Electrochemical Prevention of Biofouling Using Pt/IrO₂-Coated Titanium Electrode

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Pt/IrO₂-coated titanium was developed as the electrode for prevention of biofouling. When a potential of 0.9 V vs. Ag/AgCl was applied to the Pt/IrO₂-coated titanium electrode in seawater, 3% of marine bacteria attached to the electrode survived after 60 min. Almost no change in pH and chlorine concentration was observed after applying 0.9 V vs. Ag/AgCl in the bulk seawater. When alternating potentials of 0.9 V vs. Ag/AgCl and cycling potentials of $-0.3 \sim -0.9$ V vs. Ag/AgCl were applied, prevention of biofouling was successfully achieved in the field experiment. Also, cleaning of electrode surface was achieved electrochemically by applying the potential of 1.0 V vs. Ag/AgCl.

Key Words : Pt/IrO₂-coated Titanium Electrode, Electrochemical Method, Antifouling

1 Introduction

Marine biofouling is commonplace in immersed marine structures including cooling systems of seawater cooled power plants and heat exchangers. The efficiency of heat exchangers can be seriously decreased by formation of biofilm and attachment of higher organisms, such as mussels. Also, the speed of ships can be significantly reduced even by biofilm.^{1, 2)} The use of paints containing copper and tributyl tin compounds had been abundant due to their residual toxicities. Development of effective anti-fouling method that does not produce residual toxicity has been studied for long time however the problem remains unsolved. Investigations into the beginning of the fouling process revealed that the attachment of microorganisms observed during the first hours of operation.^{3, 4)} Biofilms are important for subsequent attachment and development of invertebrate larvae.^{5, 6)}

We have reported the electrochemical method for inactivation of microorganisms.⁷⁾ Desorption of electrochemically inactivated microbes was also achieved by applying negative potentials.⁸⁾ This electrochemical method has been applied to antifouling of seawater cooling pipes and in fishing nets using rubber^{9, 10)} and titanium nitride¹¹⁾ electrodes. However, more stable electrode materials for practical use were desired.

In the present study, Pt/IrO₂-coated titanium substrate was developed and applied to the prevention of biofouling in the field experiment. Electrochemical cleaning of the electrode surface was investigated in case of power failure.

2 Materials and Methods

2.1 Preparation of Pt/IrO₂-coated titanium electrode

A titanium substrate was etched to remove the airborne oxide on the surface, and then a thin layer of titanium hydride was formed on the titanium substrate to protect it from oxidizing during water rinsing and transfer to the plating bath. Dispersed platinum particles were coated on the surface by the electroplating bath. The titanium hydride was decomposed and a thin titanium oxide layer was formed on the titanium substrate by heating in the air. The oxide valve metals, iridium and other metals were loaded on the platinized titanium substrate with thermal decomposition of the metal chlorides, such as TaCl₅ and H₂IrCl₆, dissolved in an alcohol solution.

2.2 Electrochemical inactivation of attached bacteria

Electrochemical inactivation of marine bacteria, *V. alginolyticus* ATCC17749 was investigated as described previously.¹¹⁾ The electrode system consisted of Pt/IrO₂-coated titanium, platinum wire, and silver/silver chloride electrode as the working, counter, and reference electrode, respectively.

2.3 Field experiment

Field experiment on prevention of biofouling on Pt/IrO₂-coated titanium electrode was carried out in Kyushu. The electrode system consisted of Pt/IrO₂-coated titanium electrode, iron plate, and silver/silver chloride electrode as the working, counter, and reference electrode, respectively. Potential of 0.9 V vs. Ag/AgCl for 180 min and $-0.3 \sim -0.9$ V vs. Ag/AgCl (potential varied in 2 min cycle from -0.3 V to -0.9 V) for 20 min was ap-

plied. The size of the electrode was 140 mm × 300 mm with the thickness of 0.5 mm. Potential was controlled using power control unit containing interface board and amplifier board. The system for electrochemical prevention of biofouling consisted of three unit. (1) Electrochemical reaction monitoring unit for scheduled potential control and error monitoring, (2) power control unit for voltage output control and multi-plate control, (3) remote control and monitoring unit for data transmission and remote programming.

