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ELECTROCHEMICAL BEHAVIOR OF LOCALIZED CORROSION IN STEEL, BY SULFATE-REDUCING BACTERIA UNDER OLIGOTROPHIC CONDITIONS

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ABSTRACT

Localized corrosion of SAE1010 steel exposed to *Desulfovibrio vietnamensis* strain 7760 under oligotrophic conditions was characterized through an electrochemical noise analysis. Once the sulfate-reducing bacteria were inoculated, three evolution patterns of localization index (LI), were observed. From the start of the experiment to 135 h, LI values varied between 0.1 and 0.4. Then, the LI raised near to 1 and fluctuated between 0.1 and 1 for a long period of time (140 to 560 h). Finally it decreased and remained stable up to the end of the experiment at 0.01. This situation could indicate two different processes. After 140 h, mainly a localized corrosion process took place over the steel surface and after 560 h, a general corrosion process occurred.

According to the transients in current noise, a modulated amplitude signal with a correspondent modulated potential noise response for the initiation of pitting was observed just before LI increased near 1. At the highest LI values, the time records for current and potential have shown a typical behavior of pitting corrosion process.

In contrast, experiments with lactate as energy and carbon source for the sulfate reducing-bacteria exhibited a moderated localized corrosion process (LI, 0.1-0.3). In this case, the current and potential series did not present the characteristic signal of pitting corrosion.

The increase in LI and the presence of typical signal of pitting was discussed in terms of the utilization of cathodically produced hydrogen as a consequence of oligotrophic conditions.

Key words: localized corrosion, oligotrophic conditions, electrochemical noise, SRB.

INTRODUCTION

Oligotrophic environments can be broadly defined by their low concentration in organic substrate [1]. According to this definition, the nutritional conditions prevailing in an oil or gas pipeline may be considered as an oligotrophic environment.

Several biocorrosion-relevant microbial groups are present in pipelines of the oil industry, one of the most important anaerobic bacteria are the sulfate-reducing bacteria, SRB. The ability of SRB to use hydrogen from steel surfaces has been demonstrated experimentally. Cord-Ruwisch and Widdel reported the utilization of hydrogen from the steel surface only when organic compounds (e. g. lactate) were also present as additional substrates for sulfate reduction in a non-electrochemical experiment [2].

Under oligotrophic conditions of growth that are frequently similar to their natural environments, bacteria form biofilms because they find on surfaces the necessary nutriments to their growth. However, most of the microbiologically influenced corrosion (MIC) studies involved laboratory experiments under conditions that were completely different from those prevailing in field sites [3, 4]. Microorganisms found in natural or industrial waters were adapted to grow with very low levels of nutrients whereas microorganisms in laboratory experiments were generally grown in rich culture media.

Appropriate techniques for detection and monitoring of MIC are essential for understanding the mechanistic nature of the corrosion process. The electrochemical noise technique (EN) has been used to study onset of localized corrosion associated with pitting, crevice corrosion, stress corrosion cracking and microbiologically influenced corrosion [5, 6, 7]. Electrochemical noise (EN) is the term used to describe the spontaneous fluctuation occurring in electrochemical systems [8]. The localization index (LI) (Eq. 1) is the standard deviation of the current noise (σ_I) divided by the root mean square current (I_{rms}) (Eq. 2). The value will always be between 0 and 1 [9]. When the value of LI is lower than 0.05, the corrosion process is considered to be uniform. A value of LI between 0.05 and 0.1 corresponds to a mixed corrosion process (uniform and localized). A value of LI higher than 0.1 indicates a typical localized corrosion process [10].

$$LI = \frac{\sigma_I}{I_{rms}} \qquad (1)$$

$$I^2_{rms} = \bar{I}^2 + \overline{I^2_n} \qquad (2)$$

The noise resistance (R_n) is the standard deviation of the potential noise divided by the standard deviation of current noise (Eq. 3). A low value of R_n indicates a high corrosion rate.

$$R_n = \frac{\sigma_E}{\sigma_I} \qquad (3)$$

Pitting corrosion of some metals and alloys is always preceded by metastable pitting, which is characterized by simultaneous current and potential fluctuations. Each EN event corresponds to metastable pit and the probability of the formation of a stable pit is proportional to the number of metastable pitting events [7]. Therefore, the measurement of EN is helpful for understanding pitting initiation at an early stage.

