



## The Effect of surface treatments on the electrochemical behavior of Titanium alloy in seawater by electrochemical impedance spectroscopy (EIS)

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Received 25 Jan 2015, Revised 12 May 2015, Accepted 12 May 2015

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### Abstract

Seawater contains many minerals, dissolved gases, including oxygen O<sub>2</sub>, bacteria and other united or multi-cellular organisms, suspended solids and sediments that sometimes impart high turbidity. Chemical and biological characteristics of seawater make it a particularly aggressive environment with respect to many materials in particular titanium. Physico-chemical interactions between a metal material and its environment can lead to corrosion of material. Deterioration of metal due to microbial activity is called biocorrosion or corrosion induced by microorganisms (CIM). Because of its economic and environmental importance, CIM has been extensively over past five decades and several models studies have been proposed to explain the mechanisms biocorrosion observed. Many sectors are affected by CIM. Mention may be made example: maritime port facilities, plant thermal (heat exchangers). Biofilm formation on walls of conduits considerably reduces heat transfer, this is particularly important in case of heat exchanger tubes. We noted that treatment of surface electrode moves corrosion potential to more cathodic values. And more, the short stay of titanium in natural seawater, corrosion potential varies around -250 mV/Ag/AgCl, and then it reaches less cathodic values to longer residence time. Electrochemical impedance measurements showed the presence of one loop relative to the capacitive charge transfer phenomenon of metal/passive layer.

**Keywords:** Natural seawater, Titanium, OCP, Electrochemical impedance spectroscopy.

### 1. Introduction

Biofilms are generally composed of microbial cells and their products (extracellular polymers), which confer to them a very porous structure, in agreement with the amount of water contained (> 95%) [1, 2]. The distribution of microorganisms is not uniform. In multi-species biofilms, highly complex structures containing voids, connecting channels between these voids, and microbial clusters or layers were predominantly found [3]. With respect to mass transport, biofilms behave as inert porous layers.

In the marine environment, microbial communities adhere to surfaces (materials, rochets ... etc) grow and reproduce; this is the initial phase of biofilm formation. To survive and protect themselves from external aggressions, bacteria produce exopolysaccharides (EPS). This polymer lattice, imprisoning microorganisms, particulate matter and debris gave birth to concept of biofilm [4, 5]. The negative effects of biofilms from use of seawater on materials and equipment are numerous: hydrodynamic screen, decrease in heat transfer; for example thermal conductivity of a biofilm (0.6 to 0.7 W/mK) is close to that of water but substantially lower than that of metal alloys (stainless steel 16.30 W/mK). Thus, a film having a thickness of 55 microns decreases to 20% yield of a thermal power plant.

Biocorrosion, also called bacterial corrosion, includes all phenomena of corrosion in which bacteria directly act or through their metabolism playing a key role, either by accelerating a process already established, either by creating favorable conditions for its establishment. Presence of biofilm is likely to change any of cathode or anode reactions, and there by accelerate material corrosion. Bacterial action is here purely electrochemical, and

does not correspond to a new form of corrosion but change in kinetics of an existing corrosion where appearance of corrosion by changing operating conditions system [6-8].

The objective of this work is to study the electrochemical behavior of titanium as metal most often encountered in heat exchanger circuit desalination in natural seawater.

We selected titanium as often used as reference material regarding the resistance to corrosion in natural seawater (stress corrosion, crevice corrosion, galvanic corrosion). This behavior is attributed to the presence of a stable and protecting the surface of the metal oxide film (mainly  $\text{TiO}_2$ ).

## 2. Materials and methods

The electrochemical measurements were carried using a potentiostat (AUTOLAB) piloted by Novalab software. Tests are produced in a cell by double wall glass, volume 1000 ml, equipped with three-electrodes. Reference electrode in silver chloride Ag/AgCl, contre electrode is in platinum and working electrode is in titanium its active surface is  $1.0 \text{ cm}^2$ . Titanium that we use as the substrate of the working electrode is titanium grade 2 and has a purity of 99.2%. The 0.8% is mainly due to the Fe and C (Table1) [9 -10].

