Discussion on Cathodic Protection Effect for Steels in Salt Damaged Concrete

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ABSTRACT

In the cathodic protection (CP) of steel in salt-damaged concrete, a criterion of potential shift (depolarization:$\triangle$E) of 100 mV or high is widely accepted. However, $\triangle$E behaviour is greatly influenced by the pH change on steel surface and the supply of dissolved oxygen (DO) to steel surface. The criterion should be evaluated carefully in its application to the case of moist environment where the rate of DO is slow. The present research discusses a new evaluation method of $\triangle$E in environments of limited oxygen supply. Under these conditions, we focused on the effect of environmental improvement (increase in pH) on the surface of steel, and also examined the effect of protection by various CP designs (power supply) with the long term perspective.

Keywords. Cathodic Protection, Salt Damage, 100mV Shift, Depolarization, Protection criteria

1. INTRODUCTION

CP is attracting attention as a countermeasure against the corrosion damage of reinforced concrete structure. With regard to criterion of evaluating the effect of CP, as shown in Figure 1, $\triangle$E of 100mV is widely accepted, in which $\triangle$E is the difference between the on-potential of steel(Eon) with IR-compensation(Eio:instant off potential of steel) and off-potential of steel(Eoff) measured after appropriate passage of time following switch off (JSCE, 2001).

However, because $\triangle$E behavior greatly depends on the surrounding environment of rebars and feeding rate of oxidizing agent (cathode depolarization characteristics), in a moist environment where the feeding rate of DO is slow, criteria of 100mV may not be applicable even under impressed cathodic current. In this case, increasing protection current for satisfying 100mV shift is likely to cause reverse effects such as reduction of DO diffusion and decline in $\triangle$E speed, and increase in necessary protection current even. Supplying a

large protection current is not only uneconomical, but it will also lead to deterioration of mortar that contains anodes and invites premature decay of anode performance owing to water depletion in the vicinity of anode plates. For appropriate management, it is important to detect correctly the supply and concentration of DO in the vicinity of rebars, platinum (Pt) electrode was embedded close to rebars, and an attempt was conducted for evaluating the feeding rate of DO by measuring its electrochemical measurements (Shinoda, 2011).

On the other hand, in environments where DO supply is high, such as the case of dry concrete structures exposed to atmosphere, increase in pH and decline in concentration of chloride ions will occur due to electrophoresis accompanied by the cathodic reaction as shown in Eq(1). We call this phenomenon "environmental improvement".

$$H_2O + 1/2O_2 + 2 e^- \rightarrow 2OH^- \tag{1}$$
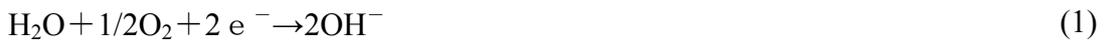
Ratio of concentration of Cl^-/OH^- will decline due to continued CP, and as the effect of environmental improvement proceeds corrosion resistance of rebars will be increased (owing to passivation or repassivation), in which increase in $\triangle E$ is observed compared to the initial value. In other words, it can be inferred that when applying CP, considering the effect of gradual environmental improvement, it is not always necessary to impress the current enough for the protection criteria from the very beginning. Therefore, changes in $\triangle E$ were monitored under CP at different current density on corroded steel in mortar (Otani, 2012).
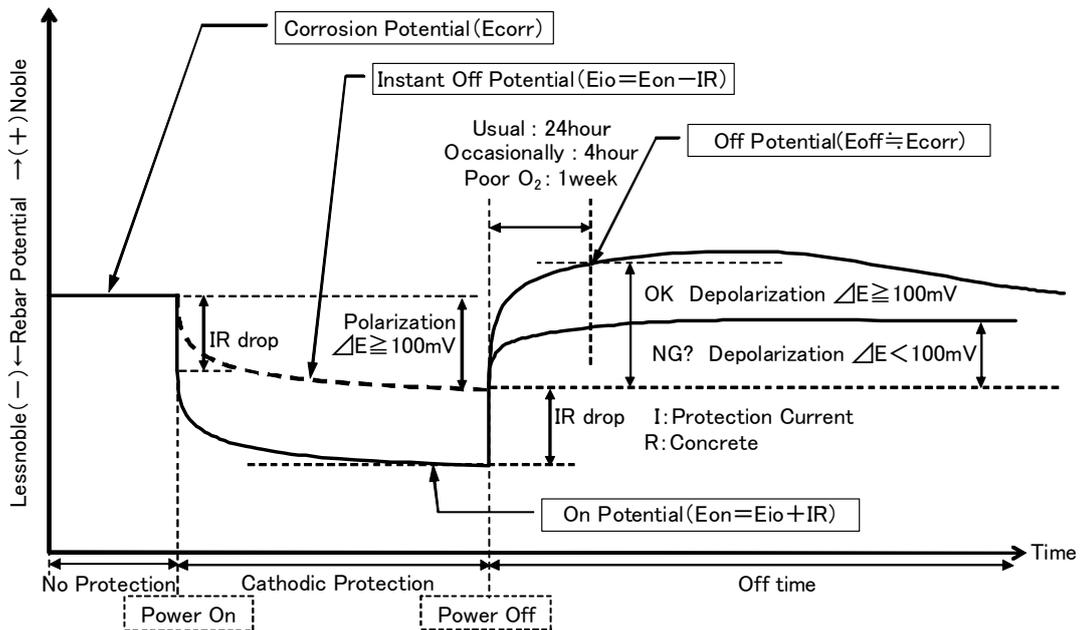
Figure 1. Outline of evaluation method for CP

