Basic research on material characteristics and installation method of the cathodic protection method using coating type secondary anode material

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ABSTRACT

In this research, concerning the cathodic protection method using MMO titanium tape as the primary anode material and the composite material combining photocatalyst and Nafion as the secondary anode material, the effect of concentration of photocatalyst and the coating amount on the corrosion protection performance was evaluated by the polarization test, and no significant difference was found. In addition, a comparative test was conducted on the different installation method of the MMO titanium tape used as the primary anode material on the concrete surface, and it was confirmed that the current easily flows when the coated surface is installed downward on the concrete side. In addition, it was found that the corrosion protection range was broadened by the coating type secondary anode material, as a result of examining the respective corrosion protection performance of the primary anode alone and the secondary anode combination.

Key words: Cathodic protection method; Primary anode material; Coating type secondary anode material; Ionic conductivity; Corrosion protection effect

INTRODUCTION

As a repair method for concrete structures under severe chloride corrosion environment, a cathodic protection method is positioned as an important technology for protecting the corrosion of reinforcement semipermanently. On the other hand, because the initial cost is high and specialized techniques is required for the cathodic protection method, it is currently not a repair method that anyone can carry out anywhere.[1]

The authors developed a cathodic protection method using a composite material combining photocatalyst and Nafion (fluorinated sulfonic acid resin) as a coating type secondary anode material, and conducted a test of its corrosion protection performance, a polarization of 100mV or more is confirmed for a concrete structure containing about 10 kg/m^3 chloride ion or less.[2] Nafion, which is the main component of the coating type secondary anode material, is a feature of this method and has ion conductivity due to protons, and its sustainability is expected by the combination with a photocatalyst. In this research, the effect of concentration of photocatalyst and the coating amount on the corrosion protection performance was evaluated by the polarization test, and the corrosion protection effect was confirmed.

In addition, the surface of the MMO titanium tape used as the primary anode material is easy to dry, and the transmission efficiency to the coated secondary anode material may be reduced as reported by previous research.[2] A comparative test was conducted on the difference in the installation method to the surface. Furthermore, the respective tests for corrosion protection performance of the primary anode alone and the secondary anode combination were conducted, these test results are reported below.

EXPERIMENTAL PROCEDURE

Constituent materials of this method

This method is an external power supply type cathodic protection method, using MMO titanium tape as the primary anode and Nafion solution with photocatalyst as the secondary anode of coating material. Nafion is a type of perfluorosulfonic acid polymer composed of a hydrophobic Teflon skeleton consisting of carbon and fluorine and a side chain having a sulfonic acid group, and its molecular structure is shown in Figure 1.

The proton H^+ of the terminal sulfonic acid group exhibits ion conductivity,[3] and the reaction of the sulfonic acid group and calcium ion is inhibited by the action of the coexistent photocatalyst, and the ion conductivity by the proton is maintained. Table 1 shows the specifications of MMO titanium tape used in this test, and Table 2 shows the physical properties of Nafion solution. The outline of this method is shown in Figure 2. The primary anode material (MMO titanium tape) was sticked to the concrete surface with a silicone adhesive, the MMO coated surface of the primary anode material was sticked upward, and the secondary anode material (coating type) was applied with a brush on it.

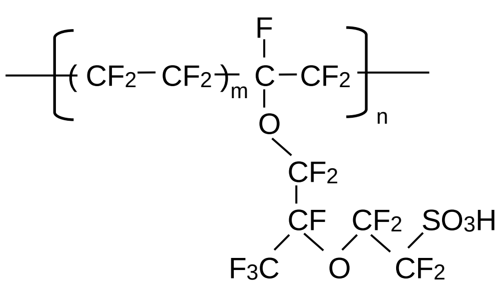

Figure 1 - Molecular structure of Nafion

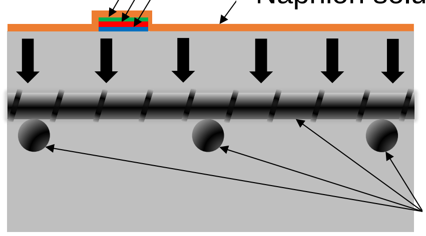

Figure 2 - Outline of the cathodic protection method using coating type secondary anode

Table 1
Specifications of MMO titanium tape

Item	Specifications
Base material	Made of titanium, ASTM B265 Grade 1 Width 20mm, thickness 0.05mm
Precious metal plating	Mixed Metal Oxide (IrO_2, Ta_2O_5)

Table 2
Physical properties of Nafion solution

Content of Naphion	Content of water	Content of VOC*	Specific gravity	Viscosity
5.0 - 5.4%	42 – 48%	47 – 53%	0.92 - 0.94	10 - 40mPa・s

*Propanol, ethanol, other

Corrosion prevention performance test 1
with regards to photocatalyst concentration and coating amount

Since the photocatalytic action by sunlight was excited and the ion conductivity of Nafion was activated, it was investigated whether the increase in the concentration of photocatalyst and the increase in the coating amount contributed to the improvement of the corrosion protection performance. Table 3 shows mix proportion of the concrete, and Figure 3 shows the reinforcement arrangement of the test specimens. Design conditions of concrete mix were nominal strength 24 N / mm^2, slump 12cm, air amount 4.5%, chloride ion content 10 kg/m^3, and sound reinforcements were used. The number of test specimens was one for each factor, and the curing period was at least one month. As a result of judging the natural potential according to ASTM standard (-350mV vs. CSE> E) before the application of this method, it was estimated that the reinforcement was corroded in the test specimen.