The aim of this work was to apply electrochemical noise analysis in order to identify characteristic events induced by SRB under oligotrophic conditions as criteria to predict type-pitting localized corrosion.

EXPERIMENTAL PROCEDURE

Organism and culture conditions.

Desulfovibrio vietnamensis strain 7760 was isolated from a oil/water sample taken from production well head (SAM-II) in Tabasco (Gulf of Mexico). Strain 7760 is a strictly anaerobic bacteria, microscopic observations showed the presence of vibrio shaped bacteria (Figure 1). Analysis of the almost complete sequence (1500 bp) of the 16S rRNA gene revealed that strain belonged to *Desulfovibrio vietnamensis* (similarity $>$ 98%).This SRB specie has active hydrogenases and is not able to use acetate as sole source of carbon and energy.

Cultures were grown in anaerobic medium containing in g/L: Na_2SO_4, 3; K_2HPO_4, 0.2; NH_4Cl, 0.2; KCl, 0.2; $MgCl_2.6H_2O$, 0.3; NaCl, 5; $CaCl_2.2\ H_2O$, 0.1; sodium acetate, 0.5; yeast extract (Difco laboratories), 0.1; bio-Trypcase (bioMérieux), 0.5; cysteine-HCl, 0.5; trace mineral element solution, 10 ml; resazurin (0,1 %), 1 ml. The pH was adjusted to 7.3 with KOH (10 N). The culture medium was autoclaved for 45 min at 110 °C.

Corrosion experiments in electrochemical cell.

A glass reaction vessel (1 L) with butyl rubber stoppers containing ports for gas, inoculum inlet and electrodes was used. Three identical steel electrodes (SAE1010) were constructed by embedding the square specimen in epoxy resin. They were used to measure EN, two of them acting as working electrodes (WE1 and WE2) and the last one acting as reference electrode. Before starting an experiment, the electrodes were polished using a 600-grit abrasive grade paper, washed in distilled water and surface sterilized with ethanol and dried in warm air. Then they were introduced under a stream of oxygen-free N_2/CO_2 (80:20, v/v) gas in the electrochemical cell containing 750 mL of the anaerobic culture medium.

Prior to inoculation, $NaHCO_3$, was added from sterile stock solutions to obtain a final concentration of 0.2 % (w/v). A 1% (v/v) bacterial inoculum grown at 35 °C on hydrogen/sulfate or lactate/sulfate medium was used.

Time records of potential and current fluctuations were monitored using a zero resistance ammeter (ZRA) manufactured by ACM Instruments (U. K). Current and potential were measured every 0.5 s, with a total number of 2048 readings, every 4.5 h during 800 h.

A preliminary test with a sterile control was realized. For the experiment under oligotrophic conditions the only energy source for the SRB strain 7760 was the cathodic hydrogen naturally generated from the surface steel. Additionally rich organic culture conditions were tested by adding sodium lactate (final concentration of 10 mM).

RESULTS AND DISCUSSION

Localization index (LI) and noise resistance (R_n) patterns.

Different patterns of LI were obtained depending on the culture conditions of the *Desulfovibrio vietnamensis* strain 7760 (Figure 2). In the absence of bacteria (control, data not shown), LI remains stable from 20 h to the end of the experiment, at a level below 0.05.

When *D. vietnamensis* strain 7760 was cultivated in the electrochemical cell under oligotrophic conditions, three evolution patterns of LI might be observed. From the start of the experiment to 135 h, LI values varied between 0.1 and 0.4. Suddenly, the LI raised near to 1 and fluctuated between 0.1 and 1 for a long period of time (140 to 490 h). Finally it decreased and remained stable up to the end of the experiment at a value of 0.01. When *D. vietnamensis* strain 7760 was cultivated in the electrochemical cell in presence of lactate, LI showed values between 0.1 and 0.4 during all through the experiment.