2. EXPERIMENTAL

2.1. Experiment evaluation protection effects in moist environment

2.1.1. Specimens

Columnar mortar test specimen with two embedded Pt sheets of surface area 2cm^2 each as shown in Figure 2, was fully immersed in sea water. Decrease in concentration level and supply in concrete was traced by two methods as shown below. Mortar test specimen was prepared from ordinary Portland cement with W/C=50% and S/C=3.
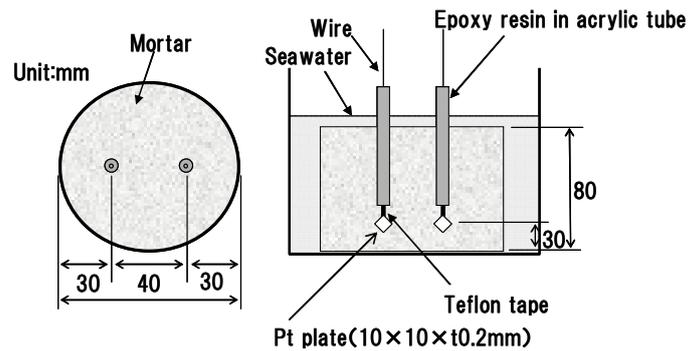
Figure 2. The shape of the mortar specimen

2.1.2. Method of evaluating the feeding rate of dissolved oxygen

(1) Cathodic polarization curve

Figure 3 shows the test apparatus. Diffusion-limited current density (i_L) was evaluated by measuring cathodic polarization curve at sweeping rate of 20mV/min using one of the Pt sheets. Sat.KClaq./AgCl/Ag electrode (SSE) was used as a reference electrode, and mixed-metal oxide (MMO) electrode, as counter electrode.
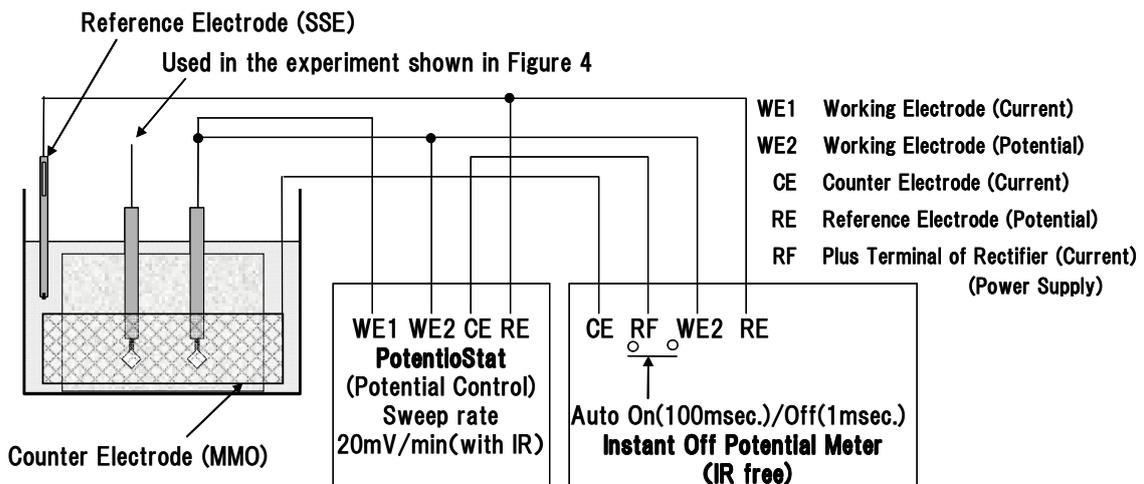
Figure 3. Measuring method of the cathodic polarization curve for Pt electrode

