

# Responce Between Electrochemical Fluctuations and Phenomenon for Localized Corrosion of Less-Noble Metals

Yasuhiko Itoi<sup>1,†</sup>, Seisho Take<sup>1</sup>, and Tooru Tsuru<sup>2</sup>

<sup>1</sup>Department of Materials Chemistry and Bioengineering, Oyama National College of Technology,  
(771 Nakakuki, Oyama, Tochigi 323-0806)

<sup>2</sup>Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology,  
(2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan)

We have been studying application of electrochemical noise (Fluctuation) analysis for localized corrosion. Foils of Zinc, Aluminum and Magnesium were used as specimens for electrochemical cell simulating localized corrosion. These specimens were dipped in sodium chloride solutions adjusted to each exponent of Hydrogen ion concentration (pH) condition of 5.5, 10, 12 respectively. Time variations of potential and current were measured in those solutions, and simultaneously the surfaces of specimens were observed using microscope with television monitor. Two types of electrochemical cells were arranged for experiments simulated localized corrosion.

The fluctuations on trendy component of short-circuited potential and short-circuited current were appeared in synchronization. It was seemed that these fluctuations result from hydrogen evolution on the aluminum active site in the crevice from the microscopic observation.

In the case of zinc and magnesium, fluctuations appeared on the trendy component of the corrosion potential. Two types fluctuation were detected. First one is the fluctuation varied periodically. The second one is the random fluctuation. It was seemed that these fluctuations result from generation of corrosion products and hydrogen evolution on the active site in the crevice of zinc and magnesium from the microscopic observation.

**Keywords** : electrochemical noise (fluctuation), localized corrosion, zinc, aluminum, magnesium, monitoring

## 1. Introduction

We have been studying applicability of ENA (electrochemical noise analysis) for characterization of crevice corrosion from the reports.<sup>1)-3)</sup>

In contrast, only a few research works<sup>4),5)</sup> appears to be available concerning ENA for crevice corrosion. Haradky and Dawson<sup>6),7)</sup> undertook detailed experimental work on noise emission on the crevice corrosion initiation but they failed to discuss the source for the detected EN signals. For the quantitative analysis of EN, elucidation of the noise signal source is indispensable.

Thus, we invested efforts of explain the mechanism of EN signal emission for crevice corrosion of zinc, aluminum and magnesium specimens and, during the curse of this work, we sought for feasibility of monitoring of crevice corrosion initiation by ENA. For the creviced Al electrode, we undertook the short-circuited electrodes method

approximating natural immersion condition to analyze quantitatively the electrochemical processes taking place inside the crevice towards the ultimate purpose of characterizing the EN signals emitted on the development of crevice corrosion. As reported earlier,<sup>8),9)</sup> we now know that there is certain correspondence between the localized corrosion type and emitted noise pattern for pitting corrosion of Aluminum. To see if the similar correlation between the localized corrosion type and the noise pattern (fluctuation patterns) exists for crevice corrosion, we studied potential fluctuation for zinc and aluminum, and power spectrum analysis for the random noise generated from the creviced magnesium electrode.

## 2. Experimental

### 2.1 Preparation of Zn, Al and Mg electrode with synthetic crevice

Test electrodes were zinc (Zn) of purity 99.99% with thickness 200  $\mu\text{m}$ , pure aluminum (Al) of purity 99.99%

<sup>†</sup> Corresponding author: itoi@oyama-ct.ac.jp

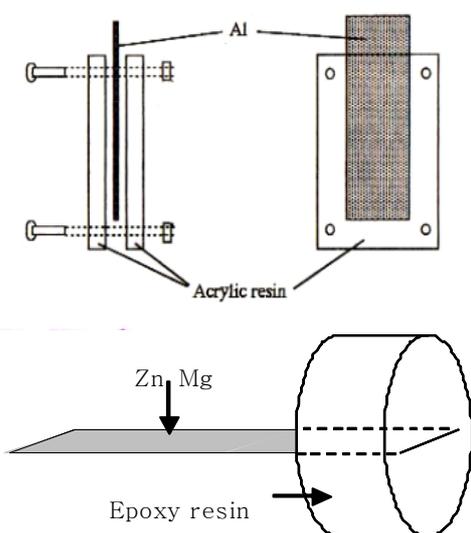


Fig. 1. Artificial crevice electrode for aluminum and buried zinc and magnesium electrodes simulated localized corrosion.

