250

THE USE OF CURRENT DENSITY MAPPING IN THE STUDY OF MICROBIAL INFLUENCED CORROSION

Michael J. Franklin, David C. White
Institute for Applied Microbiology
University of Tennessee
10515 Research Dr. Suite 300
Knoxville, Tn. 37932

Hugh S. Isaacs
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

ABSTRACT

The scanning vibrating electrode technique (SVET) was used to map current densities over carbon steel coupons exposed to bacteria. This study was initiated to evaluate the usefulness of the SVET in studies of microbial influenced corrosion (MIC). A comparison was made between current densities, at open circuit potential, of steel exposed to dilute sterile microbiological medium, and steel exposed to medium containing a culture of aerobic heterotrophic bacteria. At specific times during the analysis, small amplitude cyclic polarizations were performed. The SVET was utilized to detect localized resistance to polarization (R_p). After the samples had been exposed to the solutions for 24 hours, anodic and cathodic polarizations were applied. The SVET was used to detect localized changes in applied current. The results indicated that the SVET can be used to obtain qualitative and quantitative information regarding localized corrosion associated with MIC.

INTRODUCTION

Films of bacteria and other microorganisms often form when metal surfaces are exposed to aqueous environments. These biofilms can lead to enhanced localized corrosion of the metal. Bacteria in association with corrosion is usually indicated by the presence of tubercles containing reduced nitrogen or sulfur compounds, as well as organic acids. Although microbial influenced corrosion (MIC) has been implicated in corrosion processes for greater than fifty years (1), the mechanisms for MIC have been difficult to define.

Correlations between microbial metabolic activity and corrosion are a means to establish a microbial basis for MIC. However, studies of microbial physiology and metabolism at surfaces has received less attention than for microbes in bulk solutions. Bacteria associated with surfaces can be physiologically very different from the same bacteria in solution. This aspect is exemplified by the production of lateral flagella (2) or acidic exopolysaccharides (3), when Vibrio parahaemolyticus or Pseudomonas sp., respectively, are in contact with surfaces.

Electrochemical techniques, commonly used in determining corrosion rates, are either destructive to bacteria and/or do not provide information on localized corrosion associated with bacteria. Useful techniques for studying MIC have included anodic and cathodic polarizations. These analyses can be used to obtain Tafel parameters and polarization resistance values, which can be used in the Stern-Gerry equation to determine corrosion rate. In addition, anodic sweeps can be used to detect changes in pitting potential as a result of bacterial activity. However, anodic and cathodic polarizations require high applied currents, which can alter the physiology of bacteria. Therefore, changes in corrosion rate over time requires the use of many samples. Nondestructive techniques for studying corrosion have included potential monitoring (5) and current monitoring through a galvanically coupled cell (6).

In order to gain a better understanding of MIC, additional techniques which can detect localized corrosion and do not alter the progression of corrosion are needed. Current density mapping has been used as a nondestructive technique in biological studies (7), and corrosion studies (8). The technique is based on the principle that over corroding metal, the solution resistance produces potential fields between local anodic and cathodic sites. The current densities producing the fields can be detected with either a scanning capillary reference electrode (9) or a scanning vibrating electrode (8). The scanning vibrating electrode technique (SVET) converts fields to an alternating signal. The sign and the magnitude of this current could then be determined using a lock-in amplifier. The SVET is much more sensitive than the capillary reference electrode technique, since noise is filtered by the lock-in amplifier. Only the signal at the vibration frequency is detected.

One limitation of this technique in determining corrosion rates is that current densities are mapped at a certain distance from the metal surface, whereas the corrosion rate must be determined by the current density at the surface. Several approaches have been used to more accurately determine corrosion rates (11). Cathodic and anodic polarization techniques, have been used in conjunction with the SVET to provide information regarding localized corrosion rates (11).

In this study, the SVET was used to map current densities over carbon steel in a medium containing bacteria. In addition, localized polarization resistances were measured. At the end of the experiment, localized changes in applied current were determined for anodic and cathodic polarizations. The results indicated that the SVET can be used to evaluate localized corrosion, enhanced by bacteria.