The overall behavior of the electrochemical noise under sterile conditions corresponded to a uniform corrosion process. In presence of the SRB strain 7760, a localized corrosion process took place over the steel surface, in oligotrophic conditions and in the presence of an additional organic substrate. However, LI reached values higher in oligotrophic conditions than those obtained in presence of lactate.

These results suggest that, in oligotrophic conditions, the increase of LI and the maintenance of a localized corrosion process for a long period of time could be due to the use of cathodically produced hydrogen as the only source of energy of *D. vietnamensis* strain 7760 through the dissolution of iron. On the contrary, under rich organic conditions, the presence of an alternative energy source was reflected in the behavior of LI, which remained at a value of 0.1 considered as moderately localized and stable during all the experiment. These results did not agree with the results of Cord-Ruwish and Widdel [2] because a localized corrosion process took place independently of the presence of an organic substrate (lactate).

After 560 h of experiment, the corrosion process became uniform in oligotrophic culture conditions; then noise resistance (R_n) analysis could be used to estimate corrosion rate. Figure 3 shows that R_n had an average value of 1,500 Ohm/cm^2 after 560 h which, remained at the same value up to the end of the experiment. This value must be considered as significant for a uniform corrosion process. The high values of R_n observed during the first 560 h of the experiment did not reflect the localized corrosion process that took place as evidenced by the LI values. On the contrary, after 560 h, the R_n values indicated a significant uniform corrosion process. For this reason we consider that the combined use of R_n and LI can be recommended in order to evaluate the corrosion risks by SRB when different corrosion processes occur [11].

Typical pitting events.

Time records of potential fluctuations under open-circuit conditions and current fluctuations under short-circuit conditions were recorded. Figure 4 presents current and potential fluctuations in the time domain for the system with SRB strain 7760 after 26 h under oligotrophic conditions. Modulated amplitude transients in current with a correspondent modulated transients in potential were observed just before LI increased until reaching a value near 1.

Current and potential fluctuations in the time domain for the system with *D. vietnamensis* in oligotrophic conditions at 140 h and LI = 0.96 could be attributed to a metastable pitting event because a typical shape of transients was observed (Figure 5). The pitting initiation process is often found to result in metastable pit nucleation and propagation [12]. The current transients exhibited a relatively rapid rise followed by a slow decay with the repassivation of the pitting corrosion sites. The current from the pit was largely drawn from the capacitance of the passive film, causing the potential fall over the period of the current transient. Then it raised rather more slowly as the passive film recharged as a result of the cathodic reaction [9]. This signal pattern was always present at the highest values of LI.

The transients were always negative and had an average amplitude of 0.5 μA and 0.6 mV for current and potential noise, respectively. In a charged iron undergoing pitting corrosion experiment [7], all transients were negative and showed a similar amplitude range but occurred more frequently than those observed in our experiments.

Current and potential fluctuations in the time domain for *D. vietnamensis* strain 7760. grown in rich organic conditions, at incubation times of 50 h and 470 h, were presented in Figures 6 and 7, respectively. The signal did not present modulations nor characteristic transients of pitting and maintained the same pattern during all the test even at high values of LI.

Potential and current fluctuations were only observed when *Desulfovibrio* strain 7760 was cultivated in oligotrophic conditions. Then oligotrophic growth conditions might increase significantly the initiation of a pitting corrosion process.

CONCLUSIONS

Electrochemical noise measurements used in this study appear a convenient technique for studying microbial corrosion of iron by *D. vietnamensis* strain 7760. This technique allowed to distinguish between a uniform and a localized corrosion process that occurred in two different nutritional growth conditions of a sulfate-reducing bacteria, oligotrophic or rich organic culture medium.