We studied three different surface states:

- a. Brut.
- b. Mechanical polishing: using abrasive papers of silicon carbide (SiC) 1200, by means of a polisher electric MINITECK 233 mark.
- c. Chemical treatment: in addition to mechanical polishing, we placed the titanium electrode in acetone for 10 minutes and subsequently in ethyl alcohol at 40% for 15 minutes.
- d. Electrochemical polishing: immersion of the titanium electrode in deionized water in order to polarize -2500 mV / Ag/AgCl, for 10 minutes, creating large  $\text{H}_2$  evolution and make titanium surface shinier [11-13].

The natural seawater used (of period Mars-June 2014) was taken at the pump station (before the desalination circuit). It is characterized by a hardness Total hardness TH 706 °F, Calcium hardness  $\text{TH}_{\text{Ca}^{2+}}$  301 °F, Magnesium hardness  $\text{TH}_{\text{Mg}^{2+}}$  405 °F, Alkalimetric titre TA 0.85 °F, Total alkalinity TAC 11.5 °F and a pH 7.79.

**Table 1:** Composition of grade 2 titanium electrodes

Atom	Percentage (%)
Fe	0.3
C	0.1
O	0.25
H	0.015
N	0.03
...	...

## 3. Results and discussion

### 3.1. Mesure of corrosion potential

We carried four tests on different surface states in order to determine corrosion potential of titanium in contact with seawater (Fig. 1).

The evolution of  $E_{\text{corr}}$  in brute electrode increases with the immersion time and then stabilizen after 20 minutes at  $-0.216 \text{ V/Ag/AgCl}$ . This reflects rapid dissolution followed by formation of a passive layer on titanium surface. We note that  $E_{\text{corr}}$  corresponding to this surface state is less cathodic relative to the other three electrodes: polished, chemically treated and treated electrochemically.

Regarding the chemical and mechanical polishing,  $E_{\text{corr}}$  on these electrodes evolve in the same way and stabilized at values close  $-0.384$  and  $-0.367 \text{ V/Ag/AgCl}$  that conform from that of literature [14]. By against, the electrode was treated electrochemically allowed us to obtain a potential which change toward more cathodic values; stabilizing to  $-0.578 \text{ V/Ag/AgCl}$ .

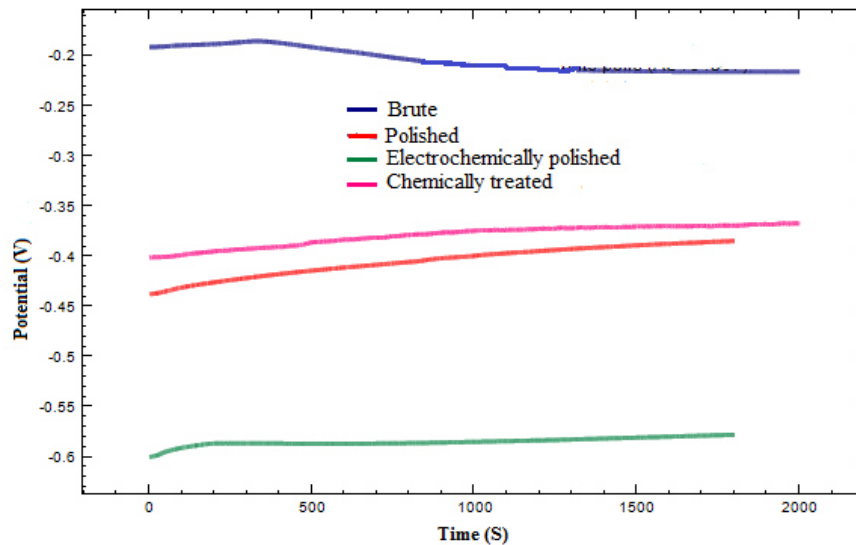
### 3.2. Electrochemical impedance spectroscopy (EIS)

To carry out the measures by EIS, the samples in question were initially immersed for a moment in the solution of natural seawater to stabilize corrosion potential  $E_0$  the impedance diagrams were then plotted to that potential. Electrochemical impedance diagrams of titanium at different surface states immersed in natural