MMO titanium tape shown in Figure.4 was sticked with a silicone adhesive at a position 50 mm from the edge, and the coating type of secondary anode material was brushed on the whole surface of the concrete with the concentration of photocatalyst and coating amount shown in Table 4, and integrated with the MMO coated surface. The amount of photocatalyst is converted by multiplying the concentration of photocatalyst by the amount of application, and the amount of Nafion is converted by multiplying the amount of application by 5.2% of the Nafion concentration. The reference electrode was placed at the center of two primary anodes, and the amount of polarization was measured. It was exposed outdoors so that it could be exposed to sunlight, and the current was supplied from an external power supply system, and the current density started from 0.1 mA/m^2.

Table 3
Mix proportion of the concrete

W/C (%)	s/a (%)	Unit amount (kg/m^3)				
		Water	Cement	Sand	Gravel	Admixture
60	46.4	162	272	856	1023	2.72

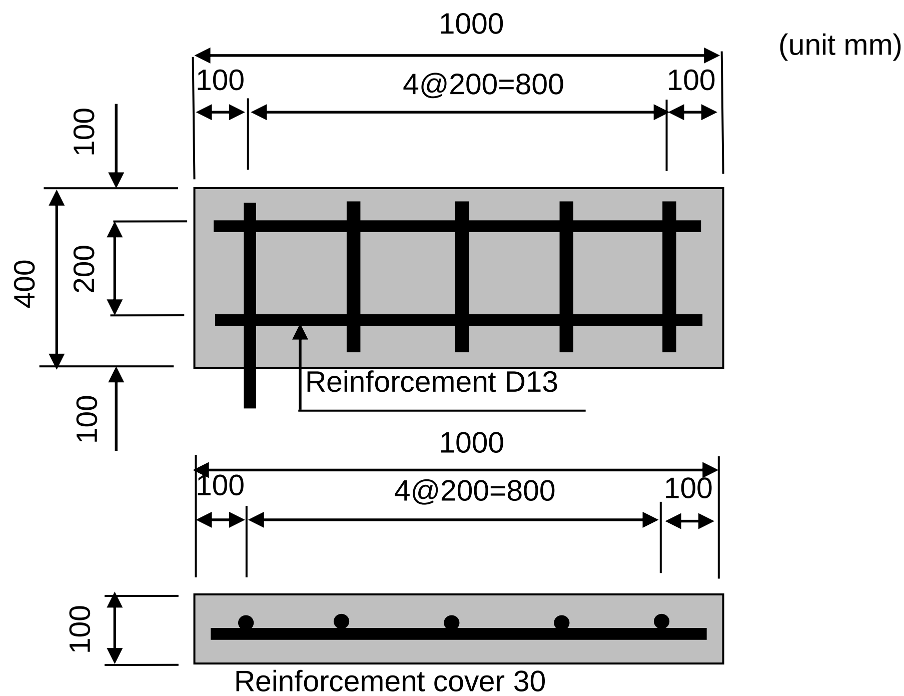

Figure 3 Arrangement of reinforcement in test specimen

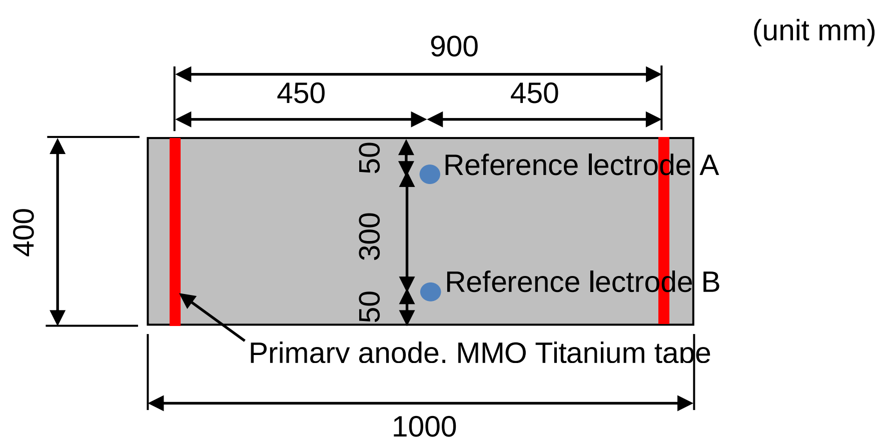

Figure 4 Arrangement of primary anode material and reference electrode

Table 4
Photocatalyst and Nafion amount calculated from photocatalyst concentration and coating amount

No.	Photocatalyst concentration	Coating amount	Photocatalyst amount	Nafion amount	Spontaneous potential
1	1%	200 g/m^2	2 g/m^2	10.4 g/m^2	-390 mV
2	3%		6 g/m^2		-476 mV
3	5%		10 g/m^2		-602 mV
4	3%	300 g/m^2	9 g/m^2	15.6 g/m^2	-370 mV
5		400 g/m^2	12 g/m^2	20.8 g/m^2	-365 mV