MATERIALS AND METHODS

Media and bacteria. A defined microbiological medium, capable of supporting the growth of the bacterium was used. The medium contained (in mg/L) NH_4Cl 50, $MgSO_4 \cdot 2H_2O$ 50, $CaCl_2 \cdot 2H_2O$ 5, KH_2PO_4 27, Glucose 50, 2-morpholinoethane sulfonic acid (MOPES buffer) 50, and trace minerals (in ug/L) $Na_2MoO_4 \cdot 2H_2O$ 0.1, $ZnSO_4 \cdot 7H_2O$ 50, $MnSO_4 \cdot H_2O$ 7.7, $CuSO_4 \cdot 5H_2O$ 2, $CoCl_2 \cdot H_2O$ 1, $NaB_4O_7 \cdot 10H_2O$ 0.8, $NiSO_4$ 0.5. The bacterial culture used, was a pure culture of a Pseudomonas sp., which was isolated from a tubercle on a steel pipe. The isolate did not grow anaerobically, and does not produce detectable levels of volatile fatty acids when grown on glucose (1g/L). The bacterium does produce copious amounts of extracellular polysaccharide when attached to a steel surface (13). When bacteria were used in these experiments, the cells were grown to late exponential phase (24 hours) on the medium described above. The cells were then centrifuged and the spent medium was removed. An equal volume of fresh medium was added to the cells, and the suspension was added to the electrochemical cell.

Electrochemical cell. The working electrodes in these experiments were coupons of C1020 carbon steel supplied by Metal Samples (Munford Al.). The steel contained by percentages; C 0.17, Mn 0.42, P 0.009, and S 0.006. The coupons, with a spot welded electrical connection, were embedded in epoxy and finished with 600 grit silicon carbide finishing paper. Thin, approximately 75 um, pressure sensitive tape (3M Co. no 92) was used to insulate the sample except for an area in the center of the coupon approximately 25 mm^2. Microshield lacquer (Pyramid Plastics, Inc.) was painted at the edge of the tape to reduce crevice corrosion. The cell had a working volume of 15 ml and contained a double contained standard calomel reference electrode (SCE) and a platinum wire for a counter electrode.

Current Density Maps. The vibrating electrode, used to scan the working electrode, consisted of an insulated platinum wire, 0.1mm in diameter. The technique for current density mapping has been described elsewhere (14,15). Briefly, the platinum wire was attached to a piezoelectric reed which was activated by applying a 10 V rms signal to the reed at 200 Hz. The peak to peak vibration was 0.04mm. The vibrating electrode was positioned 0.09mm from the working electrode surface. The alternating current was analyzed with a PAR model 116 lock-in amplifier, and a computer controlled data acquisition unit. The surface of the working electrode was scanned by moving the cell in 100 or 200 um increments with computer controlled stepper motors. The vibrating probe was calibrated with a known uniform current field, and the output voltage from the amplifier was converted into current densities, through the use of a conversion factor.

Local Polarization Resistance. For analyzing polarization resistances (R_p), a 50 mV triangular signal was applied to the working electrode at a rate of 5mV/sec. The vibrating electrode was positioned over the lacquer coating, then stepped in 0.2mm increments across the metal sample. The probe remained at each point in the transect for 40 secs. Twenty-two points were analyzed, including cathodic and anodic sites. The SVET from the lock-in amplifier, was monitored with a strip chart recorder. The ratio of change to applied current was determined by the deflection of the pen on the recorder. Local polarization resistance was determined by Ohm's law.

Anodic and Cathodic Polarizations. Cyclic polarizations were performed on some samples at the end of the exposure periods. The potential was changed at a rate of 1 mV/sec, from open circuit potential to -1.2V/SCE then to 0.0V/SCE. The vibrating electrode was positioned first over the lacquer coating. The probe then stepped across the metal sample in 0.2mm increments. The probe then returned to its original position and again stepped across the metal. This process was continued as the potential of the sample was ramped. Each transect across the sample took approximately 20 seconds. Since the potential was ramped at 1mV/sec, each transect represented an increase in potential of 20 mV. The SVET signal from the lock-in amplifier was aquired by the computer.

RESULTS

SVET analysis of sterile medium during free corrosion. The medium used in these studies was continuously aerated by bubbling with air, contained trace minerals, and an organic buffer. The medium contained chloride, sulfate, and phosphate ions in concentrations of approximately 1mM, 0.2mM, and 0.2mM, respectively. Upon exposure of the carbon steel to this medium, the open circuit potential (OCP) rose from a value of -300mV/SCE to approximately -200mV/SCE. This potential was apparently above the pitting potential of the steel, since sudden drops in potential ranging from 10 to 70 mV, occurred over the course of the experiment. The drops in potential were followed by slow increases in potential to the initial value. These potential transients were characteristic of pit initiation and repassivation (12). Fig. 1a shows a current density map over the carbon steel sample, after 22 hours of exposure of the steel to the sterile medium. One pit, with a measured current density of 50 uA/cm^2 is seen in this figure. Fig 1b is a contour map of the same pit, showing the location of the pit on the sample. Fig 1c shows the same sample after 29 hours of exposure. In this figure, the pit seen at 22 hours is not observed. Fig 1c is autoscaled, so that the minimum detectable current density can be plotted. It can be seen that less than 0.5 uA/cm^2, current densities are observed over the area formerly occupied by the active pit in Fig 1a,b.