(2) Potential decay measurement (Hydrogen electrode method)

If hydrogen (H_2) adsorption or gas coverage is created on Pt as result of cathodic reaction by maintaining the plate for a certain period of time at a potential below the H_2, Pt plate will show potential of H_2 electrode for a while. However, once H_2 on the surface is consumed due to diffusion of DO, at a certain point in time, potential suddenly will become noble and potential of H_2 electrode will no longer relevant. We call the chronic change in potential following switch off "a potential decay curve". Time required of t_H corresponds to the supply rate of DO (i_L of DO as mentioned earlier), and i_L can be estimated from t_H. In this paper, this method is referred to "H_2 electrode method". The testing apparatus for this method is shown in Figure 4. The open Pt electrode in Figure 4 worked as a working electrode for measuring cathodic polarization curve, we selected the current density of $2A/m^2$, at which Pt showed potential enough for H_2 evolution, followed by the switch off after conducting applying cathode current for 10seconds. We measured potential of Pt electrode at interval 1second up until 30 minutes after turning the switch off followed by the measurements at intervals of 2 to 30 minutes in response to rate of potential change.
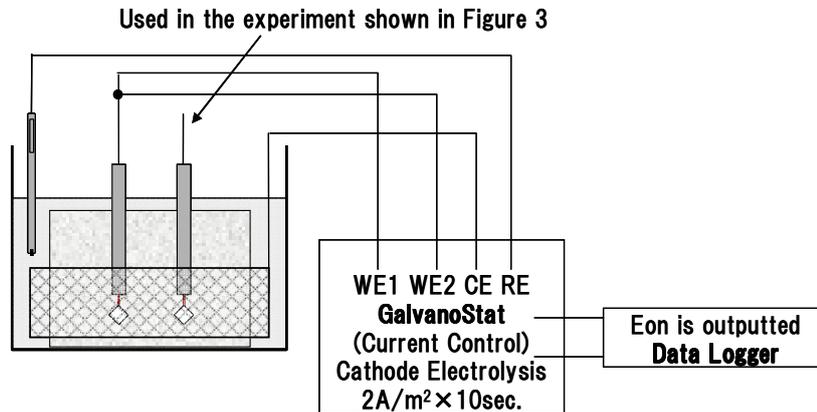
Figure 4. Mesuring method of potential decay curve (H_2 electrode method)

