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Electrochemical treatments using tin oxide anode to prevent biofouling

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ABSTRACT

Organic matter and living micro-organisms are responsible for surface modifications of any materials immersed in seawater. This phenomenon, called biofouling, has many detrimental effects and has to be prevented. Electrochemistry could be a very efficient tool for biofouling prevention in two ways, either by local biocide production through seawater electrolysis or by immobilizing electrogenerated biocides. In this paper, both strategies will be developed and illustrated in the particular case of tin dioxide as anode material. Chloride and bromide ions present in seawater are efficiently oxidized at antimony doped tin dioxide to form biocidal hypohalogenous acids, namely HOCl and HOBr. Underwater optical instruments having glass window coated with a transparent tin dioxide layer can be effectively protected against biofouling without environmental damages because hypohalogenous acids are produced at a low level and on the window itself. Another possibility explored in this paper is to perform a pre-treatment of the surface to be protected. It consists in seawater electrolysis in the presence of organic macromolecules, as for instance bovine serum albumin. In these conditions, chlorinated and brominated organic deposit is formed on the tin oxide surface as proved by EDX and XPS analyses. By testing adhesion and growth of *Escherichia coli* bacteria, it was shown that this deposit possesses biocidal property. Actually, this property is due to the presence of chloramine and bromamine groups.

1. Introduction

Any surface immersed in seawater tends to be covered by organic matter such as proteins and by living micro-organisms as bacteria within a few hours. This initial stage is followed by the development of a biofilm, a multi step process involving 3D cellular engineering with production of exopolymers and formation of an extracellular matrix. As a consequence, the biofilm thickness can reach a few micrometers or more within a few days, depending on the environmental conditions. Such a surface modification of submerged materials is called biofouling and is of great economical importance to several industries.

To fight against biofouling, it is generally admitted that it is necessary to avoid the first steps of its formation, *i.e.* macromolecule adsorption or microfouling. Adsorption can be avoided or at least limited by modifying surface properties, for instance by means of a hydrophobic coating. Microfouling can be hampered through the action of a biocide. To achieve this goal, different strategies are considered [1]. The first one is based on the release of a biocide from a coating. The oldest example is that of tri-butyl tin (TBT) mixed to marine paints. However, it is presently prohibited because of its high toxicity leading to environmental damages. Today, TBT is notably replaced by some metal cations, Cu^{2+} and Ag^{+}, produced by simple release or by anodic dissolution of the corresponding metal. Another way is to use hypohalogenous acids, namely hypochlorous (HOCl) or hypobromous (HOBr) acids. They can be generated either chemically by the slow dissolution of tablets (salt) or by the electrochemical oxidation of chloride or bromide ions. It is interesting to notice that both anions are present in seawater but at very different concentrations: 0.55 M for chloride and seven hundred times lower for bromide (8.10^{-4} M). Chloride and bromide oxidation leads to chlorine (Cl_2) and bromine (Br_2) production. It is well known that in water Cl_2 and Br_2 disproportionate into HOCl (at pH > 2.5) and HOBr (at pH > 5.7), respectively, as deduced from the potential-pH diagrams depicted in Fig. 1. Both acids are weak acid compounds. The reaction scheme is the following, X being Cl or Br:

$$2X^- \rightarrow X_2 + 2e^- \quad (1)$$

$$X_2 + H_2O \leftrightarrows HOX + H^+ + X^- \quad (2)$$

$$HOX \leftrightarrows OX^- + H^+ \quad (3)$$

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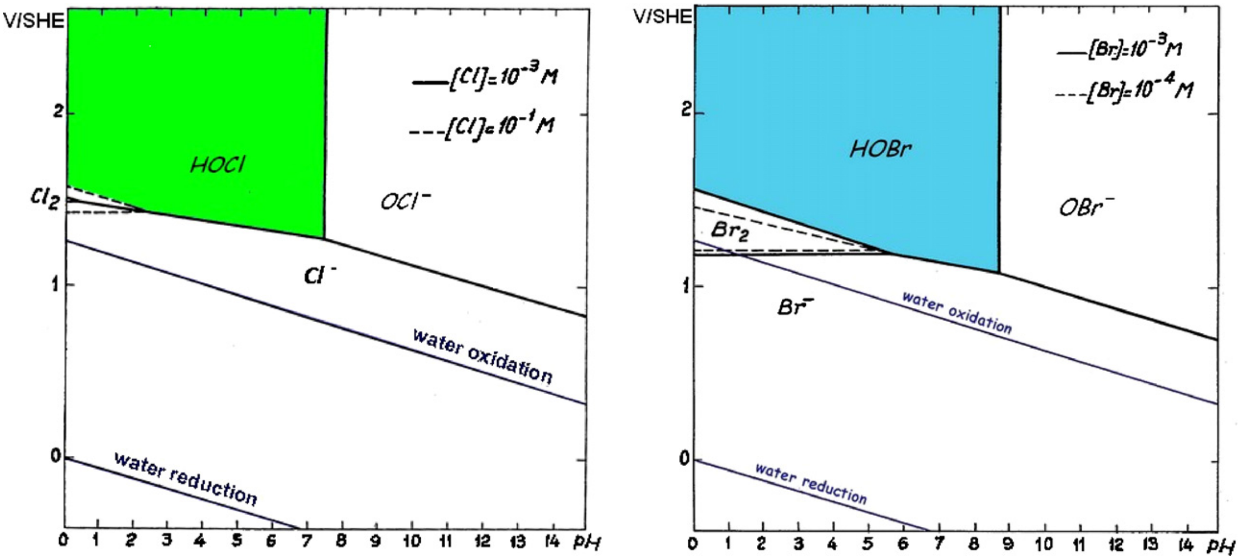