SVET analysis of MIC during free corrosion. A culture of aerobic heterotrophic bacteria, derived from a tubercle on a steel pipe, was added to the same aerated medium described. The initial OCP rose above the pitting potential for the sterile medium. However, as the bacteria colonized the steel surface, the pitting eventually stabilized, and the potential dropped to a value of approximately -620mV/SCE. The current density map shown in fig 2 was taken after 23 hours of exposure of the steel to medium containing bacteria. In this experiment, one pit had initiated and did not repassivate. The pit propagated and expanded until a large area of the surface was anodic.

Local polarization resistance. As mentioned, the SVET can be used in conjunction with linear polarization, to analyze localized resistance to polarization. The transect described in the materials and methods is shown in Fig 3a. This plot is a two-dimensional plot of the current densities at open circuit potential. This plot was taken from the three-dimensional plot shown in fig 2, for a transect 600 um parallel to the X-axis. The points at the far left and far right represent the current densities over the lacquer coating, and serve as reference points. Fig 3b shows the SVET measured local polarization resistances measured for this transect, when a triangular polarization, ± 25mV around OCP was applied to the sample. The local polarization resistances were determined by dividing the magnitude change in local current density by the change in applied potential (50mV). The measured R_p for the whole sample was 1100 ohm·cm^2. The measured values for local R_p was 1200 ohm.cm^2 directly over the anodic area, and 9000 ohm·cm^2 directly over cathodic areas.

Cyclic polarization. After 24 hours of exposure of the sample to medium containing bacteria, cyclic polarizations were performed on the sample. The result of the cyclic polarization is shown in fig 4. Increase in current due to the anodic processes was observed above -0.4V/SCE, and the increase in current due to the cathodic reaction, was observed below 1.0V/SCE.

SVET analysis of cyclic polarization. The vibrating probe was repeatedly scanned in a transect over the sample while the potential was ramped. The transect was the same as for the polarization resistance measurements (the current densities at open circuit potential for this transect are shown in fig 3a). Fig 5a shows the change in applied potential, detected by the vibrating probe, when the sample was polarized in the cathodic direction, from -620mV/ SCE to -1.2V/SCE. In this graph, the X-axis is the position of the probe over the sample, the Y-axis is potential, and the Z-axis is measured current density. The results indicated that the area of the sample which produced the largest anodic current density, at open circuit potential, produced the greatest area of change in applied current, when the sample was cathodically polarized.

Fig 5b shows the SVET measured current densities associated with the polarization of the sample in the anodic direction, from -620mV/SCE to 0.0mV/SCE. The current densities in the zones which were cathodic remained at a constant level throughout the polarization. The site which was originally anodic produced the greatest change in applied current.

DISCUSSION

<u>SVET analysis during free corrosion</u>. Current density mapping has been used to study pitting corrosion of stainless steel and iron in aggressive media (8). This study demonstrates that the SVET can be used to nondestructively locate and measure the sign and magnitude of the nonuniform current densities over carbon steel samples, exposed to bacteria. Measurements of current densities at open circuit potential showed differences between the corrosion of the carbon steel, when exposed to sterile medium, and to medium containing bacteria. The results indicated, that in the dilute aerated microbiological medium, propagation but not initiation of pits was inhibited. However, in the presence of colonizing bacteria, an initiated pit propagated, until a large area of the sample was anodic. The bacteria apparently altered conditions which induced pit propagation. The conditions altered were probably in close contact with the metal surface, since filter sterilized, spent medium did not induce pit propagation (data not shown).

<u>Polarization resistance</u>. The SVET measures current densities in solution, whereas the corrosion rate is determined by current densities at the metal surface. Factors which affect measured current densities include; the height of the probe over the surface, the vibration amplitude, and the resolution of the anodic and cathodic sites. In addition to analysis of potential fields at free corrosion potential, samples can be polarized, and changes in applied potential can be determined with the SVET. This advance provides additional information regarding the local corrosion rate. Linear polarizations can be performed to determine local polarization resistance. Small amplitude polarizations are less destructive to bacteria than large anodic and cathodic sweeps.

Polarization resistances were used in this study, to better quantitate the pitting reaction. After 23 hours of exposure of the steel to medium containing bacteria the polarization resistance measured for the whole surface was 1100 ohm·cm^2. This value of R_p is consistent with other studies of carbon steel corrosion in this same medium, affected by this same culture of bacteria (12). The values of local R_p, for a transect across both anodic and cathodic zones, showed behavior similar to the current density map. The R_p values were lowest over the anodic zones, having measured values of 1000 ohm·cm^2., and the highest values of R_p, 10^4 ohm·cm^2, were measured over the cathodic sites. During the early stages of pit propagation, values showed an even greater discrepancy between the anodic and cathodic sites, ranging from 250 to greater than 10^4, respectively (data not shown). These results indicated that measurements of R_p for whole surfaces can lead to underestimates of penetration rates, when corrosion is highly localized. The SVET offers an advantage in determining localized penetration rates, since the value of local R_p can be measured, and calculated for the area of the active anodic site. The SVET can be particularly useful in studies of MIC, since MIC is often characterized by localized corrosion.