Corrosion protection performance test 2
with regards to installation method of primary anode material

The MMO titanium tape used in this test is sticked so that the MMO coated surface is on the side of the secondary anode material and the non-treated surface is on the concrete side. Since the coating type secondary anode material transmits electricity by ion conduction, the presence of water is required. In the current specification, the surface of the MMO titanium tape is easy to dry and the transfer efficiency to the coated secondary anode material may be reduced. Therefore, the corrosion protection effect by the difference in the installation method the primary anode material on the concrete surface was examined. In addition, a water retention gel sheet was used to supply water constantly and stably when conducting the test. The number of test specimens is one for each factor, Table 5 shows the mix proportion of the concrete, and Figure 5 shows the dimensions of the test specimens and the measurement method.

Table 5
Mix proportion of the concrete

W/C (%)	s/a (%)	Unit amount (kg/m^3)				
		Water	Cement	Sand	Gravel	Admixture
60	39	180	300	669	1073	0.012

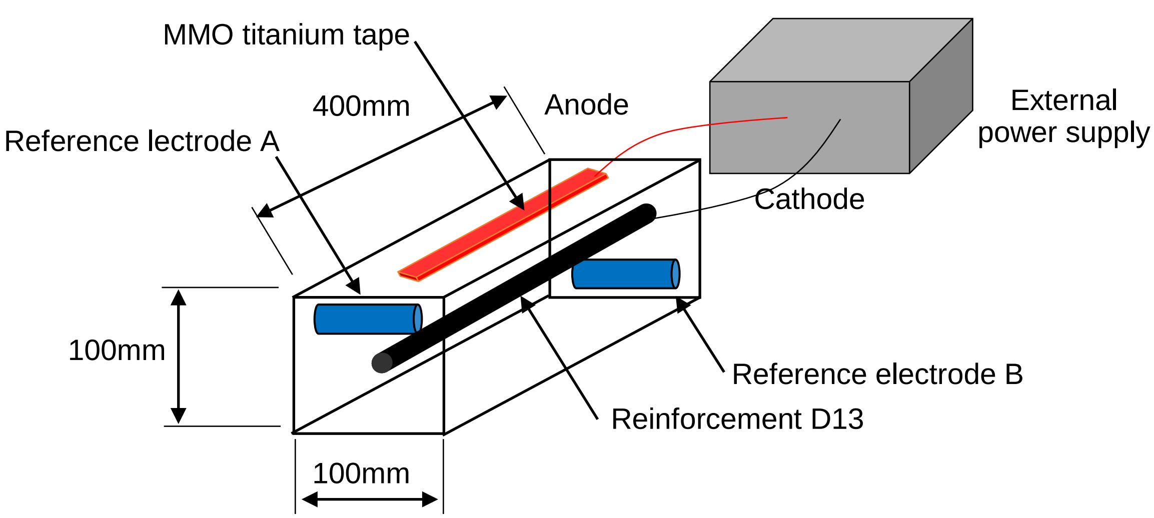

Figure 5 Dimensions of specimen and measurement method

The MMO titanium tape, the primary anode material was sticked on the top of the concrete by the application method shown in Figure 6, and the reference electrodes were placed so as to be sandwiched from both sides. It was exposed outdoors so that sunlight would shine, and energized by the external power system. The current density started from 0.25 mA/m^2 and the amount of polarization was measured. Specimen No.1 and No.2 were placed with the coated surface of MMO titanium tape facing upward, and specimens No.3 and No.4 were placed with the coated surface of MMO titanium tape facing downward. In addition, in specimen No.1 and No.3 a water retention gel sheet was placed on the MMO titanium tape, and in specimen No.2 and No.4 water retention gel sheets were placed above and below the MMO titanium tape.

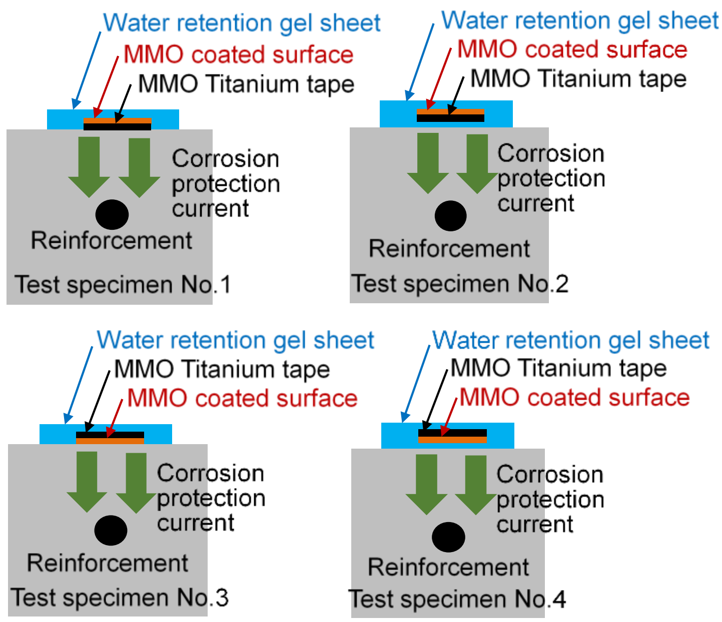

Figure 6 Installation method of primary anode material

Corrosion protection performance test 3
with regards to corrosion protection performance of the primary and secondary anode materials