2.2. CP system with current supply methods

2.2.1 Test specimen

We prepared four units of mortar test specimen from normal Portland cement with W/C=50% and S/C=2.5 after to which $10kg/m^3$ of NaCl ($6kg/m^3$ as Cl^-) was added. The value of $10kg/m^3$ of NaCl was selected for simulating high contamination of sea salt and confirming the effectiveness of CP. As shown in Figure 5, test specimens consisted of mortar of cylindrical form with dimensions of 40mm outer diameter and 90mm high, and circular steel rod 13mm outer diameter embedded. The side surface was covered with polyvinyl-chloride pipe 50mm from the bottom of mortar cylinder to upper surface. Only the bottom surface of the steel rod was allowed to corrode in seawater for 7 days prior to mortar casting. Mortar was removed from a die 24 hours after casting, and then it was hardened by keeping it wet for 14 days.
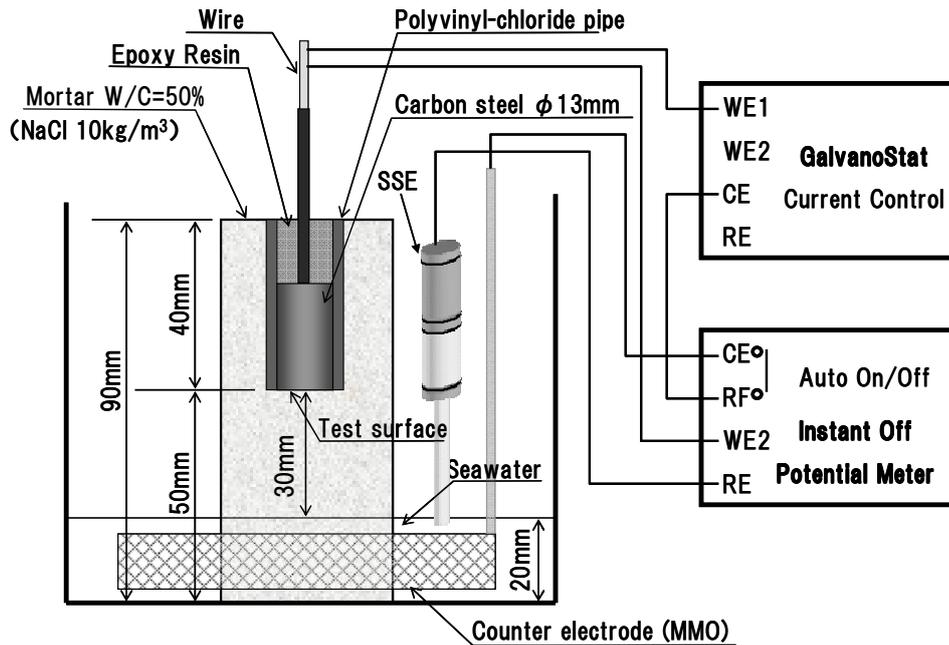
Figure 5. CP experiment for the mortar specimen

2.2.2 CP exeperiment

Prior to CP experiment, we used anode electrolysis to corrode the surface of steel specimen. This was because we had determined in corrosion potential measurement that corrosion was minor despite of burying corroded steel. Here, random anodic current was applied to steel and anode electrolysis was adjusted so that corrosion potential would be -350mVvsCSE (sat.CuSO$_4$aq./Cu electrode) and polarization resistance would be 10kΩ/cm^2 or below, and extent of corrosion is similar in all four specimens.

As shown in Figure 5, mortar specimen with corroded steel was submerged in sea water along with MMO electrode as anode. By keeping sea water up to 20mm from the bottom of mortar specimen, distance between sea water and test specimen surface was kept 30mm. As sea water level lowers during power supply period, water level was maintained by adding deionized water. Moreover, constant test environment was maintained by putting the container that was holding mortar test specimen, in a water tank kept at 25°C.

Table 1 shows power supply conditions of mortar specimens. Current density(i_c) was maintained constant not changed throughout the test period for all specimens. Potential was measured using SSE installed in sea water, and it was then converted to CSE standard.

During the test period, we took collected the log of Eon, and measured Eio randomly. Eio of specimen subjected to intermittent power supply was measured on 7th hour of power supply in each cycle. Power supply was stopped for all specimens on 6th, 23rd, and 43rd day after starting the experiment, and $\triangle$E was measured after passage of about 20hours. Moreover,

anodic and catholic polarization curves of steel were measured before power supply test and after $\triangle$E measurement. For measurement of polarization curve, Eio and current values were measured when changing Eon at every fixed step of 50mV potential at 2.5 minutes interval.

