

Modeling of Microbiologically Influenced Corrosion (MIC) of Metallic Alloys in Seawater by Electrochemical Impedance Spectroscopy in a Nano-Meter Scale

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Abstract:

Experimental data of electrochemical impedance spectroscopy (EIS) were used for the first time to predict (model) the growth of the marine biofilm on the surface of two metallic alloys in seawater. The EIS data, i.e., double-layer capacitance (C_{dl}), of UNS 1020 carbon steel and stainless steel UNS S304 were used in this study. The C_{dl} values of the formed biofilm on the alloys were measured in seawater on a frequent basis. Total exposure of alloys to the seawater ranged between 90 days to 180 days. The carbon steel was found susceptible to microbiologically influenced (induced) corrosion (MIC). A mathematical model was derived to gradually predict the growth of the biofilm formation by correlating the obtained C_{dl} of the biofilm to the thickness of the biofilm formation. The mathematical correlation was derived on taking into the account parameters such as; the dielectric constant of formed biofilm, the dielectric constant of the seawater at two temperatures 18°C and 33°C, the volume fraction of the seawater in the bio-film, the dielectric constant of corrosion products, i.e., ferrous oxides; FeO, Fe₂O₃, magnetite; Fe₃O₄, iron oxide-hydroxide; FeOOH, Ferromanganese; a mixture of MnO₂ and Fe₂O₃, Ferrous sulfate; Fe₂SO₄, Ferrosulfuric acid; FeCr in the bio-film, and the volume fraction of those corrosion products in the biofilm. The calculated thickness of the biofilms was in the range of a nanometer to a fraction of micrometer.

Introduction:

In general, a phenomenon that is relating to physical science, i.e., physical chemistry, and life science, i.e., biology, can only be manifested at interface regions between such sciences. For instance, the phenomenon of the growth of a marine biofilm, on a metallic alloy from an aqueous solution can only be investigated at the interface region between the biofilm and the aqueous solution. It is well known that interfaces are difficult regions to directly characterize. The difficulty stems from the fact that interfaces in such situations, by default are discontinuous zones between the biofilm, on the metallic alloy, and the aqueous solution. In other context direct measurements of electrochemical parameters of interfacial regions are not possible because of constrained assumptions of continuum mechanics; that biofilm should be homogeneously continuous; and the physical chemistry parameters of biofilm should contain steady-state values with respect to the time, aging, and the mass & energy of the biofilm should be in a compliance with mass and the energy constitutional (conservation) laws. However, throughout the past three decades, indirect electrochemical methods such as DC techniques, i.e., Tafel plot, cyclic polarization, linear polarization, electrochemical noise, and AC techniques, i.e., AC impedance, have been used not only to characterize interfaces, but also to measure the corresponding DC & AC electrochemical parameters in solutions.

In this study, modeling of the growth of the marine biofouling film at metal-solution interfaces will be carried out on the UNS 1020

carbon steel and stainless steel 304 samples. The growth of the marine biofouling film of both alloys will be predicted by obtained experimental data of EIS measurements for a period of 6 months under a continuous flowing seawater condition. The prediction of the growth of the biofilm will take into the account for the first time parameters such as; the dielectric constant of the formed biofilm, the dielectric constant of the seawater at two temperatures 18°C and 33°C, the volume fraction of the seawater in the biofilm, the dielectric constant of corrosion products, i.e., FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese; a mixture of MnO₂ & Fe₂O₃, Fe₂SO₄ and Ferrosulfuric acid in the biofilm and the volume fraction of those corrosion products in the biofilm.

In a recent investigation of the authors, a relationship between the double-layer capacitance (C_{dl}) of a developed biofilm on a metal sample to the thickness of the formed film is given as the Following

$$C_{dl} = (\epsilon_0 \epsilon_r A) / L \text{ -----(1)}$$

Where:

C_{dl} is the Double-layer capacitance of the formed biofilm, F

ϵ_0 the permittivity of free space, 8.85×10^{-14} Farad/cm.

A is the area of the sample exposed to the seawater, 1cm².

L is the thickness of the formed biofilm, nm, which can be obtained here by EIS, via equ.(1).

ϵ_r is the static dielectric constant of materials under the investigation, of the biofilm's materials.

In the investigation of the authors, the dielectric constant of the biofilm has been extended to account for the volume fraction of the seawater in the film, as biological membrane. So;

$$\epsilon = (\epsilon_{bf} + v_{sw} \epsilon_{sw}), \text{ where -----(2)}$$

ϵ_{bf} is the dielectric constant of the formed biofilm; $\epsilon_{bf} = 5$, when the pore fraction is equal to 0, an adhered thin layer.

