Int. J. Electrochem. Sci., 9 **(2014)** 5712 - 5721

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

The Performance of Zinc Sacrificial Anode in Simulating Marine Fouling Environment

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Received: 6 May 2014 / *Accepted:* 11 June 2014 / *Published:* 16 July 2014

Zinc sacrificial anodes with excellent merits are widely used in the marine cathodic protection of steel structures being suffered marine biofoulings. It is important to study the property of zinc anodes in marine fouling environment. However, it is very difficult to study the effect of macro-fouling on the corrosion of zinc anodes in the real ocean environment, and it is also almost impossible for the people to do this by culturing the macro-fouling in lab. In this work, the corrosion behaviour and performance of zinc anode in simulated marine fouling environment was discussed using electrochemical impedance spectroscopy, self-discharge, scanning electron microscopy and simulating methods. The results indicated that marine foulings on the surface had some protective effect on the anti-corrosion performance of anodes in the early attachment stage of fouling organisms. The corrosion rate of zinc anode was decreased sharply at the first attachment stage of the fouling organisms. The zinc sacrificial anode still possesses high current efficiency though covered with biofoulings, but its potential varies dramatically in simulated biofouling environment. Surface analysis revealed that localised corrosion occurred on the surface of zinc sacrificial anodes coated with the powder of barnacles and oysters. The experiment result shows that it is very useful and simple for us to study the effect of macro-fouling on the corrosion of zinc anodes in lab by simulating the coating of the powder of barnacles and oysters, which is consistent with the actual marine results.

Keywords: zinc sacrificial anode; marine biofoulings; macro-fouling; self-discharge; localised corrosion

1. INTRODUCTION

In the new century, ocean research has become one of the major world indices to measure the development of science and technology. Seawater corrosion and biofouling are two natural process existing at the metal-water interface simultaneously, which are important factors endangering the safe operation of offshore facilities. The low alloy steel is one of the most important metals used in marine structures, and has been in service for many years in marine applications. Cathodic protection (CP) is a major technique of improving the durability of marine applications, and it is required for long term anti-corrosion protection of the subsea steel structures [1].

In recent years, zinc alloys have been preferentially selected as sacrificial anode materials for CP of steel due to their high current efficiency, low specific weight and low cost [2]. Many studies investigated the corrosion behavior of zinc in SRB-containing marine environment [3] and simulated acid environments [4-5].

Few relevant studies about the effect of macro-fouling organism on sacrificial anodes have yet been reported. Several platforms in Bohai oilfield were investigated and found that the underwater steel structures and sacrificial anodes were basically covered by macro-fouling organism [6]. In fact, the macro-fouling organism has an important effect on the performance of anodes. With the quick growth of fouling organisms, the dissolution rate of sacrificial anodes is gradually reduced, and the macro-fouling organisms adhering seriously on the anodes may cause anode ultimate failing [7].

Because of wide distribution and high quantity, calcareous plate barnacles ever aroused people's attention in the early time. However , very few people engaged in this specialized research considering its hard difficulty and long cycle. A detailed corrosive life activities research of barnacles on stainless steel was carried out, which showed that the decomposition of organic matter in dead shell could cause acidification and crevice corrosion [8]. Ma studied the corrosion influence of attached barnacles on the metal through the observation in the actual Qingdao marine environment and proposed the barnacles flowering corrosion mechanism of localized corrosion. He thought that micro-environment of localized corrosion was caused by self-catalytic effect, secretion and death of biofouling, which could reduce the pH value up to 3 [6]. As we all know，biofouling corrosion is an important factor exsiting on the anode，similar to structures and vessels. It is necessary to study the corrosion mechanisms of macro-organisms on anode，especial the barnacles and oyster [9-10].

As we all know, It is difficult to feed oysters and other large fouling in the laboratory, especially simulate the dense fouling layer grew on the surface of actual marine structure, which formed a closed system and inhibited the material exchange between inside and outside. No researches about simulating the macro-organisms adhering layer in laboratory have been reported. But in some other researches, 2% agar was used to form the biofilm with a good similarity [11-12].

In this paper, quantitative powders of barnacles and oysters were added into 2% agar to simulate the closed dense fouling layer on the surface of zinc anode. The samples were studied by using self-discharge experiment, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). This work will be helpful on studying the effect of macro-organisms on sacrificial zinc anodes and controlling macro-fouling corrosion of the sacrificial anodes.