with thickness 100  $\mu\text{m}$  and magnesium (Mg) of purity 99.9% with thickness 240  $\mu\text{m}$ . After degreasing, aluminum was pinched between two acrylic plates and tightened using acrylic bolt/nut to form synthetic crevice, and zinc and magnesium were buried in the epoxy resin. (Fig. 1)

Aluminum specimen as localized anode was put between two transparent acrylic resin plates. This creviced aluminum and large identical aluminum specimen without crevice were arranged facing each other with electrolyte between these electrodes. This creviced aluminum and external identical one were short-circuited with each other as electrochemical coupling cell simulating crevice corrosion.

Zinc and Magnesium specimens were buried in the epoxy resin and its surface area was exposed as cross section area by cutting the epoxy resin with these buried specimens (Fig. 1), and used for electrochemical cell simulating localized anode. Time variation of corrosion potential and the short-circuited potential and the short-circuited current were measured in the sodium chloride solution adjusted to each pH.

## 2.2 Measurements of short-circuited current and short-circuited potential

To monitor the system under natural immersion condition, potential and current were monitored for the creviced Al electrode against the same Al external electrode by short-circuiting these Al electrodes. The specimen surface area ratio between the creviced test Al electrode and the external Al electrode was 1:100. Test solution was open air solution of 0.5 mol/l sodium chloride solution

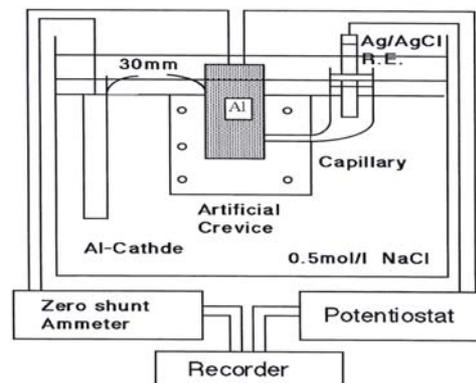


Fig. 2. Apparatus for electrochemical noise measurement

(pH6). Current was measured using zero-shunt ammeter HM-104 of HOKUTO Electrics and potential using HA-151 potentiostat of HOKUTO Electrics with reference to Ag/AgCl reference electrode shown in Fig. 2.

## 2.3 Measurements of corrosion potential

For zinc and magnesium electrodes possessing synthetic crevice as the working electrode, potential was obtained in open air test solution of sodium chloride solution of pH10 and pH12 adjusted respectively by saturated silver and silver chloride (Ag/AgCl) reference electrode. Potentiostat used for the measurements was HA-151 of HOKUTO Electrics.

## 3. Results and discussion

### 3.1 Time variation of corrosion potential and piled potential fluctuations for buried Zinc electrode.

Fig. 3 shows time variation of corrosion potential for

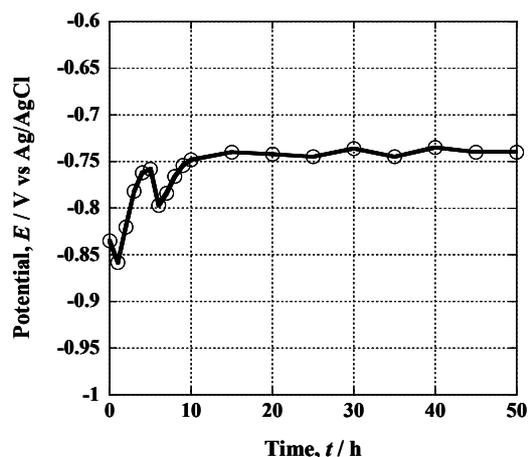


Fig. 3. Time variation of corrosion potential of buried Zn electrode in 0.5 mol/l sodium chloride solution. (pH10).