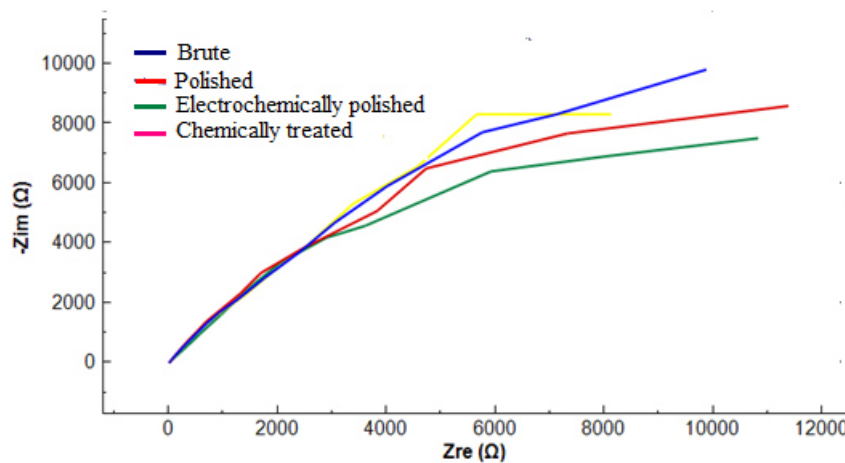
seawater at 25 ° C are shown in figure 2. Signals are applied to the system with amplitude of 10 mV, with scanning frequency of 100 kHz to 1 mHz.

**Table 2:** Evolution of  $E_{corr}$  of titanium in natural seawater depending on surface state of electrode

Surface state of electrode	$E_{corr}$ (V/Ag/AgCl)
Brute	-0.216
Polished	-0.384
Chemically treated	-0.367
Electrochemically polished	-0.578



