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ORIGINAL ARTICLE

A Short Communication on the Corrosion Behavior, O_2 Reduction and Methanol Oxidation Activity of Stainless Steel 304 After Biofilm Formation in Blacksea Water

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ABSTRACT

Corrosion inhibition, O_2 reduction and methanol oxidation activities of biofilm (BF) covered SS304 were observed by potentiostatic and potentiodynamic measurements. Corrosion inhibition character of BF grown in Black sea water can be clearly seen in pitting and activation region in alkaline environment. And in highly acidic environment, corrosion inhibition can be seen by anodic dissolution peak shift. O_2 reduction and methanol oxidation can be observed by the increase in negative currents for the potential values less than -0.6V vs. SCE and by the increase in positive currents greater than 0.4 V vs. SCE.

Key Words: Biofilm, corrosion, methanol oxidation, oxygen reduction

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1. INTRODUCTION

In different natural environments from sea water to domestic waste waters, microorganisms can synthesize surface electroactive compounds leading to the biofilm (BF) formation. Biofilms can grow faster in aqueous and nutrient rich environments involving single cell organisms, bacteria, algae, diatoms and basils [1,2].

Studies have shown that BF can be used for different purposes. For example, BF can catalyze oxygen reduction and alcohol or acetate oxidation with stainless steel (SS) electrodes in natural sea water medium and this interesting behavior can help to generate power by microbial fuel cells or by prototypes designed in marine sediments and overlying seawater. Widely investigated oxidation mechanism on SS microbial electrode was seen to be related with the microbial decomposition of alcohol and oxidation of S^{-2} (in the environment) donating electrons [3].

Initial studies on seawater biofilm grown on stainless steel cathode used in a laboratory scale fuel cell was seen to exhibit efficient oxygen reduction giving comparable current densities (1-2A/cm^2). This current density achieved was found to be related with the kinetics of electro active biofilm growth [2,4-6]. When SS electrode was immersed in natural sea water , it was seen that O_2 reduction occurs during the first phase of

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bio film growth and depends on the critical potential (-150mV vs. Ag/AgCl) , number of bacteria in the biofilm and electronic structure of passive layer [7]. In the literature, in alkaline solutions, it is reported that oxygen reduction on BF is noticed by a wave at a cathodic potential -0.6V/SCE . This wave is related mainly to the consumption of oxygen dissolved in the solution. But on the other hand, between -0.4 and 0.9 V vs. SCE, the current wave can coincide with dihydrogen formation [8].

Biofilm can also act as an interesting corrosion inhibition tool. Typically, in the biofilm formed on steel by marine environment, sulfate-reducing bacteria and iron reducing bacteria can be detected. In addition, sulfate reducing bacteria and mixed bacteria culture may act differently against corrosion. While mixed culture inhibits corrosion by reduction of iron oxides to ferrous ions assisting in the formation of green rust, sulfate reducing bacteria produces iron sulfide and increases corrosion [9]. This corrosion product maybe formed in a heterogeneous layer that consists of phosphorous and sulfur based corrosion products and biofilm [10].

In this study, in the light of the information presented above, biofilm formation was observed in Black sea water on stainless steel 304 (SS) electrode by potentiostatic measurements. After that, biofilm on the SS electrode was characterized from the point of its corrosion inhibition, O_2 reduction and methanol oxidation behavior.

2. EXPERIMENTAL

Experimental set up

Formation and characterization of biofilm formed on SS electrode in Black sea water was performed at room temperature in the experimental set up shown in Figure 1. Three electrode cell (70ml in volume) was used for electrochemical measurements. SS 304 disc was used as a working electrode, reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire separated from the working electrode environment by a coarse frit. Working electrode potential was controlled by a potentiostat (model AFCBP1 from Pine Inst.) controlled by a PC. During BF formation the sea water was continuously circulated and refreshed by a peristaltic pump. Sea water was brought from Trabzon region in Turkey.