When *D. vietnamensis* strain 7760 was cultivated in oligotrophic conditions, a localized corrosion process was first undergoing during 560 h that could be monitored by the localization index. Then the corrosion process became uniform and the noise resistance was appropriate parameter for the interpretation of electrochemical noise. In rich organic conditions the process was always localized but LI could not reach values so high than those obtained in oligotrophic culture conditions.

Metastable pitting events were identified at the highest values of LI with *Desulfovibrio vietnamensis* strain 7760 cultivated under oligotrophic conditions. In contrast the signal obtained under rich organic conditions did not present modulations nor characteristic transients of pitting. Furthermore, it maintained the same aspect during all the test even at high values of LI.

Oligotrophic growth conditions of hydrogen-utilizing sulfate-reducing bacteria might significantly increase the risk for initiating a pitting corrosion process on steel surface.

REFERENCES

1. Fry C. C., (1990) "Oligotrophs" in Microbiology of Extreme Environments. Edwards C. (ed.) Mc Graw Hill, Great Britain.
2. Cord-Ruwisch R., Widdel F. (1986) **Corroding iron as hydrogen source for sulfate reduction in growing cultures of sulfate-reducing bacteria.** *Appl. Microbiol. Biotechnol.* **25**: 169-179.
3. Campaignolle X., Caumette P., Dabois F., Crolet J. L., (1996) **The Role of Thiosulfate on the Microbially Induced Pitting of Carbon Steel**, Corrosion 96, NACE Houston TX, paper 273.
4. Videla H.A, (2002) **Biocorrosion and Biofouling of Industrial Systems. A State of the art at the beginning of the new millennium**. ICC, International Corrosion Council 15th International Corrosion Conference, Granada Spain.
5. Dawson J. L., Sculty J. R., Roberge, Reichert D. L., Dawson J. L. (Eds.) (1996) Electrochemical Noise Measurement for Corrosion Applications, ASTM STP 1277, American Society for Testing and Materials, p. 6.
6. Yang M. Z., Wilmott M and Luo J. L. (1998) **Analysis of the Electrochemical Noise of Localized Corrosion of Type A516-70 Carbon Steel,** *Corrosion* **54** (11): 869-876.
7. Yu J.G., Luo J. L. and Norton P. R. (2002) **Investigation of hydrogen induced pitting active sites.** *Electrochem. Acta* **47**: 4019-4025.
8. Bertocci U, Huet F. (1997) **Noise analysis applied to electrochemical systems.** *Corrosion* **51**: 131-144.
9. Cottis R. and Turgoose S. (1999) "Electrochemical Impedance and Noise", Corrosion Testing Made Easy, NACE International.
10. Kelly R. G., Inman M. E. and Hudson J. L. (1996) "Analysis of Electrochemical Noise of Type 410 Stainless Steel in Chloride Solutions", in Electrochemical Noise Measurement for Corrosion Applications, ASTM STP 1277 (ed) 101-103.
11. Mora-Mendoza J. L., Padilla- Viveros A. A., Zavala-Olivares G., González-Núñez M. A., Moreno-Serrano J. L., García Esquivel R. and J. Galíndez. (2003) **Electrochemical Kinetics of Sulfate Reducing Bacteria Isolated from a Gas Pipeline,** Corrosion 2003, NACE Houston TX, paper 03548.
12. Bertocci U., Koike M., Leigh S., Qiu F., Yang G., (1986) *J Electrochem. Soc.* **133**:1782.