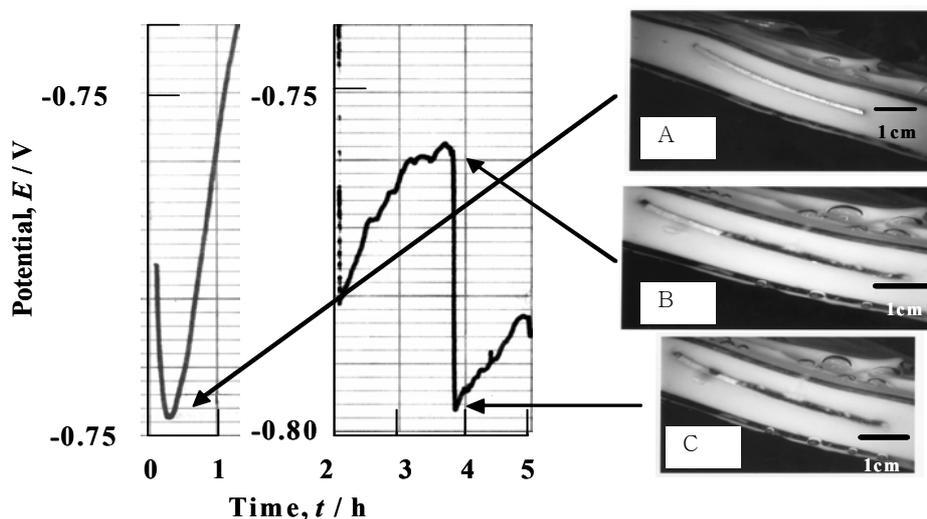


Fig. 4. Potential noise of buried Zn electrode in 0.5 M sodium chloride solution (pH10) and microscopic photographs for dissolution of zinc surface and corrosion product formation in buried zinc electrode.

buried Zn electrode in 0.5 mol/l sodium chloride solution of (pH10). The potential measured in chloride ion containing solution shifted to less noble one for that measured in the solution without chloride ion. The random noise component piled up on the potential time variation as trendy component. A part of the fluctuation is shown in Fig. 4. The fluctuations of corrosion potential appeared in the initial period after dipping indicating the rapid shift to less noble side and then to noble side slowly. This repeat was appeared few times. And then the trendy component of potential varied to noble potential with random noise as noise component.

### 3.2 Microscopic photographs of surface image for buried zinc electrode.

Fig. 4 showed microscopic photographs of surface images on creviced Zn electrode. In the first stage the surface of buried zinc was dissolved with the potential shift to less noble potential. In the second stage few hydrogen bubbles generated and corrosion products of zinc hydroxide was appeared in the dissolved crevice with the potential shift to noble potential. In the third stage the different surface area of zinc was dissolved with the potential shift to less noble potential.

These periodic variation patterns for the potential were concluded to be the consequence of the dissolution on zinc outer surface and hydroxide formation in the zinc inner surface inside the crevice formed by dissolution.

### 3.3 Short-circuit current noise generated between the creviced electrode and the external electrode and the variation of the short-circuited potential noise for creviced Al electrode.

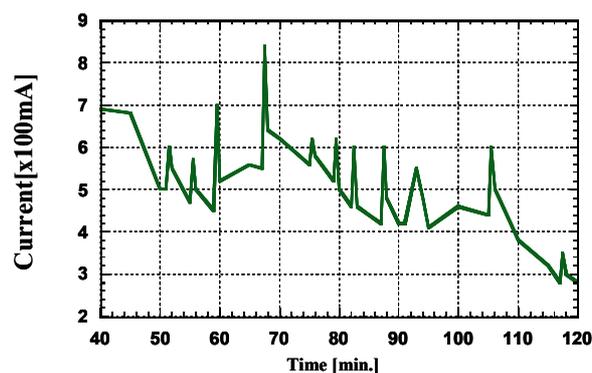


Fig. 5a. Time variation of the current between the creviced Al artificial electrode and the external Al electrode.