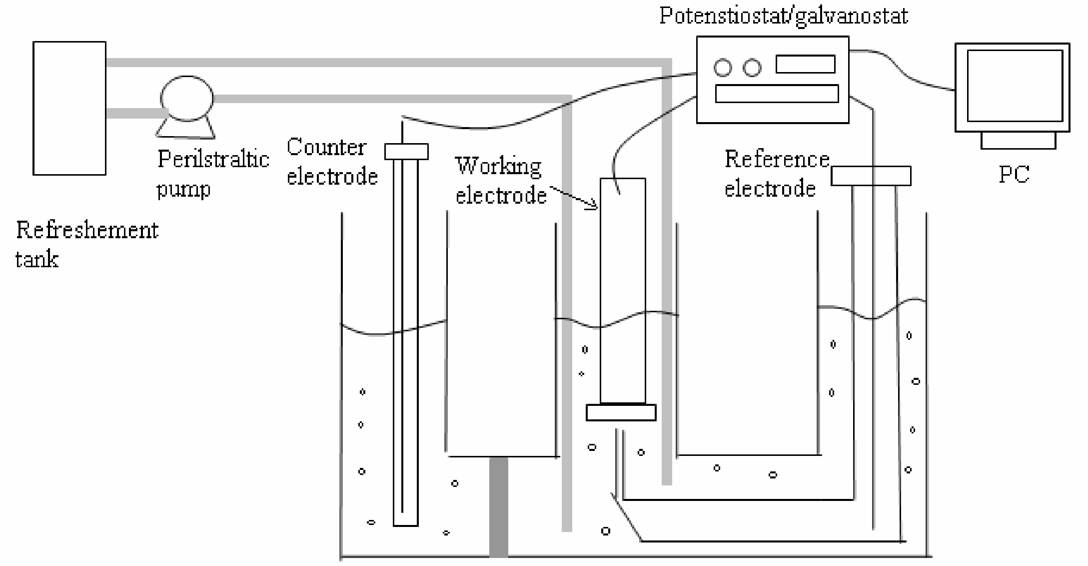

Figure 1. Experimental set up

Working electrode preparation and activation

Working electrode was prepared by using SS 304 cylindrical rod with a 0.5 cm radius and 10 cm length. The chemical composition of SS 304 was 0.08 % C, 2.0 % Mn, 0.045 % P, 0.03 % S, 0.75 % Si, 18.0 %Cr, 9.0 % Ni and 70.09 % Fe by mass. Initially, the flat surface of the SS rod was polished by an emery paper to remove rust and dirt. After that, the cylindrical rod was polished in 0.5µm alumina suspension until a flat mirror surface was achieved. In order to have flat disc surface, cylindrical rod was placed in a teflon slot. Before the experiments, disc electrode was immersed for about 10 minutes in deionized water, ethanol, nitric acid and deionized water accordingly.

Potentiostatic experiments for biofilm formation

In order to form a biofilm on SS 304 electrode surface, cell potential was kept at -1.1V for 6 days in Black sea water. Current data was recorded at every one minute. Seawater in the cell was continuously refreshed during the experiment by a peristaltic pump (Figure 1). Each day potentiostatic experiments were continued for 5.5 hours approximately. After each day potentiostatic experiment was restarted.

Cyclic voltammetry

After biofilm formation, disc electrode was characterized by cyclic voltammetry in 0.5 M NaCl pH=10 , 0.5 M H_2SO_4 and 0.5 M CH_3OH-0.5 M H_2SO_4 electrolyte environments at a scan rate of 5mV/sec and 20mV/sec between -1.1 and 1.1 V (All potential values are given with respect to SCE). pH of the NaCl solution was adjusted by HCl and NH_4OH solutions.

3. RESULTS AND DISCUSSION

Biofilm formation

In the first and second day of electrode polarization (Figure 2,3) at -1.1V, there was almost no change in the negative current, but the current then decreased over the following four days, approximately 20µA per day. This current drop is suspected to be due to the slowing rate in bacterial growth by the depletion of nutrient sources in the closed system or the elimination of the electro active bacteria by the predators such as Protozoa [6,11].