With respect to the primary and the secondary anode material, comparative tests were carried out in case of primary anode alone and the primary and the secondary anode combination. In preparation of specimen, the concrete of the same mix proportion as shown in Table 3 of 2.2 Corrosion protection performance test 1 was used, and the design conditions were also the same. The dimensions of specimen and arrangement of the reinforcement are shown in Figure 7. An arrangement of the primary anode material and the reference electrode are shown in Figure 8. It was sticked with a special type secondary anode material which have adhesive ingredients, to the MMO titanium tape of the primary anode material at a position 50 mm from the end, and the MMO coated surface was placed on the concrete side.

Moreover, in order to grasp the distribution of the polarization amount, 9 reference electrodes were prepared, a hole of φ 28 mm was made in the concrete surface, and the potential was measured. It was exposed outdoors so that sunlight would shine, and it was energized by the external power system. Starting from a current density of 0.1 mA/m^2 for the specimen area (1m×1m), measurements were made in the range up to 4mA/m^2. After that, a coating type secondary anode material with a photocatalyst concentration of 1% was coated 100m/m^2 × 2 times with a brush on the entire concrete surface, integrated with the MMO coated surface, and measurements were made in the range up to 7mA/m^2, distribution of polarization amount was similarly measured. In addition, the distribution of the depolarization amount measured after 28 days energization was measured.

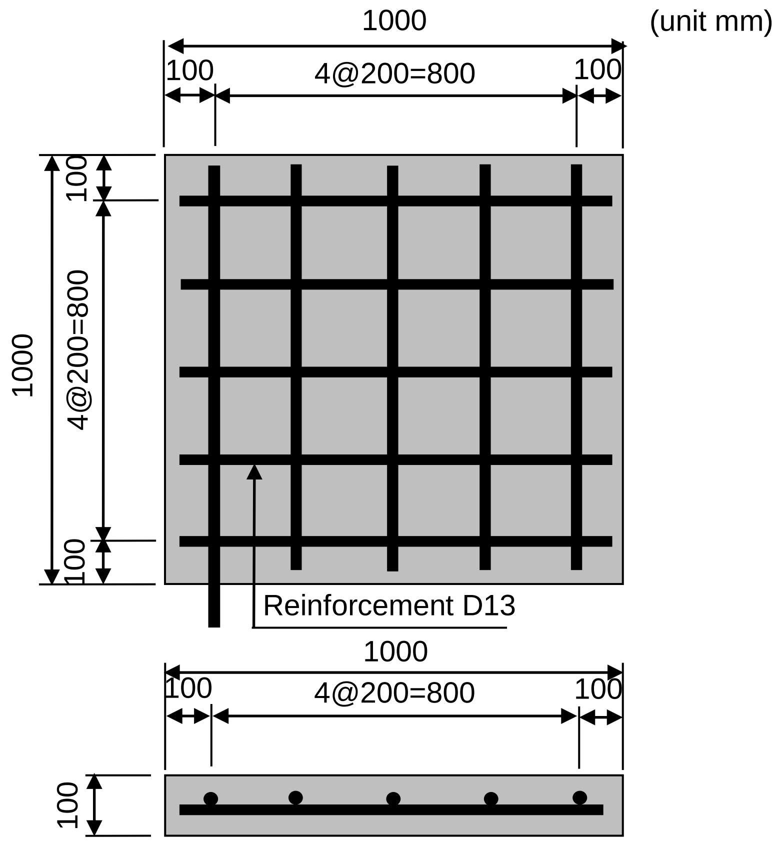

Figure 7 Dimensions of test specimen and arrangement of reinforcement

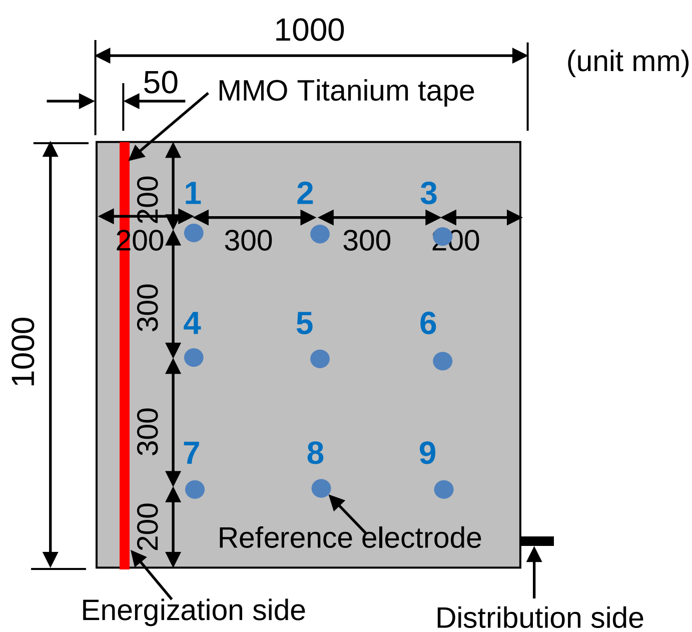

Figure 8 Arrangement of primary anode material and reference electrode

RESULTS

Corrosion protection performance test 1
with regards to photocatalyst concentration and coating amount

Test results of current density, voltage, and polarization amount at each measurement point at photocatalyst concentration of 1%, 3%, 5% (coating amount 200g/m^2) of the coating type secondary anode material is shown in Table 6, the relationship between current density and polarization amount (E-log I curve) is shown in Figure 9, The average polarization amount is calculated from the measured values of reference electrodes A and B.