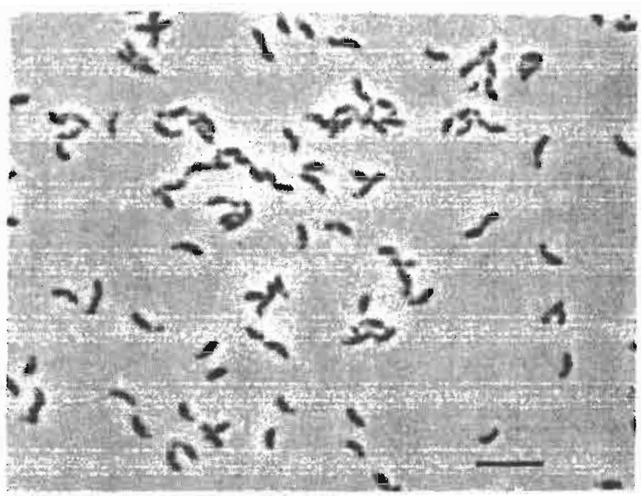

FIGURE 1 Phase contrast photomicrograph of *D. vietnamensis* strain 7760 grown with lactate as carbon and energy sources for growth. Bar represents 10 µm.

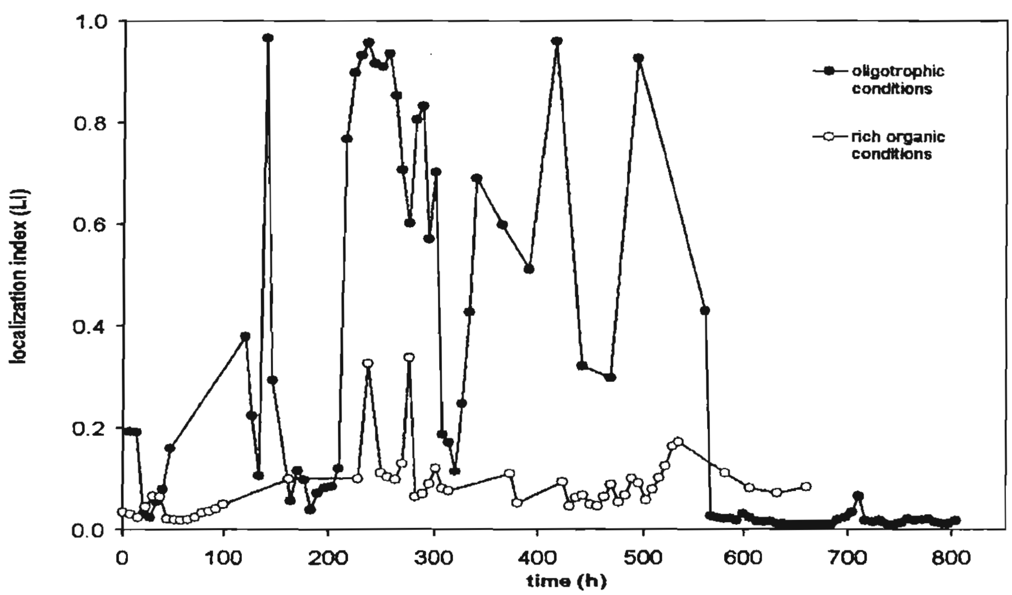

FIGURE 2 Evolution of the localization index (LI) in presence of *D. vietnamensis* strain 7760 in oligotrophic and in rich organic culture conditions (lactate).