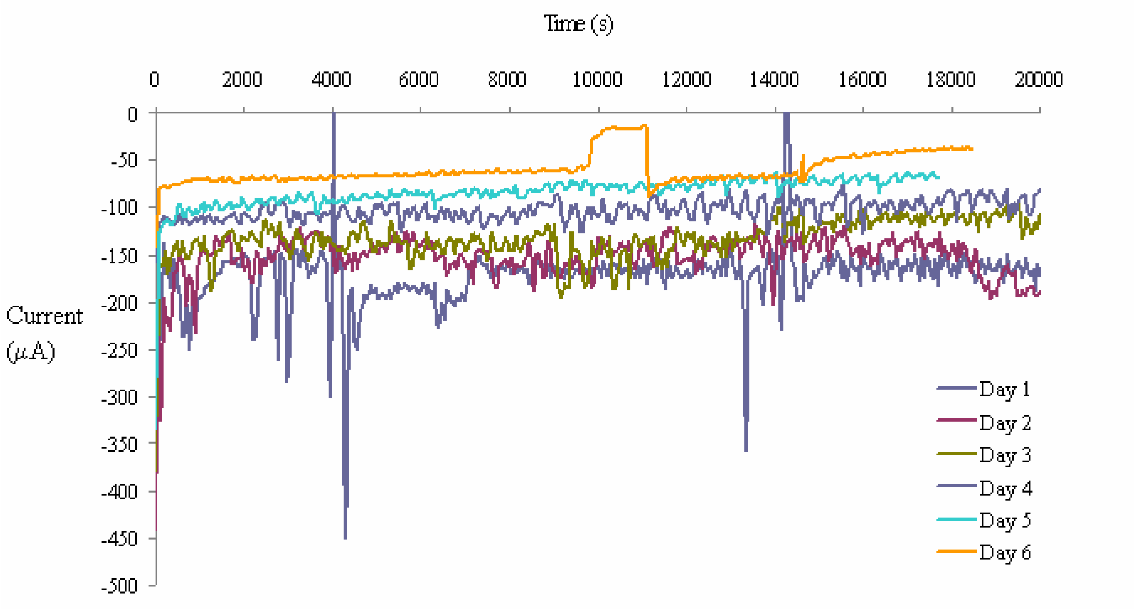

Figure 2. Current behavior obtained in a 70ml refreshed seawater on SS 304 electrode polarized at -1.1V .

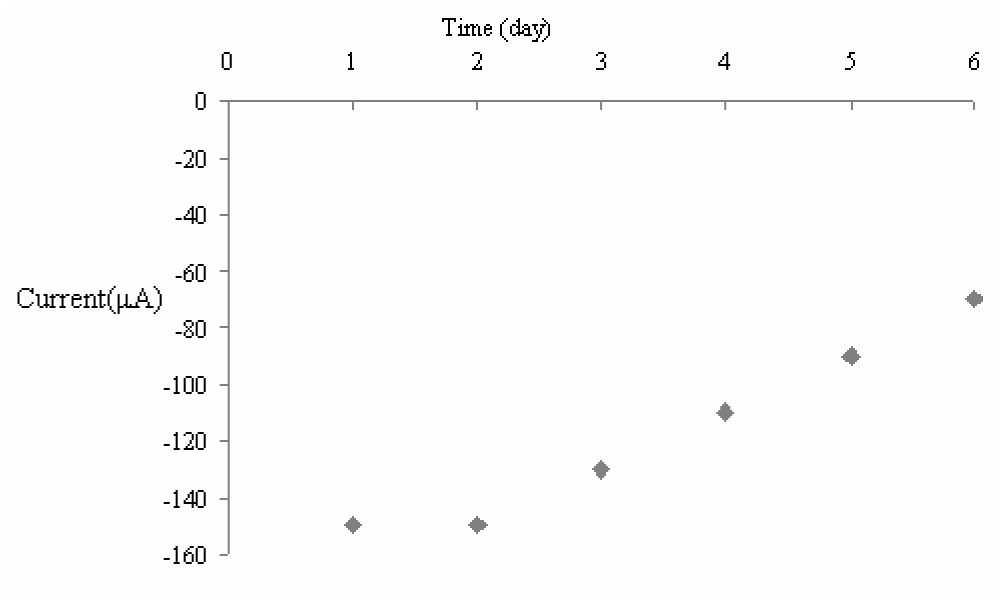

Figure 3. Current behavior obtained in a 70ml refreshed seawater on SS 304 electrode polarized at -1.1V after each day.