Table 1. Condition of CP

No.	Condition	Current density(i_c)mA/m^2		Discription
		Per steel area	Per mortar area	
1	Usual	203	21.4	In the initial stage of test, constant current was supplied at i_c of 100mV cathodic polarization
2	Small i_c (1)	15	1.6	Constant current supply at 15mA/m^2 In the initial stage, cathodic polarization of 100mV is not obtained
3	Small i_c (2)	60	6.4	Constant current supply at 60mA/m^2 In the initial stage, cathodic polarization of 100mV is not obtained
4	Intermittent	226	23.9	In the initial stage of test, intermittent power supply repeating the cycle of 8 hours power supply at i_c of 100mV cathodic polarization and 16 hours of no power supply

3. RESULTS AND DISCUSSION

3.1 A new method for the effect of protection in moist environment

Figure 6 shows consolidated temporal changes after completing submersion of each mortar specimen in sea water with respect to cathodic polarization curve of Pt plate in mortar specimen submerged in sea water and potential decay curve of Pt plate measured using H$_2$ electrode method corresponding to it. Moreover, since it is necessary to determine whether it is possible to apply this experiment irrespective of the type of cement hardened body, we have also provided data obtained from concrete specimen that was prepared in relation to this experiment and that was partially submerged in sea water.

Points marked with filled circles ($\bullet$) in the figure indicate i_L of DO on the cathodic polarization curve, and time required t_H for disappearance of H$_2$ electrode on the potential decay curve. Portions equivalent to each inflection point were taken as evaluation values.

As the potential decay curve is similar to titration curve in potentiometric titration, t_H can be considered as the time taken by DO for consuming the H$_2$ formed by under constant electric charge. In this case, because t_H can be considered a parameter that depends on the feeding rate of DO, further examining its relation with i_L evaluated from the cathodic polarization curve will appear like Figure 7.

Because almost linear relation (R^2 coefficient is 0.9619) is obtained between these two on double logarithmic axis, we could conclude that by burying Pt electrode near steel in concrete and by applying H$_2$ electrode method, we can evaluate the diffusion rate of DO supplied to the surface of steel.

The application of the criterion for CP more than 100mV for $\triangle$E may be difficult in the wet environment. This method evaluates corrosion rate under CP in such an environment and can determine the quality of the CP. For example, it may be thought that this value is equal to the corrosion rate of steel when i_L is estimated as 10mA/m^2 shown in Figure 8. When we want to decrease below corrosion rate 2mA/m^2 by CP application, it is possible to obtain a sufficient corrosion protection effect by $\triangle$E70mV or more, assuming 100mV/decade the anode Tafel slope of steel. This method has a merit to be able to set a new criterion of CP from the view point of corrosion rate.
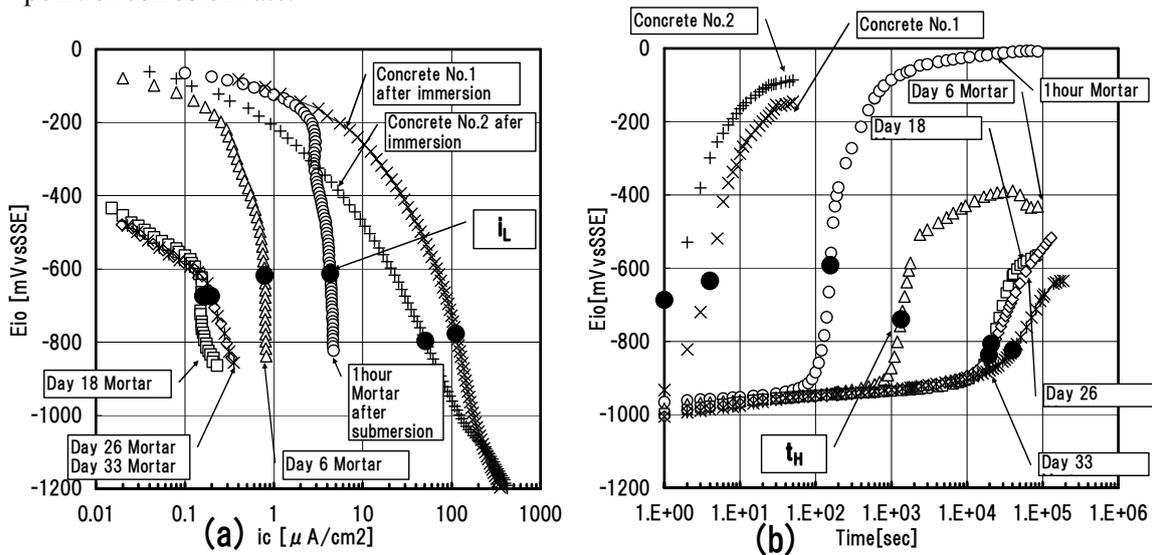
Figure 6. Cathodic polarization curves(a) and potential decay curves(b) for Pt electrodes
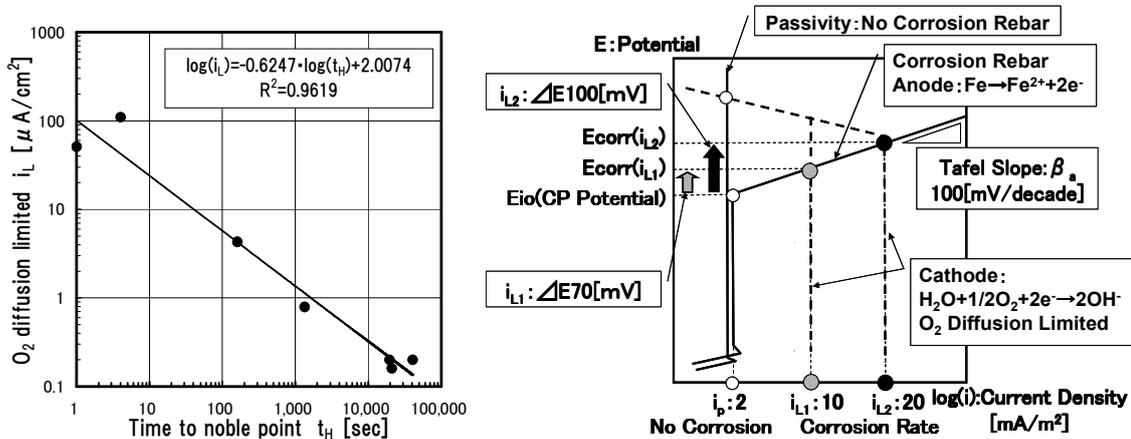
Figure 7. Relation between t_H and i_L