As shown in Figure 9, even when the photocatalyst concentration changed in the range of 1 to 5%, the difference in the polarization amount was small, and there was no large difference in the corrosion protection performance, because the difference in the amount of polarization was small at current density up to 2mA/m^2 and it is not proportional to the photocatalyst concentration, although the test specimen with 5% photocatalyst concentration has a polarization amount slightly larger than 1% and 3%. This means that even if the amount of photocatalyst is large, the ion conductivity of Nafion does not change, and it is presumed that sufficient corrosion protection performance is exhibited with a small concentration of photocatalyst of 1%.

Table 7 shows the results of current density, voltage and polarization amount at each measurement point at coating amounts of 200, 300 and 400g/m^2 (photocatalyst concentration 3%) of the coating type secondary anode material, Figure 10 shows the relationship between current density and polarization amount (E-log I curve). The average polarization amount is calculated from the measured values of reference electrodes A and B. As shown in Figure 10, the difference in the polarization amount was small even if the coating amount was different, and no significant difference was observed in the corrosion protection performance. This means that even if a large amount of the coating type secondary anode material is applied to the concrete surface, the ion conductivity of Nafion does not change, and it is presumed that a small amount of coating will exhibit sufficient corrosion protection performance.

From the above test results of the photocatalyst concentration and the coating amount, it was found that the effect on the corrosion protection effect is small when the photocatalyst amount is in the range of 2 to 12 g and the Nafion amount is in the range of 10.4 to 20.8 g.

Table 6
Test result of current density, voltage, polarization amount
with regards to photocatalyst concentration

Current (mA)	Current density (mA/m^2)	Power-supply voltage (V)	Average polarization amount (mV) Photocatalyst concentration		
			1%	3%	5%
0.04	0.10	0.85	6	9	7
0.20	0.50	1.20	61	53	61
0.40	1.00	1.75	113	97	119
0.80	2.00	2.87	189	174	227
1.60	4.00	5.09	308	284	420

Corrosion protection performance test 2
with regards to installation method of primary anode material

Test results of current density and voltage, and polarization amount at each measurement point are shown in Table 8, the relationship between current density and polarization (E-log I curve) is shown in Figure 11 when the installation method of primary anode material MMO titanium tape is different. The average polarization amount is the average of the measured values of reference electrodes A and B. As shown in Figure 11, when the coated surface of the MMO titanium tape is placed downward (Test specimen No. 3 and No. 4), the amount of polarization is increased by about 20% compared to when the coated surface of the MMO titanium tape is placed upward (Test specimen No. 1 and No. 2).

Table 7
Test result of current density, voltage, polarization amount
with regards to coating amount

Current (mA)	Current density (mA/m^2)	Power-supply voltage (V)	Average polarization amount (mV)		
			Coating amount		
			200 g/m^2	300 g/m^2	400 g/m^2
0.04	0.10	0.48	9	5	19
0.20	0.50	0.88	53	44	60
0.40	1.00	1.27	97	76	107
0.80	2.00	1.76	174	139	186
1.60	4.00	3.45	284	228	292