SVET with anodic and cathodic polarizations. By polarizing samples in combination with SVET analysis, measurements of galvanic corrosion can be made (11). Polarizations are generally destructive to the samples, and are thought to be destructive to bacteria, due to the high applied currents. However, polarization can be performed at the end of experiments, to determine the polarization characteristics of the corroding metal.

The results of the cathodic polarization, shown in fig 5a, demonstrated that the current densities were nonuniform. As the potential was lowered the current densities became more uniform across the sample. At the very low potentials, the current densities over the site which was anodic at OCP had the greatest change in applied cathodic current. This suggests that at very low potentials, the pits may become more susceptible to hydrogen evolution than the original cathodic sites. The anodic polarization also showed nonuniform current densities during polarizations. The sites originally cathodic showed no change in applied current as the potential was ramped from -620mV/SCE to 0.0V/SCE. The greatest change in applied current was observed over the anodic site. The maximum anodic current density in Fig 4 is much greater than in Fig 5b. This may be due to the transect of the probe not being positioned over the site of maximum current density. As the potential was ramped in the anodic direction, the anodic sites became more localized. Thus, the likelihood of the probe not being over the maximum anodic site increased. In any event, these results indicated that the SVET can provide better information regarding penetration rates at localized sites.

Use of SVET in MIC studies. Localized corrosion of metals exposed to untreated waters is often attributed to activity of microbes. Studies have suggested that different physiological types of microbes can facilitate the cathodic or the anodic reactions. For example hydrogenase positive sulfate reducing bacteria have been implicated in cathodic depolarization of iron (1), and iron reducing bacteria have been implicated in anodic depolarization of carbon steel (16). This study presents the usefulness of the SVET in characterizing localized corrosion associated with MIC, and demonstrates that the SVET may provide information to test these theories. Studies characterizing microbial physiology and metabolism are also progressing. For example, Mittelman (personal communications) has applied an autoradiographic technique for characterizing activity of microbes at a surface. Bacteria are fed specific radiolabelled substrates. Incorporation of these substrates into cell material is then detected by autoradiography. In this way, localized microbial metabolic activity can be detected. In addition, we are investigating the use of Fourier Transform Infrared Spectroscopy to localize and characterize bacteria on surfaces. These studies together with in situ analysis of localized metal corrosion may aid in correlating microbial activity to corrosion processes.

CONCLUSIONS

1) The scanning vibrating electrode technique can be used to nondestructively detect the location, sign, and magnitude of nonuniform current densities over metals which are exposed to microbial influenced corrosion.

2) Linear polarizations, cathodic and anodic polarizations, can be used in combination with the SVET to obtain quantitative information for local corrosion sites.

3) A culture of aerobic heterotrophic bacteria enhanced pit propagation of carbon steel in a dilute aerated microbiological medium.

4) Recent advances in studies of microbial physiology, genetics, and metabolism in combination with <u>in situ</u> techniques for measuring corrosion should advance testing of microbial metabolism versus localized corrosion.

ACKNOWLEDGMENTS

The authors thank Ken Sutter for his assistance. This research was supported by contract from the Office of Naval Research (ONR N0014-87-K-0012).

REFERENCES

1. von Wolzogen Kuhr, C.A.H., and L.S. van der Klugt. Water, vol. 18, p. 147, 1934.

2. Belas, R., M. Simon, and M. Silverman. J. Bacteriol. vol. 167, p. 210, 1986.

3. Bartlett, D.H., M.E. Wright, and M. Silverman. Proc. Nat. Acad. Sci. USA, vol. 85, p. 3923, 1988.

4. Nivens, D.E., P.D. Nichols, J.M. Henson, G.G. Geesey, and D.C. White. Corrosion, vol. 42, p. 204, 1986.

5. Scotto, V., R. Di Cintio, G. Marcenaro. Corrosion Sci. vol. 25, p. 185, 1985.

6. Gerchakov, S.M., B.J. Little, P. Wagner. Corrosion vol. 42, p. 689, 1986.

7. Nuccitelli, R. Ed. <u>Ionic Currents in Development</u>, Alan R. Liss, Inc., New York, 1986.

8. Isaacs, H.S. Corrosion Sci. vol. 29, 1989.

9. Isaacs, H.S. in <u>Electrochemical Corrosion Testing</u>, ASTM STP 727, Mansfeld F., and U. Bertocci Eds. American Society for Testing and Materials, p. 3-33, 1981.