Figure 8. A new method to evaluate CP effect

3.2 Effect of protection under various power supply conditions

Figure 9 shows temporal changes in i_c of Eon and Eio of each specimen. In the figure of Eon and Eio, potential was increasing in all specimens up to 6th day of power supply. From the 6th day onward, potential of No.1, No.3, and No.4 showed decreasing trend at the time of

power supply. This is perhaps due to decline in the feeding rate of DO to the surface of steel. In specimen No.2, where power was supplied at small i_c, potential did not decline.
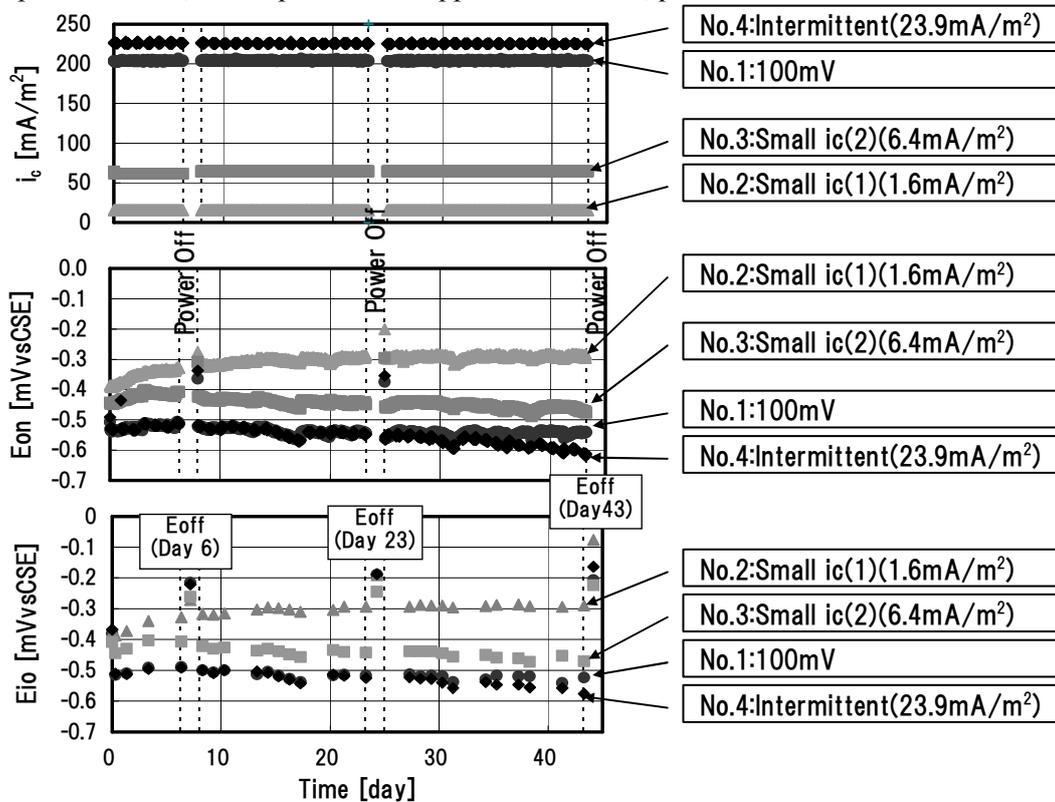
Figure 9. Change in i_c , Eon and Eio with time