2. EXPERIMENTAL

2.1 Specimen preparation

The zinc anodes used in the experiment are composed of the following (mass ratio): 0.5% Cd, 0.098% Pb, 0.012% Cu, 0.045% Fe, Zn balance. The specimens used to study the EIS performance of zinc sacrificial anode were cut to the size of 10 mm×10 mm×5 mm, ground to 2000 grit, degreased with actone, risnsed with distilled water, and then embedded with an exposed experimental area of 1cm^2. Some samples were cut into 20 mm×18 mm×5 mm as self-discharge specimen, treated according to GB 5776-2005 (China) and abraded with emery papers up to a grit size of 2000# and degreased with ethanol using an ultrasonic bath, then dried in 105 ^{0}C ±2 ^{0}C for 30 min, weighed at a 10^{-4}g accuracy using an electronic analytical balance and stored in a desiccator. 3.6cm^2 of work surface area of self-discharge sample was kept and other surface was sealed with silicone rubber seal. The samples were kept in a silica gel desiccator and sterilised by ultraviolet irradiation for 30 min before the test.

All samples were divided into three kinds of contrastive types, including blank zinc samples(A), zinc samples coated with 2 ml agar(B) and zinc samples coated with 0.1 g mixed powder of barnacles and oysters into 2 ml agar(C). The seawater from Qingdao Jiaozhou Bay was used as the solution for all experiments.

2.2 Current efficiency test

The self-discharge measurement was carried out on the basis of GB/T 17848-1999. The anode specimens were suspended vertically in filtered seawater for a period of 240 h. The constant current density was kept at 1 mA/cm^2. Auxiliary cathodes were made of carbon steel. The areas' ratio of cathode to anode was 60:1. Routine tests are carried out to determine the anode efficiency. The corrosion products were removed ultrasonically in a freshly prepared solution of saturated NH_4OOCCH_3 for 2-3 h. Then the specimens were rinsed with distilled water, dried in warm air and then weighed to determine their mass loss. An analytical balance with a precision of 0.0001 g was used and the specimens were weighed before and after the self-discharge test.

The anodes’ efficiency was calculated as follows:

$$Q=k*(M_2-M_1)/(m_1-m_2) \tag{1}$$

where Q is the actual electric capacity （A.h/kg）; k is a ratio, k=843.3 (A.h/kg）; M_1 and M_2 are the mass of Cu coulometer before and after the discharge test (g); m_1 and m_2 are the mass of anodes before and after the discharge test (g).

$$Q_0=A*X+B*Y+C*Z... \tag{2}$$

$$\eta(\%)=(Q/Q_0)*100\% \tag{3}$$

Where Q_0 is the theory of electric capacity（A.h/kg）; A, B, C are the percentage of anodes’ components (%); X、Y、Z are the theoretical electric capacity of each anodes’ components （A.h/kg）; η is the anodic current efficiency (%).

Three identical anode couples were used in the self-discharge test. The average results and the standard deviation of data were calculated accordingly.

2.3 Electrochemical tests

The electrochemical measurements were carried out using a SI1260 and 1287 Electrochemical Measurement System in a conventional three-electrode cell, with a large platinum foil as the counter electrode and a saturated calomel electrode as the reference electrode. The EIS measurements were carried out over frequencies ranging from 100 kHz to 10 mHz with a 5 mV amplitude signal at OCP. The experimental data were analyzed by the software ZsimpWin [13].

2.4. Surface analysis test

The surfaces of all the kinds of samples that were exposed to seawater were analysed through SEM. All samples were immersed for 2 h in a 5% glutaraldehyde solution and then sequentially dehydrated using 50%, 75% and 100% ethanol–PBS solutions (15 min each). Afterwards, the samples were analysed by SEM to determine their corrosion morphologies.

3. RESULTS AND DISCUSSION

3.1 The result of self-discharge experiment

A high performance sacrificial anode should be characterized with sufficiently negative and stable E_{ocp} and high anodic current efficiency. In addition, the corrosion products on the anode should fall off easily, and the surface of anode should dissolve uniformly [14].So we just judged the performance of zinc anodes adhered by macro-organisms by using these parameters.