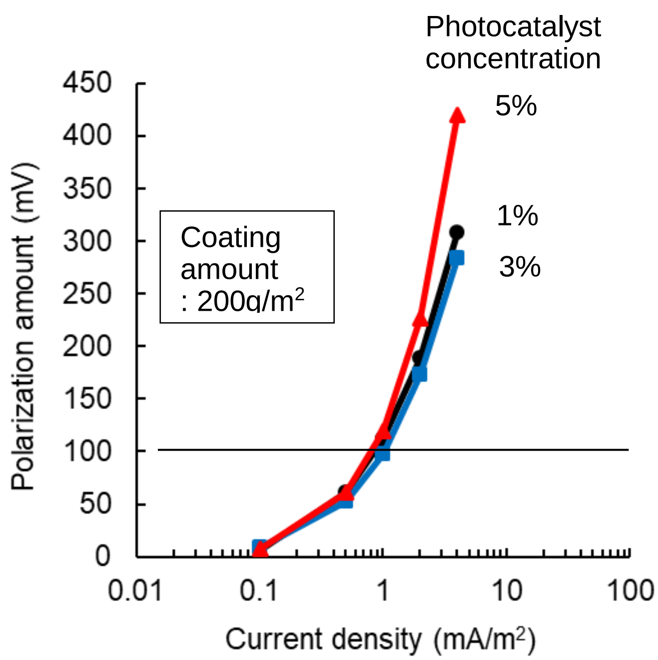

Figure 9 Test result of E-log I with regards to photocatalyst concentration

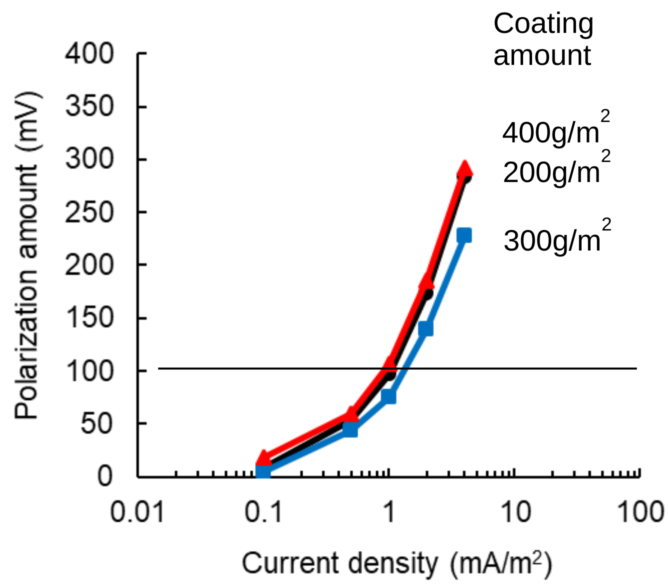

Figure 10 Test result of E-log I with regards to coating amount

This is because the coated surface of the easy-to-dry primary anode material is kept on the concrete side and water is retained by the water contained in the concrete, and the current of the primary anode material is discharged from the coated surface, so the current flows directly to the concrete side. Thus, it is presumed that current flowed to the coated secondary anode material efficiently.

The polarization amount of 18% in the comparison of specimen No. 1 and No. 2 and 5% in the comparison of specimen No. 3 and No. 4 is increased, compared with the case when one water retention gel sheet was placed on top of the MMO titanium tape (Test specimen No. 1 and No. 3) and the case when the water retention gel sheets were placed above and below the MMO titanium tape (Test specimen No. 2 and No.4). It is presumed that the water retention gel sheet inhibited the current from flowing directly to the concrete side, and the current was likely to be retained in the water retention gel sheet, making it difficult for a part of the current to flow to the coated secondary anode. For primary anode material, it was found that it is desirable to send a current to the concrete side with the coated side of MMO titanium tape facing down.

Table 8
Test result of current density, voltage, polarization amount
with regards to installation method of primary anode material

Current (mA)	Current density (mA/m^2)	Power-supply voltage (V)	Depolarization amount (mV)			
			No.1	No.2	No.3	No.4
0.01	0.25	0.03	37	33	57	32
0.02	0.50	0.09	72	50	98	89
0.04	1.00	0.16	118	93	146	125
0.08	2.00	0.29	168	137	203	209
0.16	4.00	0.50	239	197	288	275

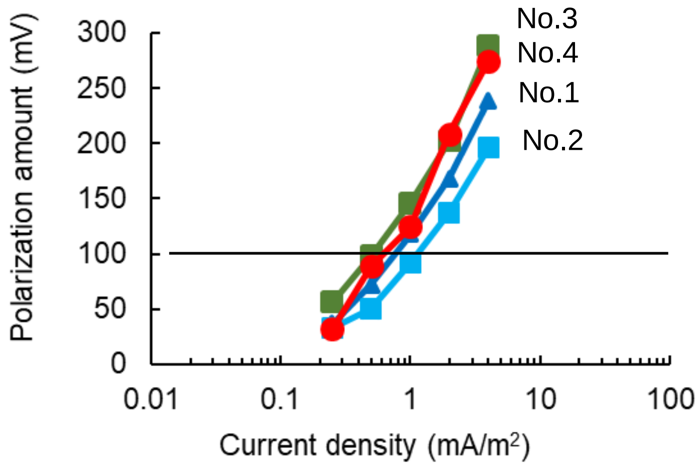

Figure 11 Test result of E-log I
with regards to installation method of primary anode material

Corrosion protection performance test 3
with regards to corrosion protection performance of primary and secondary anode materials

Table-9 shows the test results of current density, voltage and polarization amount at each point in case of the primary anode material alone, and Table-10 shows the test results in case of the primary and the secondary anode material combination, and the polarization amounts measured after 28 days of energization are shown in Table-11. In addition, as a result of confirming to what extent the corrosion protection effect affects based on Table-9, Table-10, and Table-11, the distribution map of polarization amount is shown in Figure 12 and 13, the distribution map of depolarization is shown in Figure 14. The measured values were used at 9 points of the reference electrodes 1 to 9 among 81 intersections of the distribution map, and the values calculated by the difference method were used for the remaining intersections. The amount of polarization at a current of 4.00 mA are used in Figure 12, and the amount of polarization at a current of 7.00 mA are used in Figure 13, each distribution map was created in order to clearly show the spread of the corrosion protection current by the coated secondary anode material.