10. Isaacs, H.S. CORROSION/89 paper no. 28. National Association of Corrosion Engineers, New Orleans, La., 1989.

11. Isaacs, H.S. Corrosion Sci. vol. 28, p. 547, 1988.

12. Isaacs, H.S., and Y. Ishikawa. J. Electrochem. Soc. vol. 132, p. 1288, 1985.

13. Franklin, M.J., D.E. Nivens, A. Tunlid and D.C. White. abst. American Society for Microbiology, Miami, Fla. 1988..

14. Ishikawa, Y., and H.S. Isaacs. Boshoku Gitjutsu, vol. 33, p. 147 1984.

15. Isaacs, H.S., and Y. Ishikawa. CORROSION/85, paper no. 55, National Association of Corrosion Engineers, Boston, Ma, 1985.

16. Obuekwe, C.O., D.W.S. Westlake, J.A. Plambeck, and F.D. Cook. Corrosion. vol. 37 p. 632, 1981.

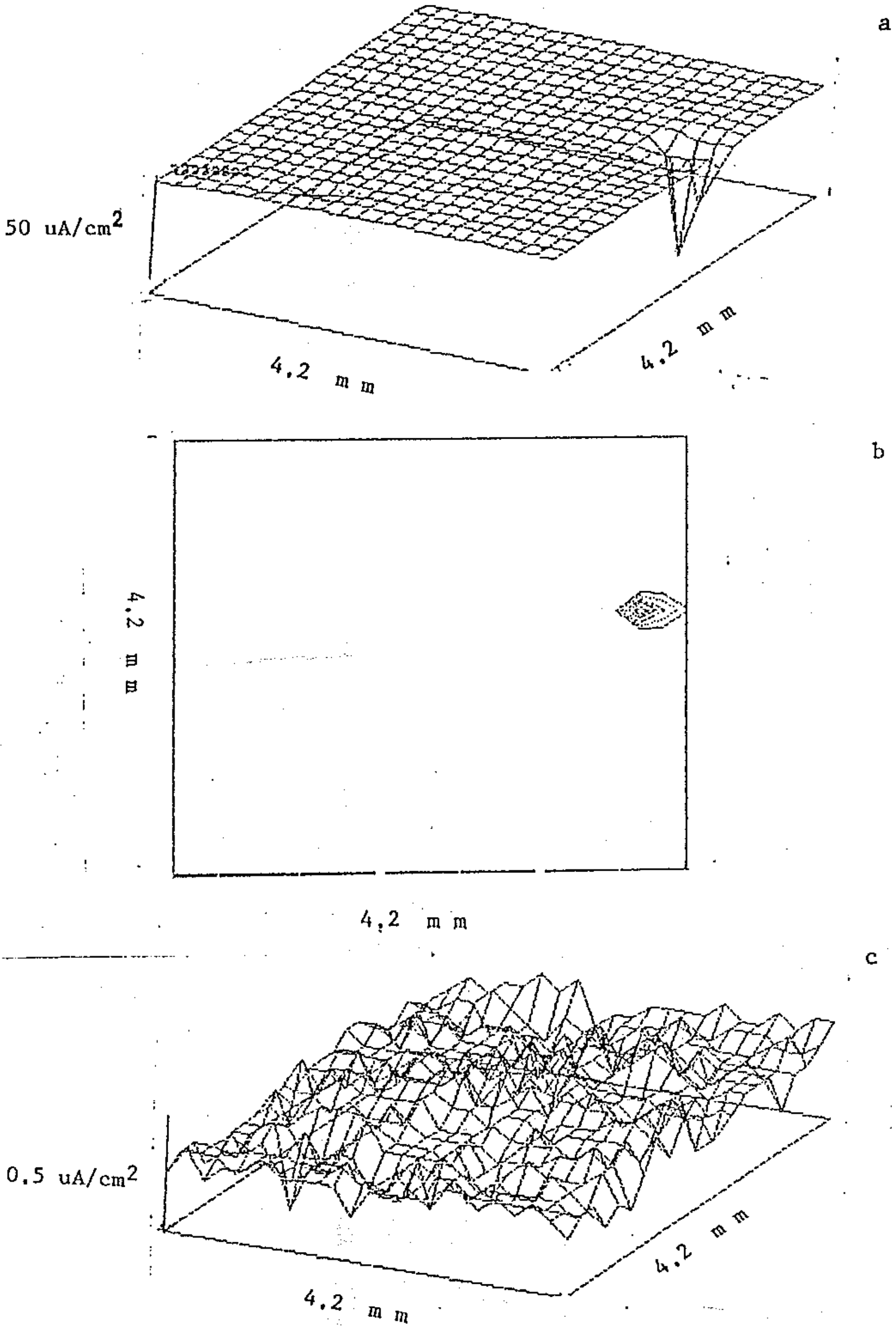

Fig. 1. Current density maps over carbon steel samples, obtained with the scanning vibrating electrode technique. a) SVET analysis after exposure of the steel to sterile medium for 22 hours. b) Contour map of the same sample. c) SVET analysis for the same sample after 29 hours of exposure to the sterile medium.