The stable OCP, average OCP, actual electric capacity(Q), the theoretical electric capacity (Q_0) and anode current efficiency(%) (calculated by Eqs. (1)–(3)) of zinc sacrificial anodes in the self-discharge test were summarized in Table1. The OCP of all the anode samples were stable enough, between - 0.9000 V with - 0.9900 V. The results showed that Ocp(A)<Ocp(B)<Ocp(C). The OCP became positive when the surface of anode was coated with agar, also coated with powder of barnacles and oysters. It could be concluded that the attached macro-foulings inhibited the transportation of corrosive media (special Cl^- and O_2), which causing protective effect in early stage, so the average OCP became positive gradually too. As time going on, the average OCP varied greatly，especial the zinc samples coated with powder of barnacles and oysters(C) [15-16]. Its maximum offset was 359.22 mV, while the other samples (A and B) were only 1.55 mV and 57.76 mV separately. In this condition, the powder layer of barnacles and oysters must have some actions on the corrosion performance of zinc anodes [17].

Table 1. Potential measurements and current efficiency for specimens

No.	OCP （V）	OCP averange(V)	Q_0 （A.h/kg）	Q （A.h/kg）	η
A	-0.9832	-0.98165	824.5777	795.162	0.9643
B	-0.9398	-0.88204	824.5777	806.966	0.9786
C	-0.9240	-0.56478	824.5777	811.561	0.9842

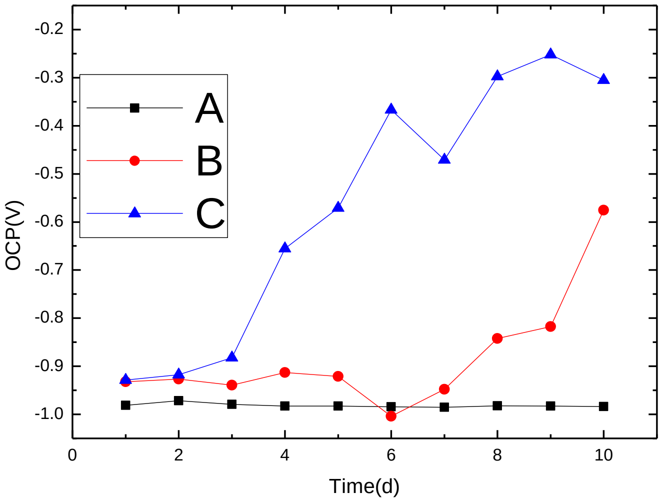


Figure 1. Working potential-time curve for blank zinc samples (A), zinc samples with agar (B), and zinc samples coated with powder of barnacles and oysters (C)

Fig. 1 shows the variations in E_{ocp} of the sacrificial anodes with time. Curves (A) show that the E_{ocp} of blank zinc anodes is stable during the self-discharge experiment time, while the potential value of sample with agar（B） exhibited slight fluctuation from the 1st to 7th day, then increased rapidly. The reason was that the agar formed a barrier to inhibit the substance exchanges to some extent. The zinc specimen coated with powder of barnacles and oysters(C) had steady potential at the beginning, but the potential shifted positively from the 3rd day, which is greater and more obvious than sample coated only with agar (B). From this, we could conclude that the attachment of simulating macro-fouling layer inhibited the material transport, so the formation of macro-fouling layer can reduce the corrosion rate significantly at the early stage of biofouling process. The potential shift increased with the surface attachment increase of fouling community. Based on Fig 1, it can be concluded that zinc anode possesses stable performance without any micro-fouling or macro-fouling attachment. However, when biofouling occurred, it became instable and varied hugely. So it’s very necessary to discuss whether zinc samples could have sufficient cathodic protection when they were being suffered fouling organisms.

Current efficiency is an important indicator of evaluating the performance of the sacrificial anode. The quantity of electric charge increases with the increase of current efficiency. With the increased thickness of coated layer（from A to C）on the surface, current efficiency enlarged slightly.

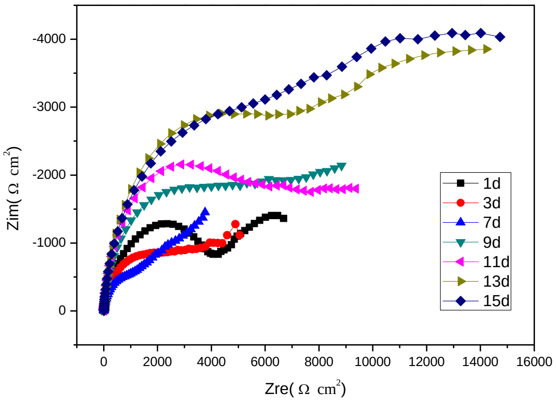
All samples exhibited a high current efficiency higher than 90%. So at the first stage of biofouling process, the attachment of barnacles and oysters could increase the current efficiency of anode.