3 Results and Discussion

3.1 Electrolysis of seawater using Pt/IrO₂-coated titanium electrode

Figure 1 shows the effect of applying potential on change in pH and chlorine concentration in seawater using Pt/IrO₂-coated titanium electrode. Electrolytic generation of chlorine was measured using a chlorine electrode (detection limit of chlorine, 0.02 ppm; model 97-70, Orion Research Inc., Boston, MA). Almost no change in pH and chlorine concentration was observed when potentials in the range of 0~0.9 V vs. Ag/AgCl were applied for 60 min to a Pt/IrO₂-coated titanium electrode in seawater. When potentials of above 1.0 V vs. Ag/AgCl were applied, slight decrease in pH and increase in chlorine concentration was observed. It was confirmed that application of the potentials below 0.9 V vs. Ag/AgCl could minimize the generation of chlorine and change in pH by electrolysis of seawater.

3.2 Electrochemical inactivation of marine bacteria using Pt/IrO₂-coated titanium electrode

The effect of applying constant potentials on survival ratio of marine bacterium, *V. alginolyticus* was investigated. The survival ratio decreased gradually above 0.7 V vs. Ag/AgCl. The survival ratio after applying 0.9 V vs. Ag/AgCl for 60 min was 3%. Also, time course of survival ratio of marine bacteria adsorbed on Pt/IrO₂ coated titanium electrode was measured at 0.9 V vs. Ag/AgCl. The survival ratio decreased sharply and was 70%, 25%, and 10% after 1 min, 5 min, and 15 min, respectively. It was shown that it is possible to kill 95% of adsorbed ma-

rine bacteria by applying 0.9 V vs. Ag/AgCl for 30 min.

3.3 Field experiments

Figure 2 shows the photograph of the electrodes immersed in Matsuura bay (Nagasaki, Kyushu, Japan) for 1 year. When alternating potential of 0.9 V vs. Ag/AgCl (180 min) and cycle potentials between -0.3~-0.9 V vs. Ag/AgCl (20 min) was applied, attachment of macro-organisms were not observed. In contrast, the concrete surface immersed for same period was covered with a lot of organisms. It was shown that attachment of macroorganisms was prevented electrochemically.

3.4 Elimination of microorganisms by the electrochemically generated chlorine at low concentration

In case of power failure or the trouble in application of the potentials, elimination of attached microbes was investigated by applying higher potentials. Detachment of marine bacteria was investigated. The number of cells on the electrode surface decreased slightly after applying 0.9 V vs. Ag/AgCl for 60 min compared to no applied potential. In contrast, when 1.0 V vs. Ag/AgCl was applied for 10 min after applying 0.9 V vs. Ag/AgCl for 60 min, almost 70% of attached cells were detached. The number of detached cells increased slightly with applying higher potential. It was shown that cleaning of electrode surface is possible by applying the potentials of 1.0 V vs. Ag/AgCl. Detachment of cells at these potentials might be due to the generation of chlorine (chlorine concentration was 1.29 ppm after electrolysis for 60 min at 1.0 V vs. Ag/AgCl) or the generation of radicals at low concentrations. This process can be used for the elimination of the microorganisms in case of power failure or the trouble in application of the potentials.

In conclusion, electrochemical prevention of biofouling was achieved using Pt/IrO₂-coated titanium as the electrode. This material was electrochemically active and chemically stable. Electrochemical prevention of biofouling was successfully achieved in the field experiment by applying potentials of 0.9 V vs. Ag/AgCl (180 min) and cycled potentials between -0.3~-0.9 V vs. Ag/AgCl

Fig. 1 Effect of applied potential on chlorine concentration (■) and pH (●) of seawater after electrolysis using Pt/IrO₂ coated titanium electrode. Constant potentials were applied for 60 min in 30 mL of seawater. Electrode area was 4.0 cm².

Fig. 2 Field experiment of electrochemical prevention of biofouling using Pt/IrO₂ coated titanium electrode. Experiment period was from November 2001 to November 2002 in Matsuura bay. Left: Pt/IrO₂ coated titanium electrode with potential application (0.9 V vs. Ag/AgCl, 180 min; -0.3~-0.9 V vs. Ag/AgCl, 20 min). Right: Concrete surface immersed for same period.

(20 min), alternatively. Cleaning of electrode surface could be carried out electrochemically by applying the potential of 1.0 V vs. Ag/AgCl.

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