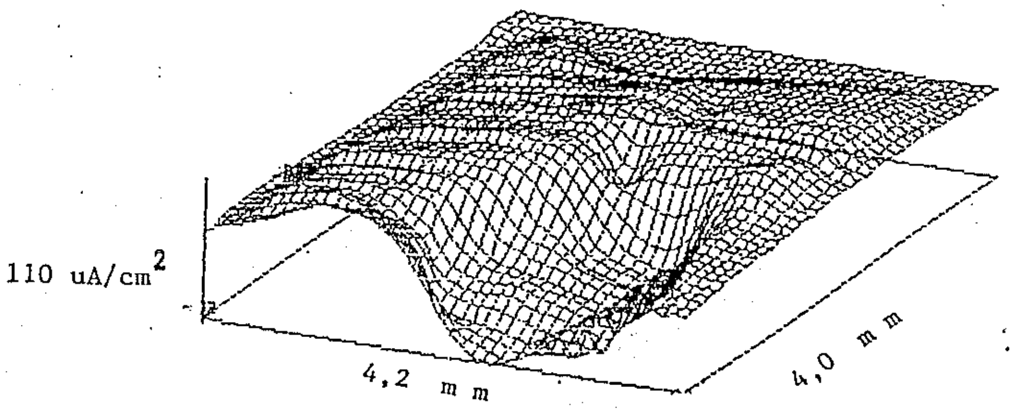

Fig. 2, Current density map over carbon steel sample, obtained with the scanning vibrating electrode technique. SVET analysis was obtained after 23 hours of exposure of the steel to medium containing aerobic bacteria.