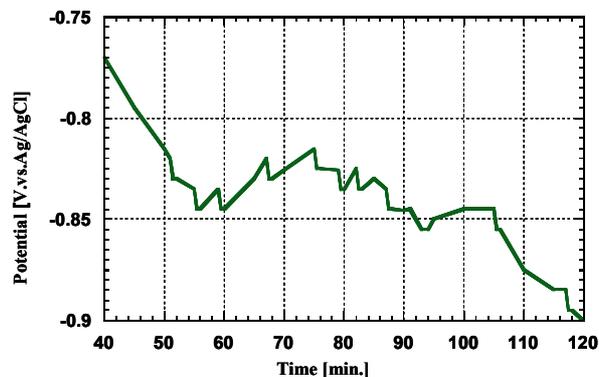


Fig. 5b. Time variation of the potential between the creviced Al artificial electrode and the external Al electrode.

Fig 5 reproduces the observed variations of the short-circuit current (a) and the short-circuit potential (b) between

the creviced Al electrode and the identical external electrode. In the potential monitoring setup, capillary was employed to measure the potential at a location as near as possible to the crevice. The monitored current was positive and accordingly the external electrode acted as the cathode and the creviced electrode as the anode. Thus, on this basis, an equivalent electric circuit for the crevice corrosion system was composed. In the initial 50 min, both the current and the potential varied only very slowly and no noise was detected for either the current or the potential. After 50 min, fluctuation of the current and fluctuation of the potential appeared to emerge in synchronization. For example, when potential shift towards less noble side occurred in spike, the current rise suddenly in correspondence and, on the steady recovering ennoblement of the potential, current tend to decreased moderately. These periodic variation patterns for the current and the potential were concluded to be the consequence of  $H_2$  bubble formation and its departure after certain extent of the growth from the Al surface inside the crevice as presented earlier.<sup>1)</sup>

After the test, acidification of the solution (to a level pH2~3) inside the crevice was varied using a pH test paper and the weight loss the creviced Al specimen was also ensured.

### 3.4 Time variation of corrosion potential and piled potential noise for creviced Mg electrode.

Fig. 6 shows time variation of corrosion potential for creviced Mg electrode in sodium chloride solution of  $10^{-6}$  mol/l (pH12). The potential measured in chloride ion containing solution shifted to less noble one for that measured in the solution without chloride ion. The random noise component piled up on the potential time variation as tren-

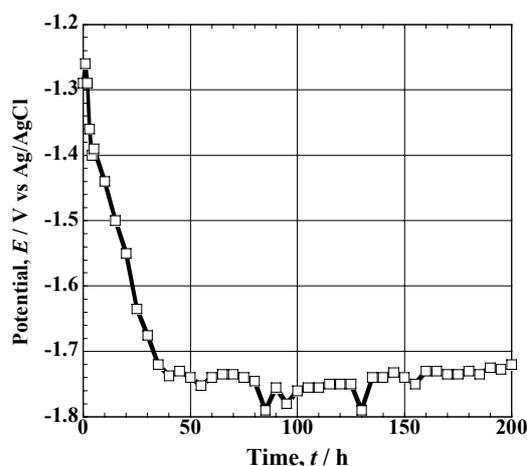


Fig. 6. Time variation of corrosion potential of creviced Mg electrode in  $10^{-6}$  mol/l sodium chloride solution. (pH12).