Cyclic voltammetry

Initially, SS304 electrode without BF were characterized by cyclic voltammetry in order to see regions of corrosion, passivation and hydrogen evolution. Figure 4 shows five different regions during cyclic voltammetry. Region A where potential is less than -1V shows the region of both dihydrogen formation and oxygen reduction. Region B is the activation-passivation region where iron hydroxide and iron oxyhydroxide forms according to the mechanism given below [12]:

$$Fe + 2OH^- \leftrightarrow Fe(OH)_2 + 2e^-$$

$$Fe(OH)_2 + OH^- \leftrightarrow FeOOH + H_2O + e^-$$

Current drop in region B is followed by pitting region C at a potential greater than 0.0V. After the formation of chromium oxide/iron oxyhydroxide mixed oxide layer (region D), a current plateau forms where the electrode surface is covered by a layer of chromium rich oxide which is known as chromium passivation [13].

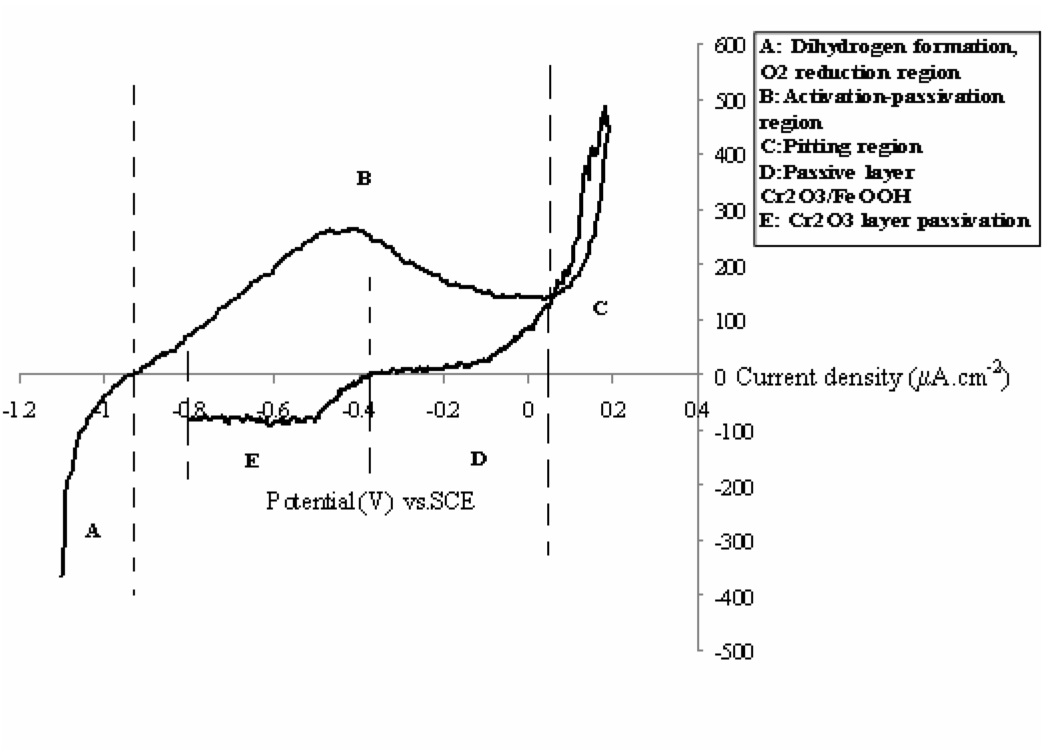

Figure 4. Cyclic voltammogram for stainless steel electrode in aerated 0.5M NaCl pH 10 solution recorded at 5mV/s before BF formation.

