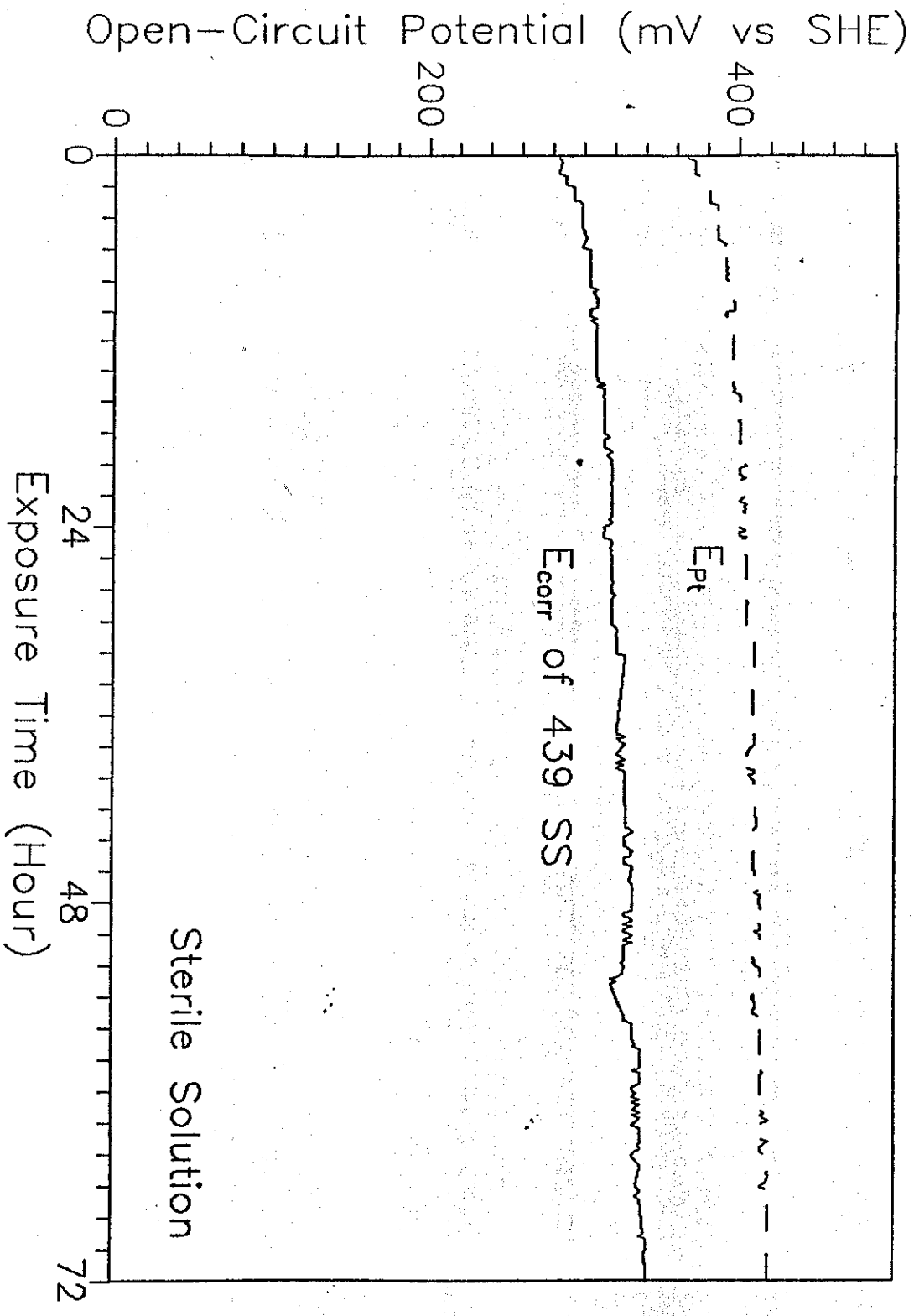

Open-Circuit Potential (mV vs SHE)
0
200
400
Exposure Time (Hour)
0
24
48
72
E_{Pt}
E_{corr} of 439 SS
Bacterial Solution

Fig. 3


Open-Circuit Potential (mV vs SHE)
0
200
400
Exposure Time (Hour)
0
24
48
72
E_{Pt}
E_{corr} of 439 SS
Sterile Solution

439 S.S (Bacteria) (3)
1000 x