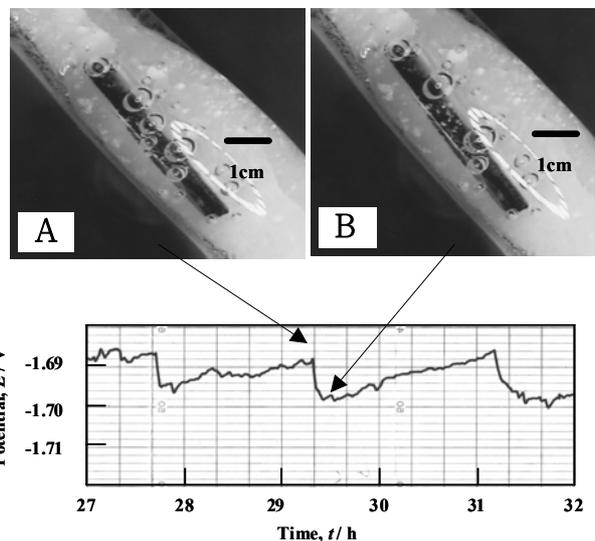


Fig. 7. Potential fluctuation and noise of buried Mg electrode in  $10^{-6}$  mol/l sodium chloride solution (pH12) and microscopic photographs of  $H_2$  bubbles generated in buried Mg electrode.

dy component. A part of the random noise is shown in Fig. 7.

### 3.5 Microscopic photographs of hydrogen bubbles on buried Mg electrode

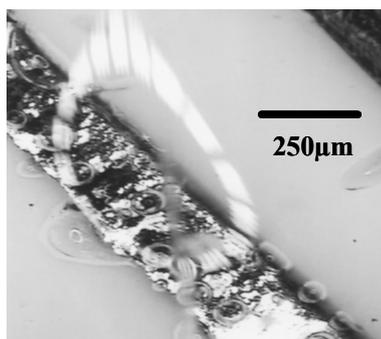
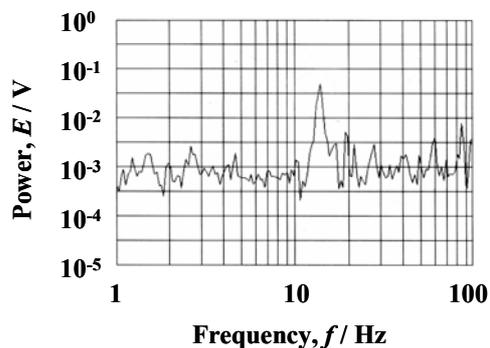
Fig. 7 showed microscopic photographs of hydrogen bubbles on creviced Mg electrode. Hydrogen micro bubbles generate and combine with each other to rather big size with the shift to a noble potential and then detached from blocked surface with appearance of active site with the shift to less noble potential.

### 3.6 Power spectrum analysis for random noise generated from creviced Mg electrode

Fig. 6 shows the example of power spectrum for random noise of creviced Mg electrode in sodium chloride solution. There was a distinctive feature. The spectrum peaks are generated irregularly in the frequency region of 1~20 Hz. This feature indicates the change of phenomenon in the crevice. Hydrogen micro bubbles generate and combine with each other to rather big size and then detached from blocked surface with appearance of active site. It seems that the peak frequency of power spectrum corresponds to the period of the generation of hydrogen bubbles.

## 4. Conclusions

(1) The big fluctuation on the time variation of corrosion potential in the initial period for buried zinc electrode results from the dissolution of zinc substrate and the for-



**Fig. 8.** Example of power spectrum for random noise generated from buried Mg electrode in sodium chloride solution and microscopic photographs of  $H_2$  bubbles generated from on buried Mg electrode.

mation of hydroxide in the crevice formed by the dissolution of active site of buried zinc electrode.

(2) By arranging short-circuit between the creviced Al electrode and the external Al electrode, the former acted as the anode and the latter as cathode indicating that the natural crevice corrosion system was correctly simulated by this configuration. Potential of the creviced Al electrode

varied in synchronization with the fluctuation of the short-circuited current noise being correlated with the  $H_2$  bubble forming and detaching process.

(3) The time variation of parameters of power spectrum explained the change of phenomenon in the crevice of buried magnesium electrode. Hydrogen micro bubbles generated and combined with each other to rather big size and then detached from blocked surface with the appearance of active site.

(4) We propose new monitoring method. In the first step, the time variation of trendy component of corrosion potential would be discussed. In the second step, the noise component piled up on the corrosion potential would be discussed and judged.

(5) It will be proposed that reference electrode is set up near the best position having the possibility for crevice corrosion generation as the best monitoring model.

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