Eoff measured after stopping the power supply on 6th day, 23rd day, and 43rd day from starting the experiment, increased with time for all specimens. Figure 10 shows changes in $\triangle$E with time for each specimen. $\triangle$E of specimen No.1 and No.4 exceeded 250mV on 6th day, and especially increase in $\triangle$E after that for specimen No.4 subjected to intermittent power supply is large. However, $\triangle$E declined somewhat in specimen No.1 on 43rd day. In specimen No.3, on 6th day we could obtain $\triangle$E of 100mV, which is the protection criteria, and it increased after that as well. In specimen No.2, where power was supplied at the smallest i_c , although $\triangle$E was 55mV on 6th day, it became 102mV on 23rd day, satisfying the protection criteria.
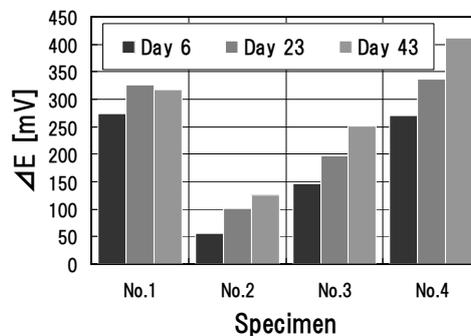
Figure 10. Change in $\triangle$E with time for each specimen

Figure 11 shows the change with time in the anodic and cathodic polarization curves of the steel. While the change with time in the cathodic polarization behavior of all test pieces is small, the anodic polarization can be assessed as having increased, resulting in enhanced passivation. This is presumed to be an effect resulting from the environment improvements of the steel surface, namely, the rise in pH and decrease in Cl^- concentration of the steel surface due to the supply of protection current (Mochizuki,2010). Further, based on this result, the aforementioned rise in Eoff is clearly the result of passivation.