As seen in Figure 5. corrosion behavior of SS304 was greatly changed after BF formation. Activation region and pitting region was masked by the corrosion inhibition of BF layer. In addition, reduction current was seen at a potential greater than -0.6V which was much more positive than -1V on a bare electrode surface. This indicates that on BF covered SS 304 electrode, negative current was greatly enhanced by oxygen reduction.

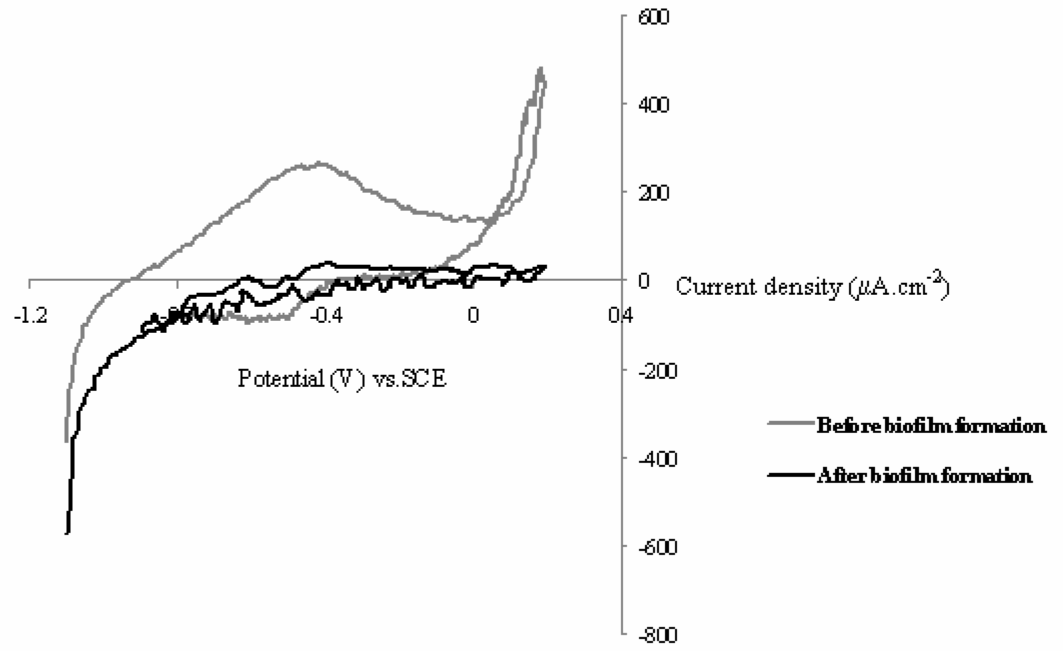

Figure 5. Comparison of stainless steel electrode before and after BF formation in aerated 0.5M NaCl pH 10 solution recorded at 5mV/s.

Corrosion behavior of BF covered SS 304 in a highly acidic environment was also studied. It was seen that anodic dissolution current peak shifted to a little more positive potential on BF covered SS 304 with a slight current drop. This indicates that a slight corrosion delay can be observed by the formation of BF layer in highly acidic environments (Figure 6).