3.2 EIS measurement

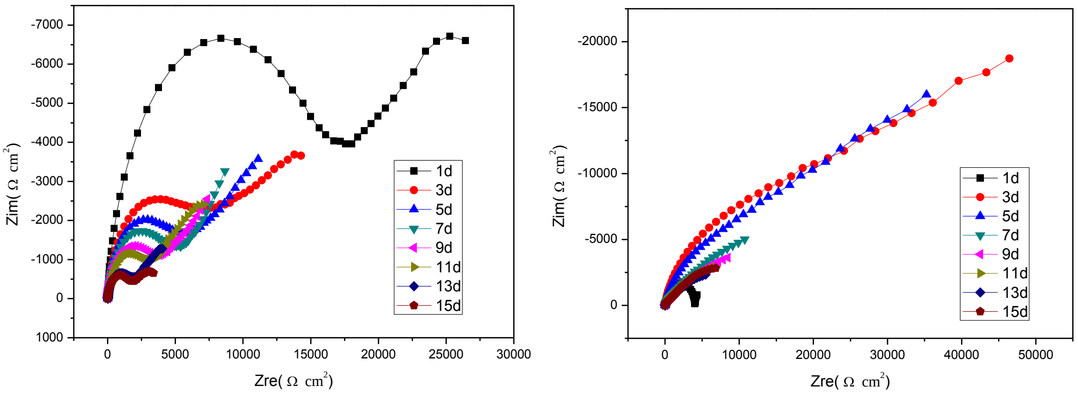
Fig. 2 showed the Nyquist plots of the sacrificial anodes immersed in seawater for 15 days. Two corresponding equivalent circuits (EC) for modelling the EIS data were proposed and depicted in Fig. 3[13]. In Fig.3, Model (a) was used for the 1st day experiment of all the three kinds of samples, whilst Model (b) was used for the experiment data from the 2nd day to the 15th day of all the three kinds of samples. R_s is the solution resistance, Q_f is the capacitance of the surface film. R_f is the resistance of the surface, Z_w is the diffusion impedance, Q_{dl} is the capacitance of the double layer and R_{ct} is the charge transfer resistance. The charge transfer resistance R_{ct} can characterise the corrosion rate of the metal, and the corrosion rate increases when R_{ct} decreases [18]. The changes in the electrochemical parameters of the anodes were partially shown in Table 2-4.

As can be seen from Table 2, the R_{ct} value for the blank zinc sample was reduce gradually from the 1st day to the 3rd day, which was considered as that zinc was an active anode material, when it was immersed in seawater, the surface will soon be dissolved, so the R_{ct} value dropped rapidly[19-21]. From the 3rd day to the 9th day, R_{ct} increased gradually, and the maximum value of the 9th day reached to 6539 $\Omega\cdot cm^2$. The reason was that a protective film of corrosion products was formed on the anodic surface, which could prevent the direct contact between the metal and corrosive media and inhibit the erosion of aggressive media[22]. At the 11th day, R_{ct} decreased obviously. With time going on, the corrosion products became loose and porous gradually, the corrosion rate increased again.

The similar trend could be obtained from Table 3 for the sample coated with agar. Being compared with the blank zinc sample, the sample coated with agar showed a better anti-corrosive feature. However, the different conclusion could be drawn from Table 4 for the sample coated with powders of barnacles and oysters. The R_{ct} value increased obviously from the 1st day to the 3rd day, and then decreased. It became stable from the 11th day.

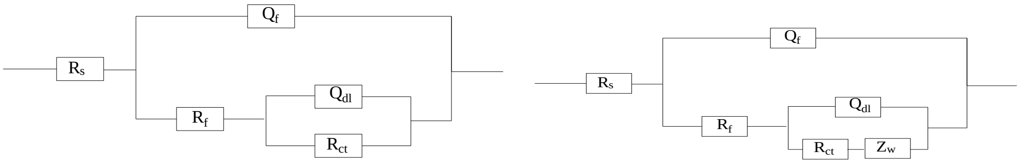


(A)



(B) (C)

Figure 2. Nyquist plots of Zn samples: black (A), coated with agar (B) and coated with powder of barnacles and oysters (C)



(a) (b)

Figure 3. Equivalent circuit for the EIS data.