Fig. 1. Potential-pH diagrams (Pourbaix diagrams) of chlorine and bromine species at the salt concentration levels encountered in seawater.

with acid dissociation constant (pKa) of 7.5 and 8.7 for the $HOCl/OCl^-$ and $HOBr/OBr^-$ couples, respectively. The acidic forms are known to be more active against bacteria than the salt ones. The biocidal activity arises from the oxidizing power of Cl(+I) and Br(+I). Fig. 2 shows the pH dependence of the concentrations of these species in aqueous solution. The pH of seawater being close to 8, it can be concluded that in this medium the acid form is dominant for the hypobromous acid/hypobromite couple whereas the ionic form is dominant for the hypochlorous acid/hypochlorite couple. Then in seawater, bromine is more efficient than chlorine with respect to their biocidal effect. Potential-pH diagrams for the chlorine and bromine systems depicted in Fig. 1 points out the oxidizing power of HOCl with respect to bromide ions. As a consequence, HOCl reacts rapidly with bromide ions to form hypobromous acid [2–4]:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (4)$$

Therefore, in solution, as long as the concentration of HOCl added or electrogenerated remains lower than the bromide concentration, only HOBr is present in the medium.

In practice, the electrogeneration of HOCl and HOBr is currently employed to provide an active protection against marine biofouling by local production of oxidants at the vicinity or (directly on) at the very surface of the device to be kept clean. The latter method has been particularly developed in our lab in collaboration with IFREMER. In the case of optical windows, a transparent electrode has to be deposited in front of the device. Antimony doped tin dioxide (ATO) has been found to be the best candidate to serve as a transparent and stable anode to oxidise chlorides and bromides present in seawater [5]. The advantages of such a configuration are a low energy consumption and a very limited production of biocidal compounds, associated with a low environmental impact. This process will be presented in the first part of this paper.

A new route, currently under development, consists of immobilizing electrochemically generated biocides. Recently, it was established that HOCl is able to react with proteins adsorbed at an ATO electrode [6,7]. Using bovine serum albumin (BSA) as a model protein, chlorination was found to be very effective during electrolysis of a BSA-containing aqueous chloride solution [8]. In this paper, it will be shown that bromination and chlorination of BSA similarly also occurs during electrolysis of BSA-containing seawater. Furthermore, during electrolysis, aggregation of proteins takes place via intermolecular cross-linking bonds. The so-prepared organic film contains bromamine and chloramine groups with antibacterial properties, as it will be shown in the second part of this paper.

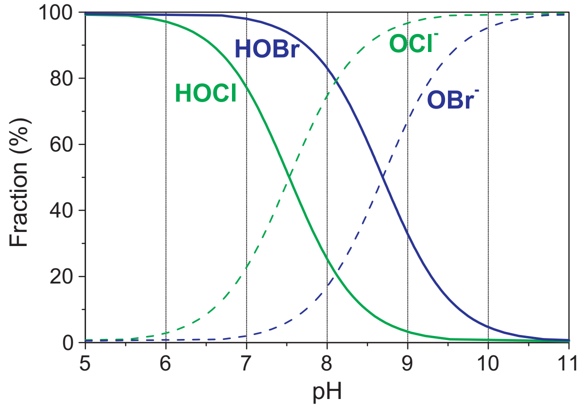

Fig. 2. Percentages of concentrations of the species corresponding to the dissociation equilibrium of the $HOCl/OCl^-$ (pKa = 7.5) and $HOBr/OBr^-$ (pKa = 8.7) systems.

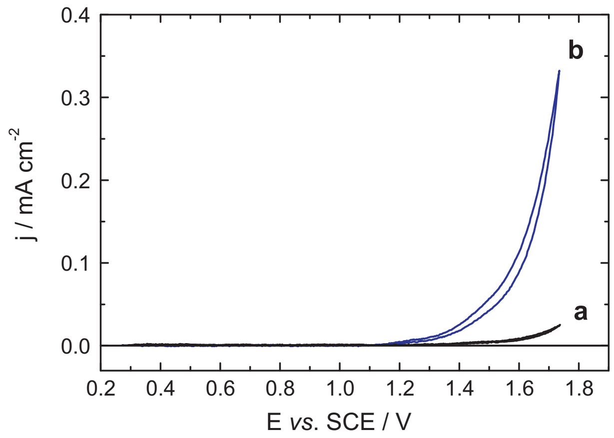

Fig. 3. Comparison of the electrochemical behaviour of (a) fluorine-doped (FTO) and (b) antimony-doped (ATO) tin oxide films in seawater. Potential scan rate: 1 mV s^{-1}.