As shown in Figure.12, a high polarization amount of 200 mV or more was obtained within 200 mm from the primary anode material, but the polarization amount decreased extremely at a distance of 200 to 450 mm, and the polarization amount of 110 mV or less was obtained at a distance of 450 to 750 mm. Next, when the primary anode material was stuck and the coating type secondary anode material was coated, as shown in Figure. 13, a high polarization amount of 200 mV or more was obtained within 300 mm from the primary anode material, but the polarization amount gradually decreased at a distance of 300 to 450 mm, and it slowly decreased at a distance of 450 to 750 mm. It was found that by applying the coating type secondary anode material, the corrosion protection current spreads over a wide range by the ion conductivity, and the corrosion protection range is expanded.

A direct current with a its density of 0.64 mV/m^2 was applied for 28 days to confirm the change in potential due to the energization for a fixed period, and the results of the depolarization test are shown in Figure14. As shown in Figure 14, it was found that the corrosion protection current was diffused uniformly and widely as compared with Figure 13 before energization. In particular, the corrosion protection current is diffused at a distance of 450 to 750 mm. This is estimated to be stable due to the diffusion of the corrosion protection current by 28 days energization. Comparing the distribution map Figure 13 and Figure 14, the polarization amount of reference electrode 9 is the lowest at 52 mV in Figure 13 and the depolarization amount of reference electrode 3 is the lowest at 61 mV in Figure 14, which showed the different trends. The results of polarization tests other than this test also showed that the polarization amount on the distributing side on the lower right tends to decrease, and the polarization amount also tends to decrease along the direction of distributing immediately after energization. On the contrary, in the depolarization test, it is estimated that the corrosion protection current is diffused and stabilized as a whole by energization for a fixed period (28 days), and a high depolarization amount is maintained on the distributing side. However, the cause of the lowest depolarization amount of the reference electrode 3 (Figure 14) positioned in the opposite direction is unknown. Therefore, it is necessary to continue energization and check how the distribution tendency of the depolarization amount changes in the future, and to confirm the influence of the corrosion protection effect.

Table 9
Test result of current density, voltage and polarization amount
In case of primary anode material alone

Current density (mA/m^2)	Power-supply voltage (V)	Polarization amount (mV)								
		No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
0.10	0.56	14	12	12	25	14	8	19	7	2
0.40	0.82	34	19	19	53	25	18	50	13	4
0.70	1.11	68	27	40	91	39	24	84	25	3
1.00	1.44	87	39	44	122	55	34	118	37	8
2.00	2.24	143	61	71	189	144	59	214	59	21
4.00	3.56	218	88	113	283	127	81	264	88	30

Table 10
Test result of current density, voltage and polarization amount
in case of combination primary and secondary anode material

Current density (mA/m^2)	Power-supply voltage (V)	Polarization amount (mV)								
		No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
0.10	0.77	7	11	2	9	6	3	10	2	1
0.40	0.99	28	17	12	39	17	11	42	9	4
0.70	1.25	54	26	24	71	31	22	77	18	11
1.00	1.50	67	35	34	88	45	31	100	28	16
2.00	2.18	123	57	63	147	77	54	155	52	30
4.00	3.26	201	76	93	235	119	77	235	82	39
7.00	4.69	288	118	131	342	159	107	338	110	52

Table 11
Test result of current, voltage and depolarization amount
in case of combination primary and secondary anode material

Current (mA)	Power-supply voltage (V)	Depolarization amount (mV)								
		No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8	No.9
0.64	58.51	343	144	61	358	142	133	306	140	147

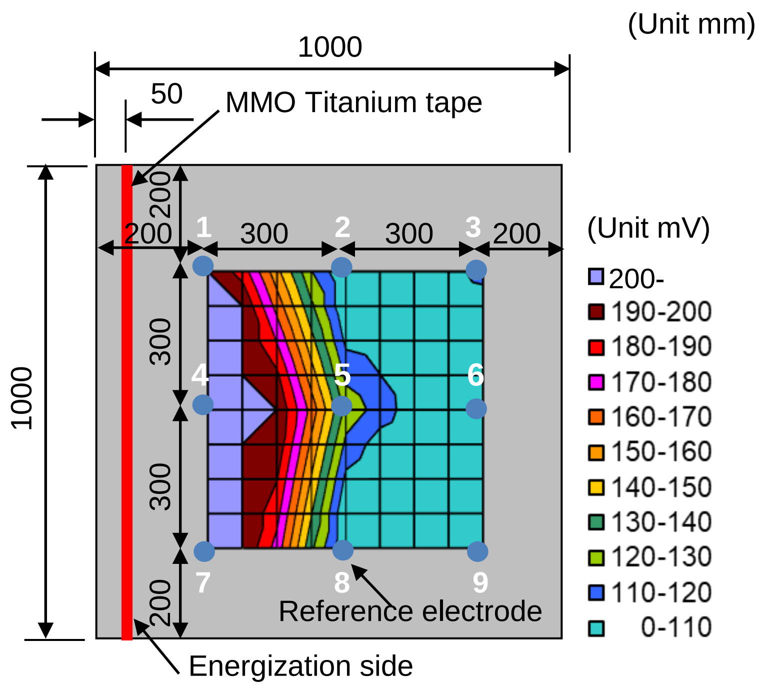

Figure 12 Distribution of polarization amount in case of primary anode material alone