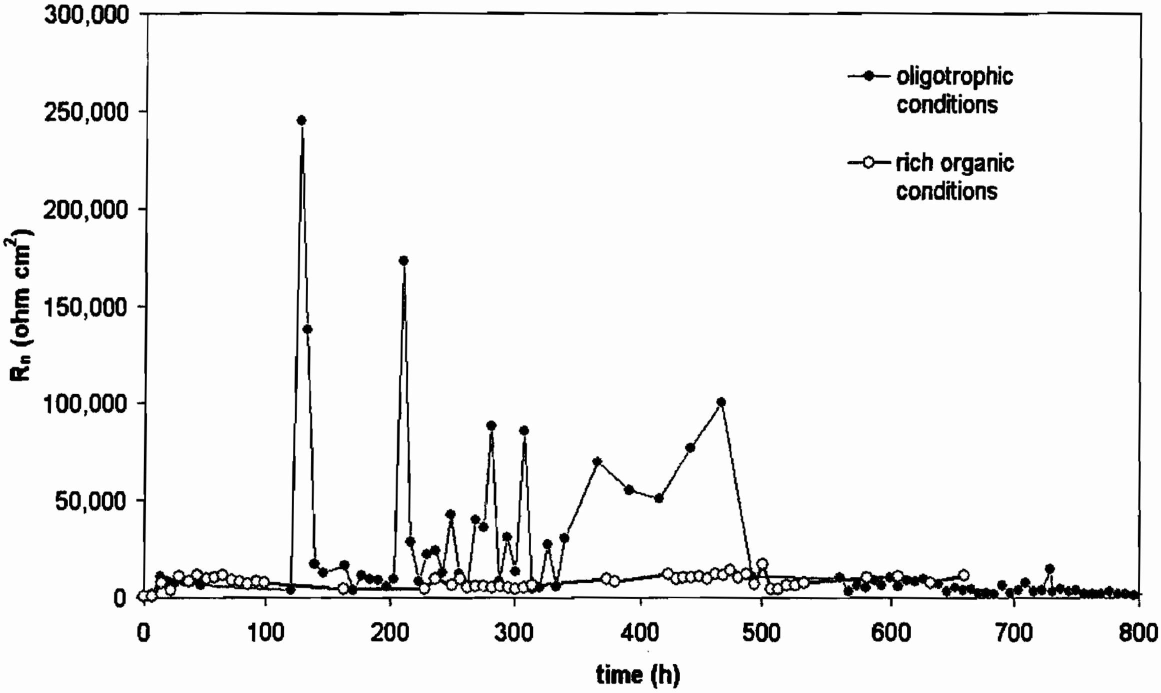

FIGURE 3 Evolution of the Resistance noise (R_n) in presence of *D. vietnamensis* in oligotrophic conditions and in rich organic conditions (lactate).

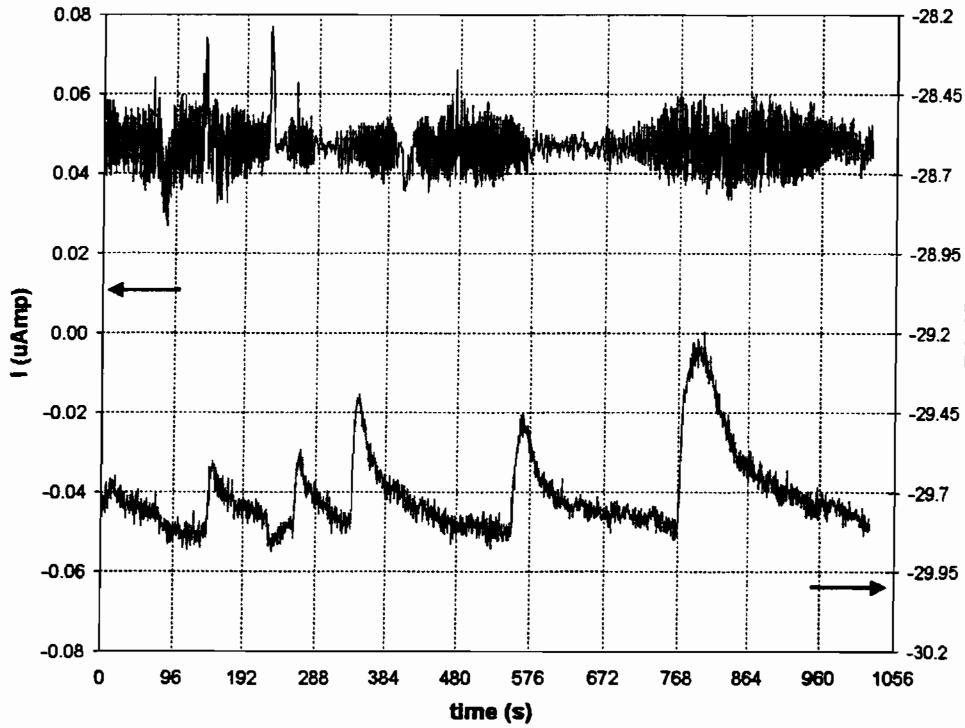

FIGURE 4 E and I records for the system in presence of *D. vietnamensis* strain 7760 in oligotrophic culture conditions showing the modulated current and potential signals after 26h of exposition.