ϵ_{sw} is the dielectric constant of the seawater, $\epsilon_{sw} = 70.2$ at 18°C¹⁰ and $\epsilon_{sw} = 67.4$, at 33°C¹⁰.

v_{sw} is volume fraction of the seawater in the film. The value of $v_{sw} = 50\%$ and 75% is considered in the film as film grows outward of the surface of the alloys. The value of $\epsilon_{sw} = 70.2$ at 18°C¹⁰ will be considered at exposure time of 0, 1, 5, 10, 20, 30, 60, 90 days, from the November to the February season. Furthermore, the value of $\epsilon_{sw} = 67.4$ at 33°C¹⁰ will be considered at an exposure time of 130, 150, 180 days, from the March to May season.

In the present work, dielectric constant (ϵ) of bio-film (Equ.2) has further extended to account for not only the volume fraction of the seawater in the film, the dielectric constant of the seawater at two temperatures 18°C and 33 °C, and the volume fraction of the seawater in the biofilm, but also to take into consideration for the first time the

dielectric constant of corrosion products (ϵ_{cp}), i.e., FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese; a mixture of MnO₂ & Fe₂O₃, Fe₂SO₄, and Ferrochromium FeCr, in the bio-film, and the volume fraction (v_{cp}) of those corrosion products in the bio-film. So Equ.2 becomes;

$$e = (e_{bf} + v_{sw} e_{sw} + \sum v_{cp} \epsilon_{cp}) \text{ ----- (3)}$$

where:

$\sum v_{cp} \epsilon_{cp}$ is the summation of the number of the dielectric constant of the corrosion products (ϵ_{cp}) time the volume fraction of the corrosion products (v_{cp}). By substituting for the value of e in Equ. 3 into Equ.1, and solving for the thickness of the biofilm (L), the value of L becomes:

$$L = \{(e_{bf} + v_{sw} e_{sw} + \sum v_{cp} \epsilon_{cp}) / (\epsilon_0 A)\} / Cdl \text{ ----- (4)}$$

Therefore, It is expected that the corrosion products in the formed biofilm of the UNS 1020 carbon steel samples will be FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese; a mixture of MnO₂ & Fe₂O₃, and Fe₂SO₄ based on the composition of the steel samples; 0.18-.23% C, 0.3-0.6% Mn, and balanced of Fe. Likewise, It is expected that the corrosion products in the formed biofilm of the UNS S304 stainless steel samples will be Ferromanganese (a mixture of MnO₂ & Fe₂O₃) and Ferrochromium; FeCr based on the composition of the stainless steel samples; 18-20% Cr, 8-12% Ni, 2% Mn, 1% Si, 0.08% C, and balance of Fe. The values of

ϵ_{cp} of the corrosion products at room temperature can be obtained from the literature: ϵ_{cp} of FeO=14.2; ϵ_{cp} of Fe₂O₃=14.2; ϵ_{cp} of Fe₃O₄=14.2; ϵ_{cp} of FeOOH=14.2; ϵ_{cp} of Fe₂SO₄=14.2; an average value of ϵ_{cp} of a mixture of the oxides MnO₂ & Fe₂O₃ (Ferromanganese)= 5.1; and an average value of ϵ_{cp} of FeCr: Ferrochromium= 1.65.

In addition, the value of the volume fraction (v_{cp}) of corrosion products in the biofilm at UNS 1020 carbon steel samples is assumed around 3% and 5% for an accumulation of FeO, Fe₂O₃, Fe₃O₄, FeOOH & Fe₂SO₄ with respect to the volume fraction of seawater (v_{sw}) of 50% and 75%, respectively. In addition, the value of the volume fraction (v_{cp}) of corrosion products in the biofilm at UNS S304 stainless steel samples is assumed 1% and 3% for each of Ferromanganese; a mixture of MnO₂ & Fe₂O₃ and FeCr with respect to the volume fraction of seawater (v_{sw}) of 50% and 75%, respectively.

Consequently, Equ.4 describes the relationship between the double-layer capacitance of the biofilm (from EIS) and the thickness of the biofilm which accounts for the volume fraction of the seawater in the film, the dielectric constant of the seawater at two temperatures 18°C and 33°C, the volume fraction of the seawater in the biofilm, the dielectric constant of corrosion products (ϵ_{cp}), i.e., FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese; a mixture of MnO₂ & Fe₂O₃, Fe₂SO₄, and Ferrochromium FeCr, in the biofilm, and the volume fraction (v_{cp}) of those corrosion products in the biofilm.