Table 2. Electrochemical parameters of blank zinc samples

Time	R_s ($\Omega\cdot cm^2$)	Q_f (F/cm^2)	R_f ($\Omega\cdot cm^2$)	Q_{dl} (F/cm^2)	R_{ct} ($\Omega\cdot cm^2$)
1	6.253	$4.197*10^{-6}$	1267	$4.437*10^{-5}$	3590
3	7.094	$2.051*10^{-5}$	1218	0.0003186	2237
7	7.514	$2.7*10^{-5}$	1020	0.0003991	2668
11	7.244	$1.119*10^{-5}$	3965	0.0001883	5922
13	6.66	$1.161*10^{-5}$	4453	$8.56*10^{-5}$	514.1
15	6.113	$1.284*10^{-5}$	3841	$7.658*10^{-5}$	48.48

Table 3. Electrochemical parameters of the zinc samples coated with agar

Time	R_s ($\Omega\cdot cm^2$)	Q_f (F/cm^2)	R_f ($\Omega\cdot cm^2$)	Q_{dl} (F/cm^2)	R_{ct} ($\Omega\cdot cm^2$)
1	10.44	$2.943*10^{-6}$	5003	$3.204*10^{-5}$	21380
3	7.703	$3.788*10^{-6}$	3248	0.0001908	17480

7	8.81	$3.334*10^{-6}$	2786	$8.463*10^{-5}$	3532
11	8.323	$3.301*10^{-6}$	750.3	0.0001606	6739
13	8.173	$5.795*10^{-6}$	1100	0.0004073	3760
15	8.456	$1.372*10^{-5}$	1672	0.0008056	2059

Table 4. Electrochemical parameters of the zinc samples coated with powder of barnacles and oysters

Time	R_s ($\Omega\cdot cm^2$)	Q_f (F/cm^2)	R_f ($\Omega\cdot cm^2$)	Q_{dl} (F/cm^2)	R_{ct} ($\Omega\cdot cm^2$)
1	13.69	$7.308*10^{-6}$	4111	0.0158	27560
3	12.09	$1.096*10^{-5}$	7606	$5.185*10^{-5}$	84750
7	11.87	$3.208*10^{-5}$	955.3	0.0002134	24880
11	11.86	$3.795*10^{-5}$	550	0.0003399	14130
13	11.76	$4.21*10^{-5}$	425.6	0.0004155	12450
15	11.83	$3.402*10^{-5}$	551.7	0.0003334	14880

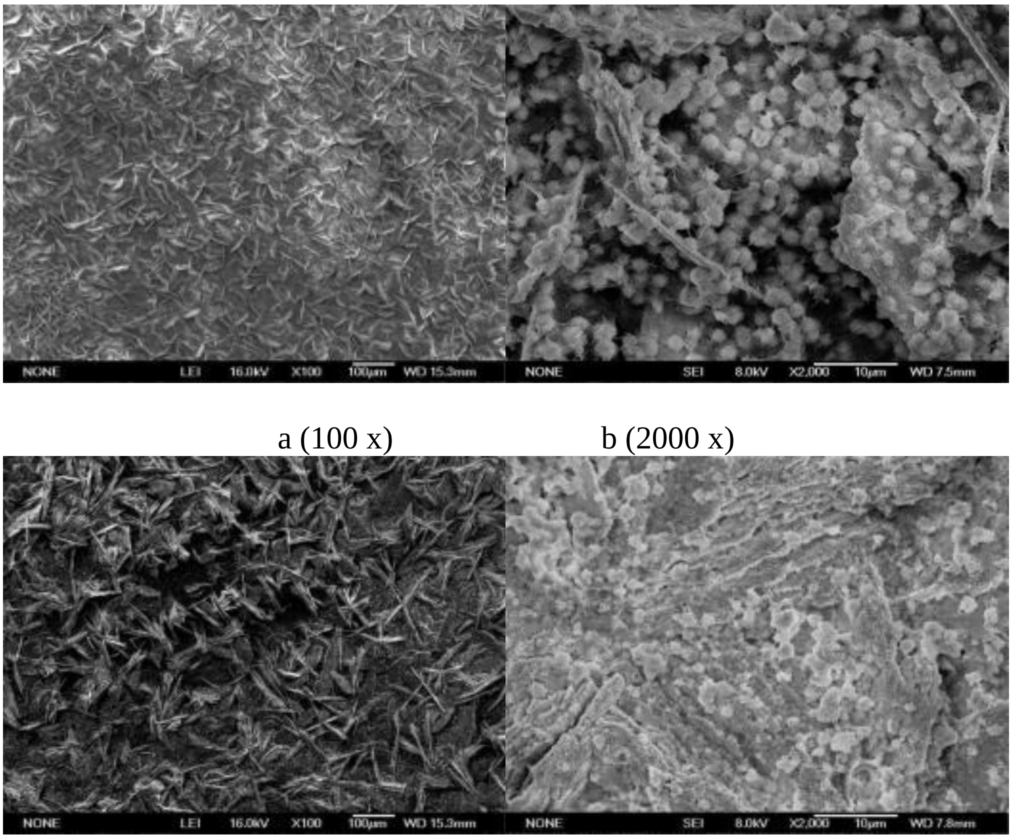
Comparing the three kinds of zinc samples, we could found that the R_{ct} value of zinc sample coated with powders of barnacles and oysters (C) was obviously larger than the others. It could be concluded that the macro-fouling community simulated by the powder of barnacles and oysters played a good seal role, which hindered Cl^- and dissolved oxygen, and inhibited the corrosion to some extent. The simulated macro-fouling attachment had formed a dense protective layer on the surface of anode, which inhibited the corrosion rate obviously [14].