According to the results of this experiment, the conduction in all test pieces resulted in the enhancement of passivation and increased anodic polarization resistance. This holds true in cases where conduction is performed using a low i_c as well as in cases where conduction is performed intermittently. Therefore, results of this experiment proved that for achieving 100mV shift it is not necessary to supply power at a large i_c, rather it can be achieved by applying CP considering environmental improvement of the surface of steel.
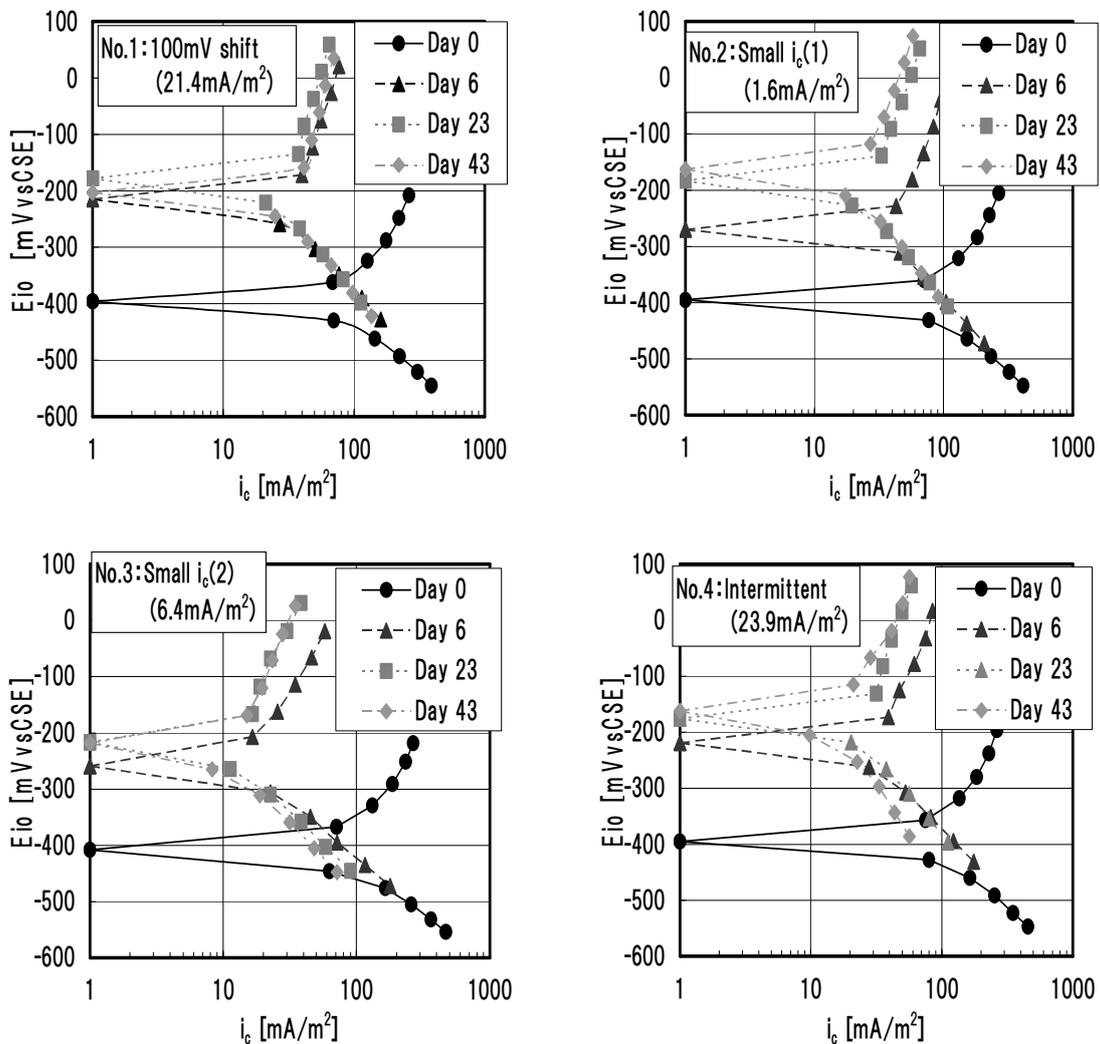
Figure 11. Change in anodic and cathodic polarization curves with time

4. CONCLUSION

1) We could detect H_2 evolvement on Pt embedded in concrete and temporarily use this Pt as H_2 electrode. By measuring time t_H (potential decay curve) from subsequent change in potential until its termination as H_2 electrode, diffusion rate i_L of DO was evaluated. We confirmed that this method (H_2 electrode method) can also be applied for evaluation of corrosion in concrete environment.

2) In the environment with smaller diffusion rate of DO, in order to prevent over-protection, it is necessary to monitor diffusion rate of DO in the same environment and to evaluate corrosion rate.

3) In the environment with high diffusion rate of DO, even if current supplied is lower than the requirement in the beginning of CP, it is possible to satisfy protection criterion ($\triangle$E of 100mV or above) after long run by the effect of environmental improvement on the surface of steel.

4) In the CP in consideration of environmental improvement of steel surface, types of power supply methods such as intermittent power supply can be proposed.

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