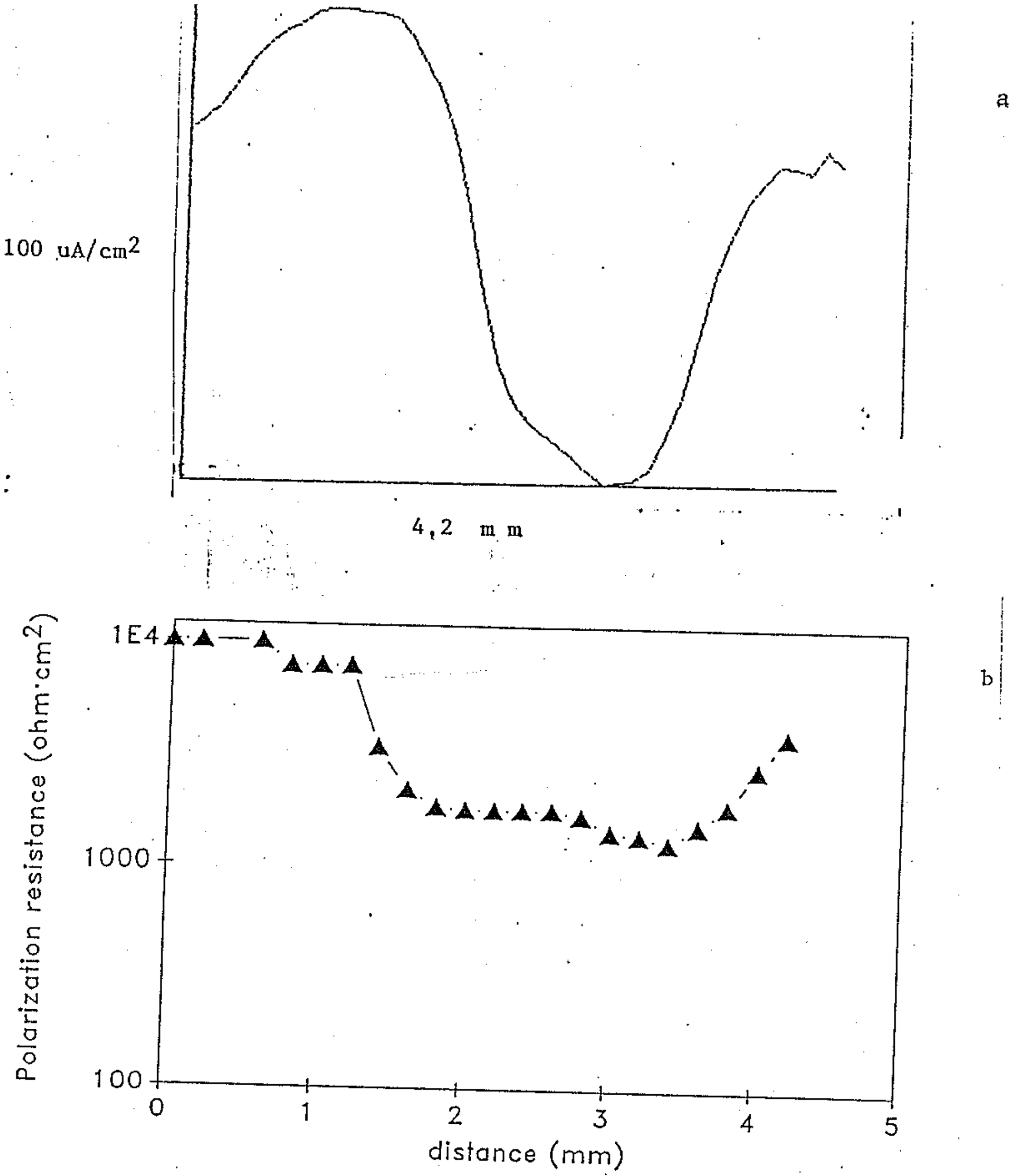

Fig. 3. a) Current densities, at open circuit potential, for a transect across the carbon steel sample. Transect was taken from fig. 2, 600um parallel to the X-axis. b) polarization resistance measurements, obtained with the SVET for the transect in fig. 3a.

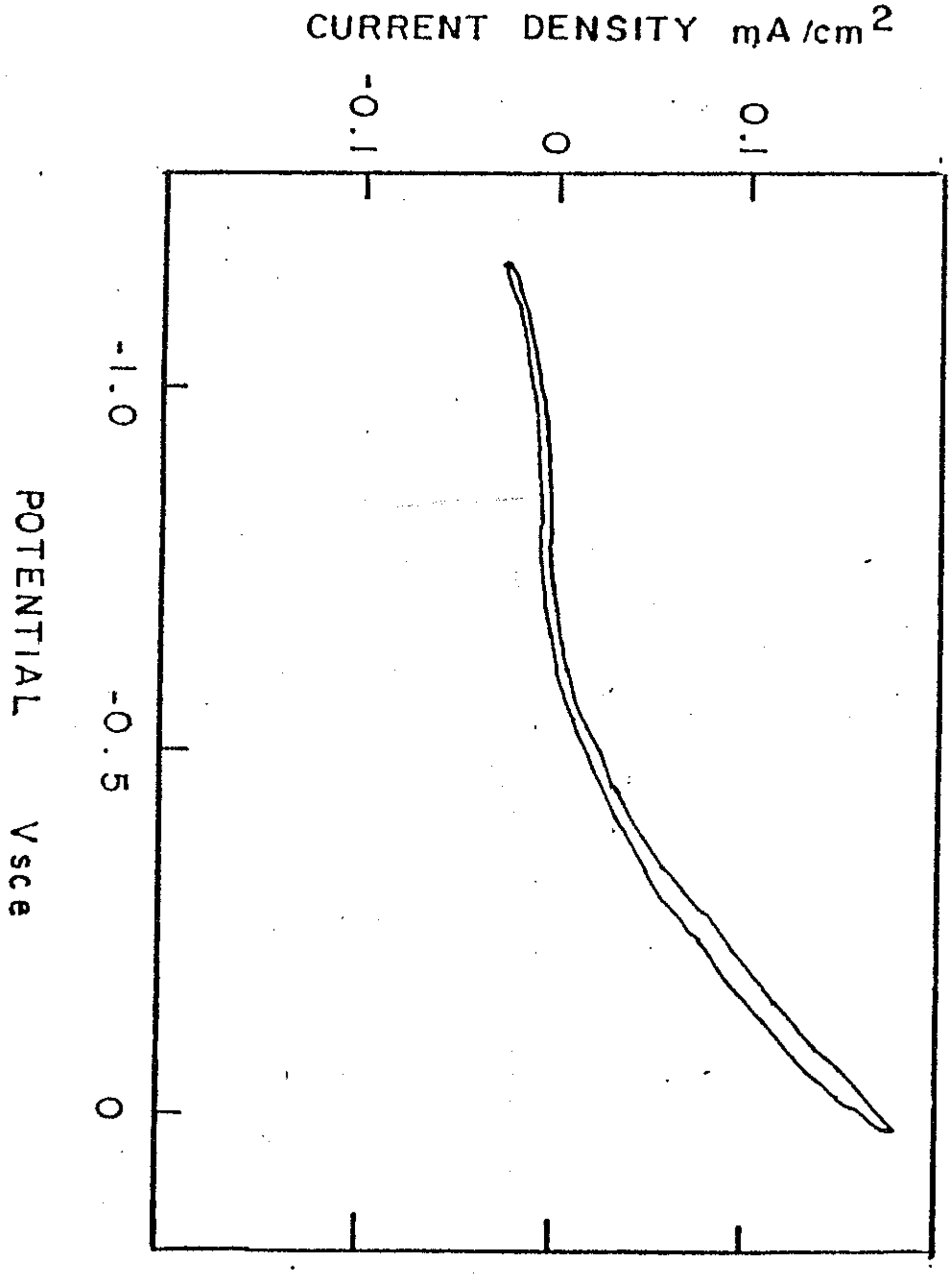

Fig. 4. Cyclic polarization for the carbon steel sample after 24 hours of exposure to medium containing bacteria.