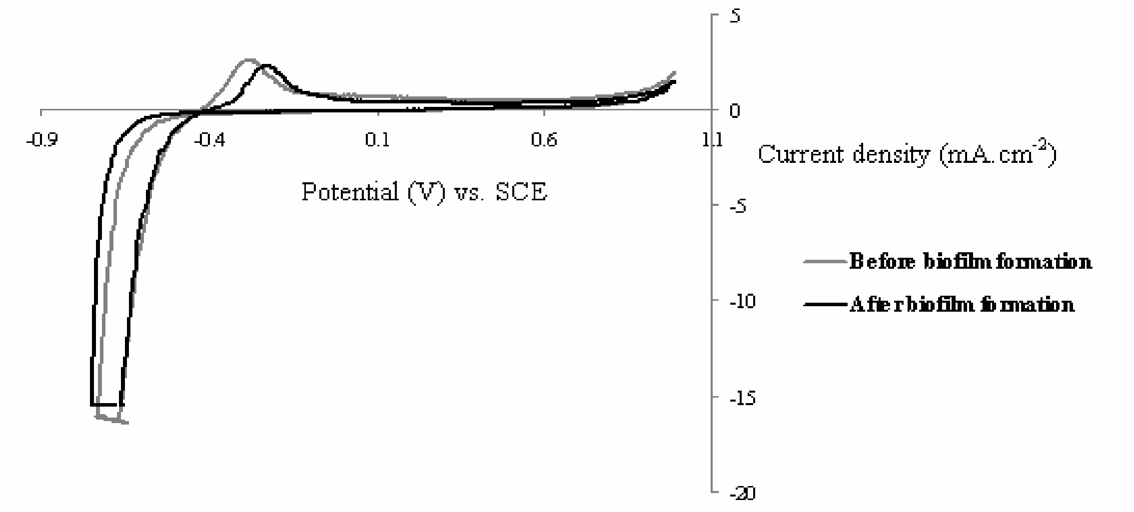

Figure 6. Comparison of stainless steel electrode before and after BF formation in 0.5M H_2SO_4 solution recorded at 20mV/s.

In order to see if the BF layer is electrochemically active for alcohol oxidation, SS 304 electrode was scanned in 0.5M H_2SO_4+ 0.5M CH_3OH electrolyte solution before and after BF formation (Figure 7). It was seen that anodic dissolution of bare electrode surface increased after addition of methanol in the acidic electrolyte. But after BF formation, anodic dissolution was suppressed. In addition, oxidation currents were observed after 0.6V vs. SCE on BF covered electrode which is most probably related with methanol electro-oxidation.

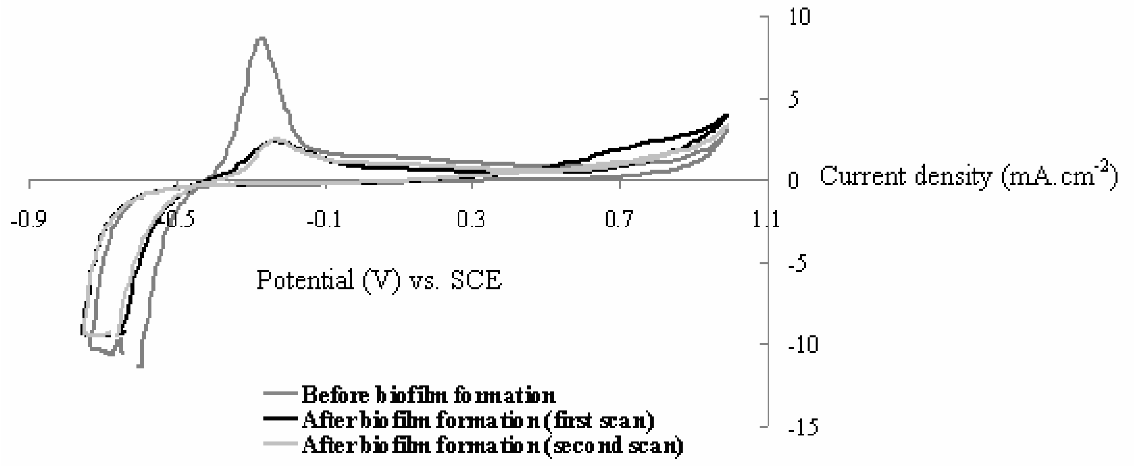

Figure 7. Comparison of stainless steel electrode before and after BF formation in 0.5M H_2SO_4+ 0.5M CH_3OH solution recorded at 20mV/s.

4. CONCLUSIONS

During biofilm formation in Black sea water, after second day negative current decreased which was suspected to be due to slowing rate in bacterial growth or predators. BF formed on SS 304, almost masked pitting corrosion and activation regions. In highly acidic environment, BF coverage shifted anodic dissolution in the positive direction. O_2 reduction and methanol oxidation activities on BF covered SS304 can also be observed during cyclic voltammetry.

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