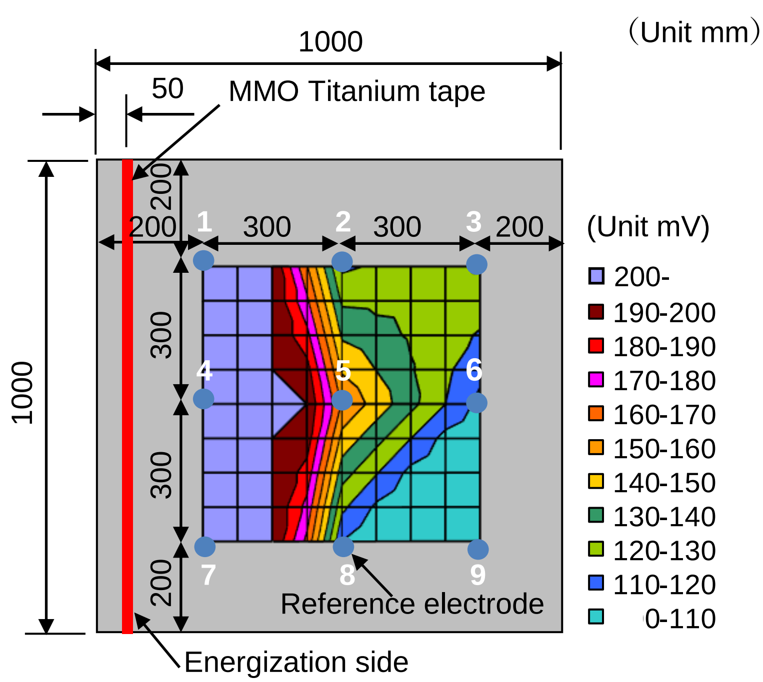

Figure 13 Distribution of polarization amount in case of combination primary and secondary anode material

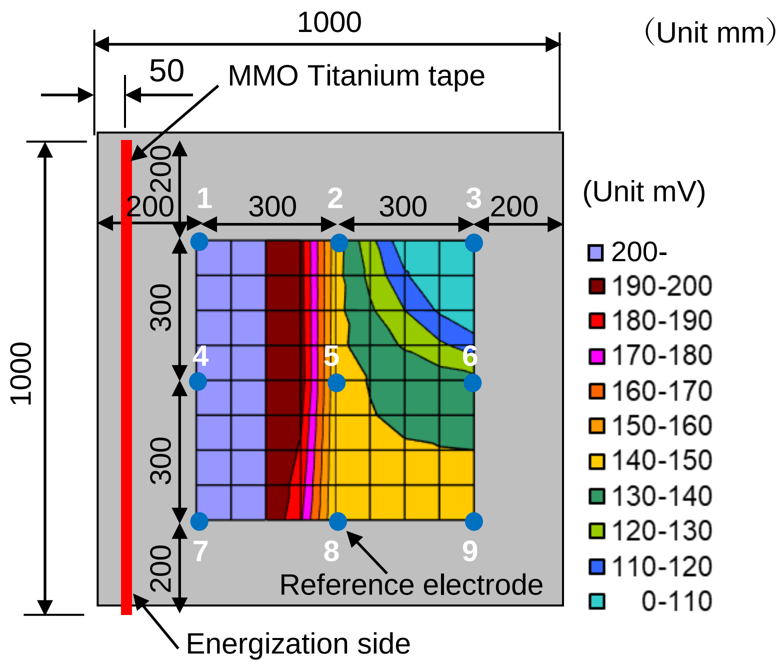

Figure 14 Distribution of depolarization amount in case of combination primary and secondary anode material

CONCLUSIONS

In this research, concerning the cathodic protection method using MMO titanium tape as the primary anode and the composite material combining photocatalyst and Nafion as the secondary anode, the effect of concentration of photocatalyst and the coating amount on the corrosion protection effect was evaluated by the polarization test, and the corrosion protection performance was confirmed. Moreover, the installation method of the primary anode on the concrete surface was changed, and its comparative tests were conducted, and the corrosion protection performance of the primary anode alone and the combination with the secondary anode was examined. The findings obtained by this research are shown below.

Within the range of 1 to 5% of the photocatalyst concentration of the secondary anode material od coating type, the influence of the amount of photocatalyst on the amount of polarization is small and no difference is found in the corrosion protection performance. It was confirmed that the catalyst concentration of 1% exhibited sufficient corrosion protection performance. Within the range of 200 to 400g/m^2 of the coating amount of secondary anode material, the influence of the coating amount on the polarization amount is small, and a large difference is not found in the corrosion protection performance. It was confirmed that the coating amount of 200g/m^2 exhibited sufficient corrosion protection performance.

By placing the MMO coated surface of the primary anode material downward on the concrete side, water is retained by the water inside the concrete, and a current flows directly to the concrete side, so that the secondary anode material can function efficiently. It was confirmed that the current flowed to the secondary anode material efficiently. It was found that by applying the secondary anode material, the corrosion protection current spreads over a wide range by the ion conductivity, and the corrosion protection range is expanded. It was found that the corrosion protection current spreads uniformly over a wide range and it is stable in the amount of depolarization after 28 days energization.

Finally, as shown in Table 11, the voltage is as high as 58.51 V, so it is necessary to keep the voltage below 5 V that can be used as a general cathodic protection method.

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