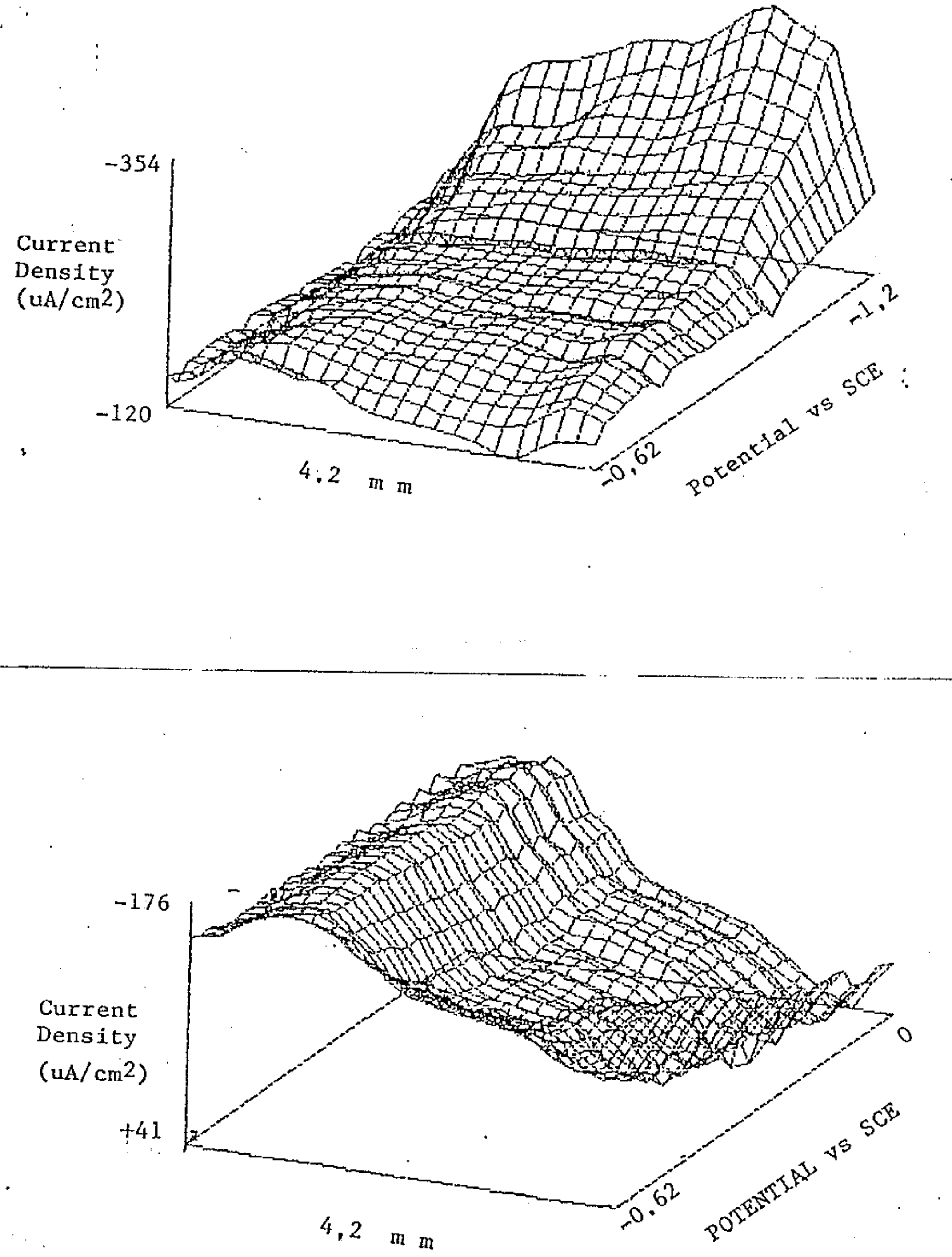

Fig. 5. Cyclic polarization for the carbon steel sample after 24 hours of exposure to medium containing bacteria. Changes in applied current detected by the SVET, as described in the materials and methods. a) Cathodic polarization, potential ramped from OCP, -620mV/SCE to -1.2V/SCE at 1mV/sec. b) Anodic polarization, potential ramped from OCP to 0V/SCE at 1mV/sec.