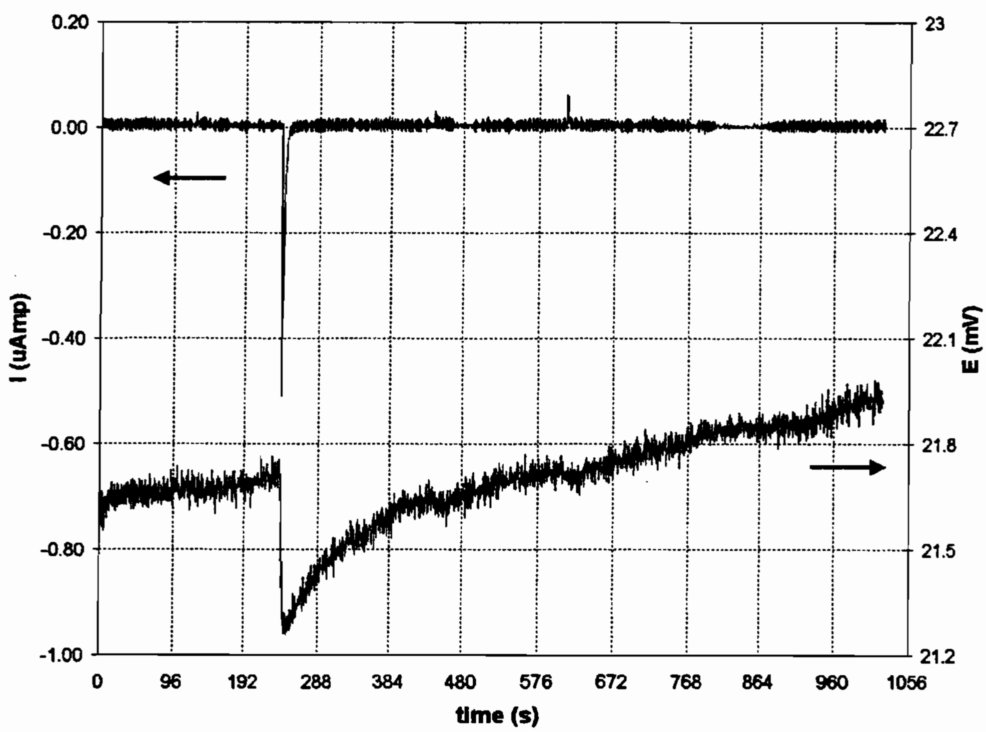

FIGURE 5 E and I records for the system in presence of *D. vietnamensis* strain 7760 in oligotrophic culture conditions after 140 h of exposition and LI = 0.96, showing the typical behavior of pitting corrosion.