**Figure 1:**  $E_{corr}$  for different states of titanium surface immersed in natural seawater versus time.

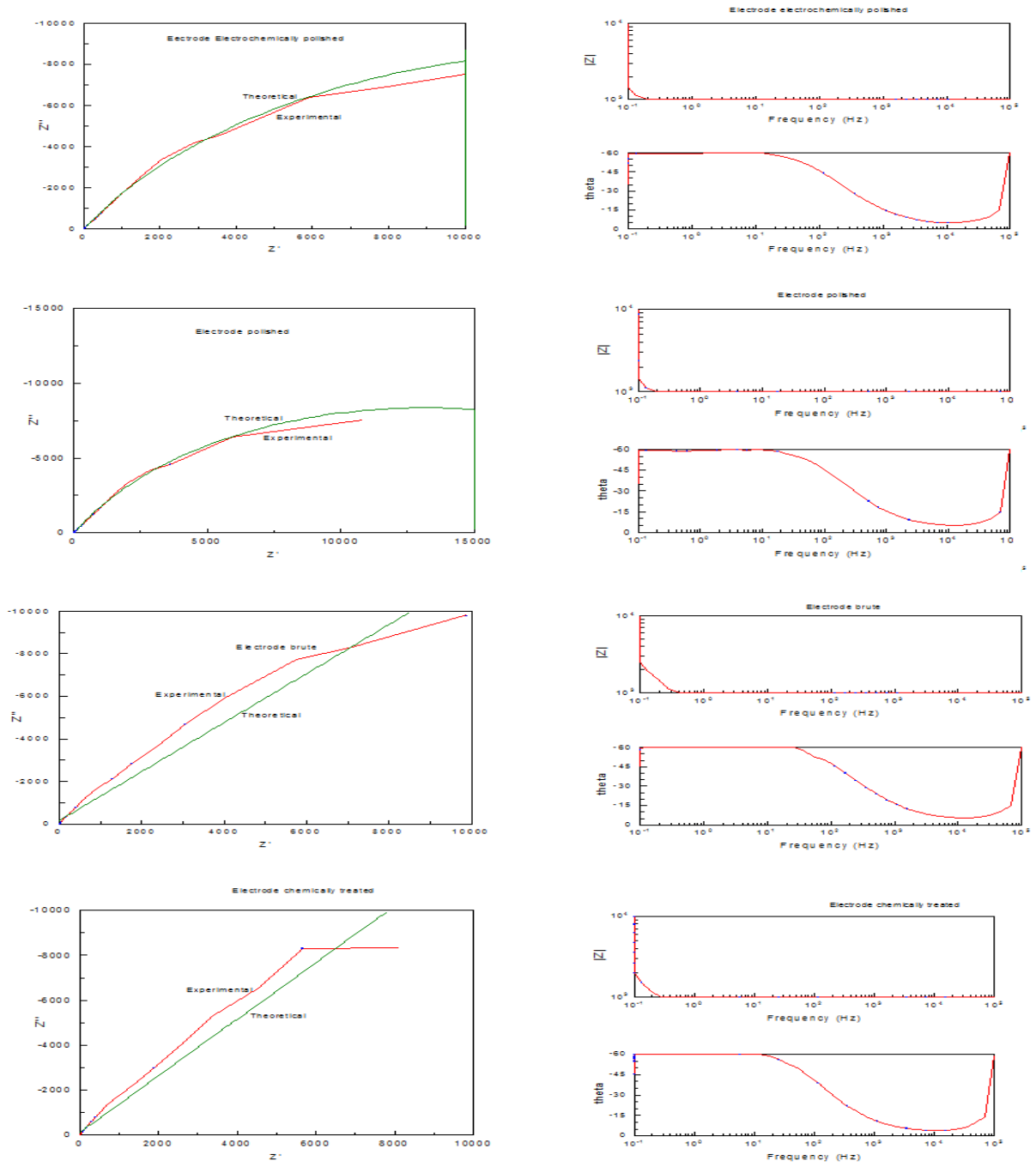


**Figure 2.** EIS Nyquist diagrams of various surface of titanium.

Nyquist diagrams for the four surface states show the presence of capacitive loop relative to charge transfer phenomenon of interface metal / passive layer.

We found that high-frequency, high frequency resistance  $R_{HF}$  on brute titanium is higher relative to such of the three types of samples (polished, chemically treated and electrochemically polished). Similarly, the polarization resistance  $R_p$  relating to state of brute surface is superior to those of the other surfaces. It is worth taken into account that the surface of electrode brute has made reinforce formation of a layer of corrosion products of titanium.

Figure 3 shows the conformity of the impedance experimental curve with the simulated. We note that the two curves are superposed and therefore we can conclude that the electrical equivalent circuit that we have chosen is the Titanium / solution interface.



**Figure 3.** Conformity of EIS diagrams of experimental and theoretical curves of Titanium/NSW interfaces.

The equivalent circuit and electrochemical parameters measured for this system are shown together in figure 4 and table 3. In fact, the immersion of metal electrode in the solution leads to a pure activation kinetics, but not limited by the phenomenon of mass transport and the total impedance  $Z$  can be written [15]:

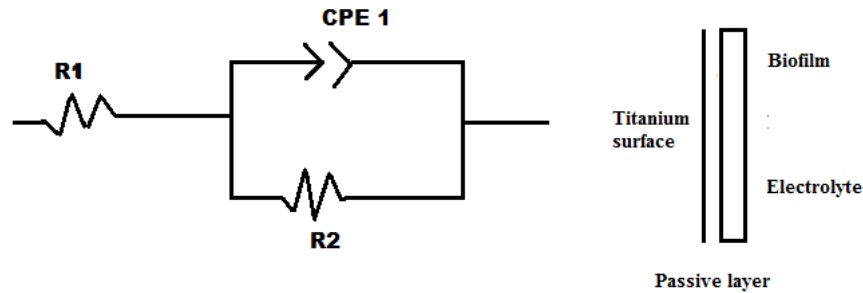
$$Z = R_e + \frac{R_t}{1 + j\omega C_{dc} R_t}$$

With  $R_e$ : electrolyte resistance,  $R_t$ : charge transfer resistance and  $C_{dc}$ : double layer capacitance.

It is an evolution of blocking electrode model where resistance  $R_t$  reflecting charge transfer is connected in parallel with double layer capacitance  $C_{dc}$  [16].

**Table 3.** Electrochemical parameters of surface electrode electrochemically polished immersed in NSW.

Electrochemical parameter	Value	Error %
$R_s$ ( $\Omega$ )	8.832	9.128
CPE- T	0.00115	6.7745
CPE- P	0.72692	2.7607
$R_p$ ( $\Omega$ )	10155	19.454



**Figure 4.** Equivalent circuit for the case of an electrode immersed without mass transport phenomenon.

### Conclusion

The behavior of brute Titanium in natural seawater showed that  $E_{corr}$  is about  $-0.216$  V/ Ag/AgCl, and change to more cathodic value  $-0.578$  V/Ag/AgCl for the electrode treated electrochemically.

The results of electrochemical impedance spectroscopy confirm that the polarization resistance  $R_p$  relating to state of brute surface is superior to those of the other surfaces.

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(2015) ; <http://www.jmaterenvironsci.com>