3.4 Surface morphology examination

3.4.1 Corrosion morphology of zinc anodes

SEM observations of zinc aondes coated with agar and samples coated with powder of barnacles and oysters were conducted after the 15 days EIS measurement, which were shown in Fig.4 (a and b, for aondes coated with agar) (c and d, for aondes coated with powder of barnacles and oysters agar) respectively.

Figs. 4 showed that the corrosion product of zinc samples coated with agar was spiculate and petal-like, while the corrosion product of zinc samples coated with powder of barnacles and oysters was sheet and squamous. The pitting corrosion occurred on both kinds of zinc samples, especially on the surface of zinc samples coated with agar, which with larger and deeper pitting corrosion morphologies than others. The trend of local corrosion would infect the anode dissolution in the subsequent process [19-21]. In the real ocean environment, a survey had been made and showed that the fouling organisms covering on the marine facilities could cause oxygen concentration cell and promote localized corrosion in oxygen-depleted zone [6,23]. In addition, when the barnacles and oysters die they are decomposed by bacteria, which can also cause localized corrosion [24]. Thus the influence of biofouling covering on marine anode is to reduce the average corrosion rate and promote the localized corrosion [25], which is fully consistent with the simulated experiment in our paper. Therefore, we should fully consider the effect of fouling organisms on the sacrificial anode and the protected steel structure in the design of cathodic protection.



a (100 x) b (2000 x)

C (100 x) d (2000 x)

Figure 4. SEM images of zinc aondes coated with agar (a and b), and samples coated with powder of barnacles and oysters (c and d)

4. CONCLUSIONS

(1) The effect of macro-fouling on the corrosion of zinc anodes in lab was studied by simulating the coating of the powder of barnacles and oysters on the surface of samples, which is first proposed in the paper and consistent with the actual marine results.

In this paper, the corrosion behaviour and working performance of zinc sacrificial anodes have been studied firstly in simulated marine fouling environment. From the investigation, the following conclusions can be drawn:

(2) The macro-fouling community simulated by the powder of barnacles and oysters played a good seal role, which increased the anti-corrosion performance at the first attachment stage of macro-fouling.

(3) The zinc anodes coated with agar played a better anti-corrosion performance than the blank

zinc anodes because of the inhibition of Cl^- and dissolved oxygen. However, it played a worse anti-corrosion performance than the zinc anodes coated with powder of barnacles and oysters.

(4) Self-discharge experiment showed that marine biofilms had some protective effect on anodes in the early attachment stage of fouling organisms. The zinc sacrificial anode still possesses high current efficiency when subjected biofoulings. However, the potentional varies damatically in simulated biofouling environment.

(5) The result of SEM shows that local corrosion occurs when surface was covered with simulated fouling layer, which is fully consistent with the zinc anode samples immersed in real seawater.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China (No. 41376003 and 41006054).

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