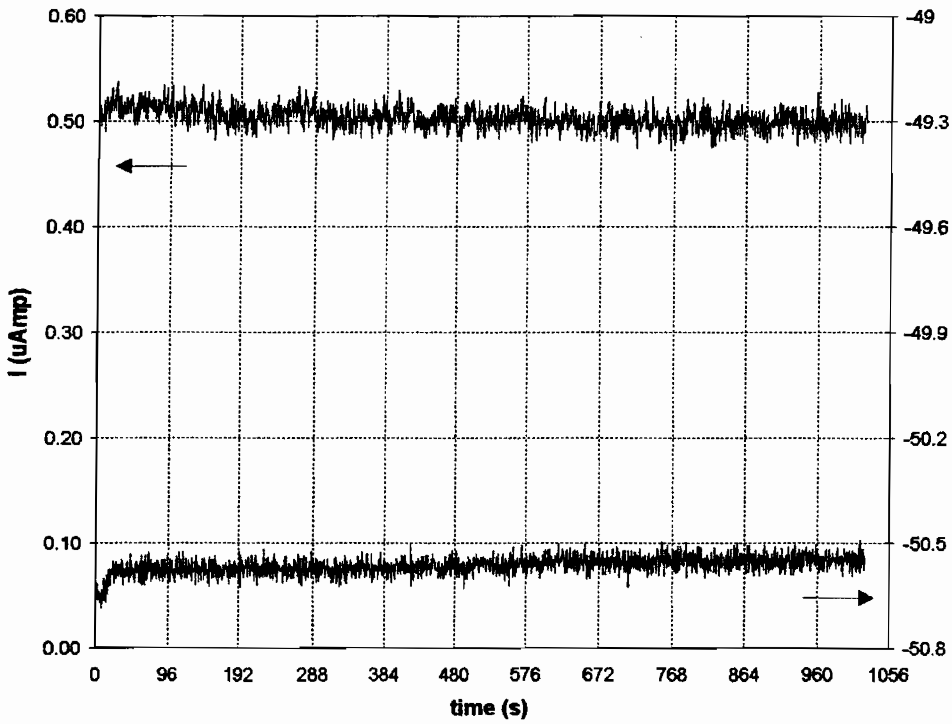

FIGURE 6 E and I records for the system in presence of *D. vietnamensis* strain 7760 in rich organic culture conditions after 50 h of exposition.

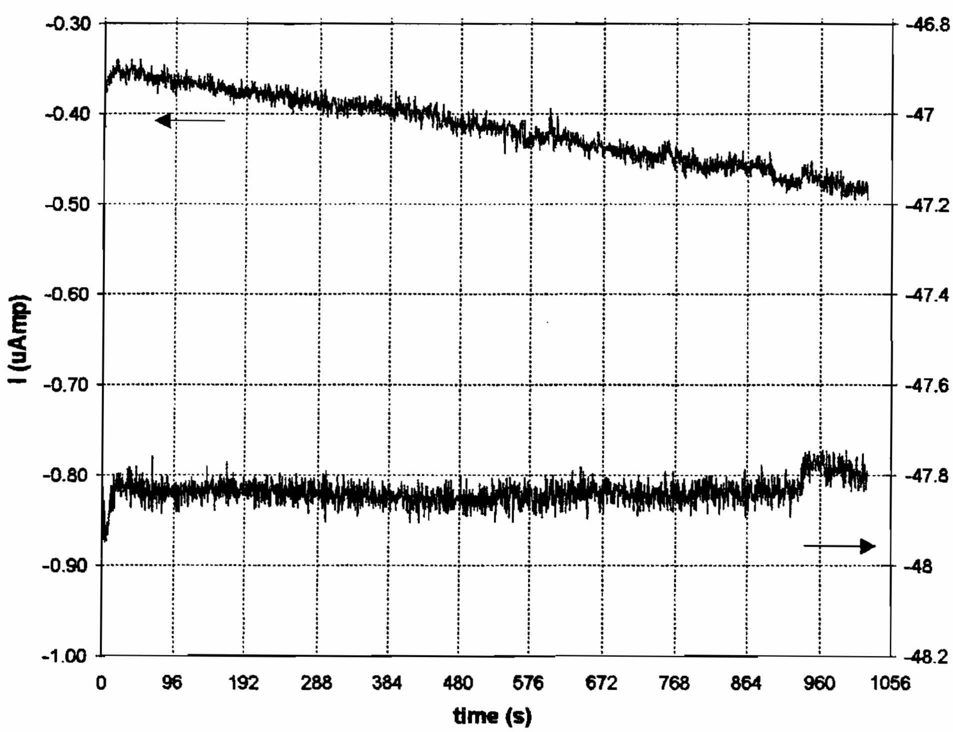

FIGURE 7 E and I records for the system in presence of *D. vietnamensis* strain 7760 in rich organic culture conditions at 470 h of exposition.

Padilla-Viveros A.A., Garcia-Ochoa E., Alazard Didier (2004)

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Corrosion NACE 2004: International Symposium, 59, New Orleans (USA), 2004/03/28