Protection of Iron against Corrosion in Various Solutions by Coverage of Passivated Iron with a Two-Dimensional Polymer Coating Prepared by Using Octyltriethoxysilane and Healing Treatment in 0.1 M NaNO₃*

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In order to shorten the time required for preparation of an ultrathin polymer coating on a passivated Fe electrode, a self-assembled monolayer of 16-hydroxyhexadecanoate ion HO(CH₂)₁₅CO₂⁻ adsorbed on the electrode was modified with 1,2-bis(triethoxysilyl)ethane (C₂H₅O)₃Si(CH₂)₂Si(OC₂H₅)₃ and octyltriethoxysilane C₈H₁₇Si(OC₂H₅)₃. Further, the passivated and polymer-coated electrode was healed by treatment in 0.1 M NaNO₃. The time for passive film breakdown, *t*_{bd} and the protective efficiency, *P* (%) were determined by monitoring the open-circuit potential and repeated polarization measurements during immersion in 0.1 M KClO₄, 0.1 M NaNO₃, 0.1 M Na₂SO₄ and 0.1 M NaCl for many hours. The *t*_{bd} values were 57.4, >240, 19.2 and 9.0 h, respectively. Breakdown of the passive film was markedly suppressed by coverage with the polymer coating and healing treatment. The *P* values of the electrode in these solutions were extremely high, more than 99.9% before *t*_{bd}, indicating that complete protection of substrate Fe against corrosion was accomplished by covering the electrode with the healed passive film and polymer coating unless the passive film was broken down.

Key words : passivated iron, self-assembled monolayer, two-dimensional polymer, healing treatment, octyltriethoxysilane, passive film breakdown, complete protection

1. Introduction

For protection of passive film from breakdown and Fe substrate from corrosion, an ultrathin (5.4 nm in thickness), ordered (self-assembly) and interconnected (two-dimensional polymer) coating was prepared on passivated Fe. An Fe electrode was passivated in a borate buffer solution at 8.49 of pH by anodic polarization and derivatized in a solution of sodium 16-hydroxyhexadecanoate NaHO(CH₂)₁₅CO₂ (NaHOC₁₆A) to prepare a self-assembled monolayer (SAM) of 16-hydroxyhexadecanoate ion HO(CH₂)₁₅CO₂⁻ (HOC₁₆A⁻) on the surface of passivated Fe, [FeO]OH¹⁾, as

The SAM was modified with 1,2-bis(triethoxysilyl)ethane (C₂H₅O)₃Si(CH₂)₂Si(OC₂H₅)₃ (BTESE) and water,

$$x[\text{FeO}]\text{O}_2\text{C}(\text{CH}_2)_{15}\text{OH} + x(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3 + 4x\text{H}_2\text{O}$$

Subsequently, the electrode was modified with octadecyltriethoxysilane C₁₈H₃₇Si(OC₂H₅)₃ (C₁₈TES) to form a two-dimensional polymer²⁾⁻⁴⁾,

This polymer coating is called BTESE + C₁₈TES-modified HOC₁₆A⁻ SAM.

In order to prepare an ordered and close packed polymer coating, the HOC₁₆A⁻ SAM was modified in an acetone solution of C₁₈TES at a low concentration, 5 × 10⁻⁴ M (mol dm⁻³) for many hours (93 h, for example). Hence, it took more than 143 h to prepare the coating on the passivated Fe electrode.

Protection of the passive film against breakdown was examined by monitoring the open-circuit potential, *E*_{oc} of the passivated and polymer-coated electrode in 0.1 M NaCl²⁾. The *E*_{oc} value of this electrode was high, more than 0 V vs. SCE (saturated calomel electrode) in the initial region of the immersion time, *t*, indicating the presence of a passive film on the electrode surface. However, the value abruptly decreased to -0.30 V vs. SCE thereafter, being indicative of passive film breakdown and thus, the time required for passive film breakdown, *t*_{bd} was determined as being 8.5 h. Because *t*_{bd} of the passivated electrode was less than 5 min, it was concluded that the polymer coating adsorbed on the passive film prevented breakdown markedly. Further, the protective efficiency, *P* [See Eq. (7).] obtained by polarization measurement of the polymer-coated electrode in 0.1 M NaCl after immersion

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for 4 h was extremely high, 99.9%, leading to a conclusion that complete protection of Fe from corrosion in 0.1 M NaCl was accomplished by coverage with the passive film and polymer coating unless the passive film was broken down²⁾.

The t_{bd} values of the passivated and polymer coated Fe electrode were 45.2 and 12.7 h in 0.1 M KClO₄ and 0.1 M Na₂SO₄, respectively^{5),6)}. Because the values of the passivated electrode in the respective solutions were 10.2 and 0.63 h, passive film breakdown was markedly prevented by covering the passive film with the polymer coating. The P values of the polymer-coated electrode were more than 99.9% in both solutions before t_{bd} , indicating complete protection of Fe against corrosion before breakdown^{5),6)}.

Since NO₃⁻ acts as an inhibitive anion rather than an aggressive one for passive film breakdown of Fe, the t_{bd} value of the passivated and polymer-coated electrode was more than 480 h in 0.1 M NaNO₃. The P values were more than 99.9% during immersion for 72 h but decreased to 98.4% in the region of t up to 480 h because the cathodic reduction of NO₃⁻ and NO₂⁻ occurred for repairing defects within the passive film. No pitting corrosion was observed on the surface and hence, breakdown was suppressed with NO₃⁻ inhibitor predominantly⁷⁾. Thus, healing treatment of the passivated and polymer-coated electrode was markedly effective for prolongation of t_{bd} .

The two-dimensional polymer coating of BTESE + C₁₈TES-modified HOC₁₆A⁻ SAM was prepared on the passivated Fe electrode and treated in 0.1M NaNO₃ for 48 h to heal the passive film. The t_{bd} values of this electrode in 0.1 M KClO₄, 0.1 M Na₂SO₄ and 0.1 M NaCl were markedly increased to >360, >240 and 24.8 h, respectively. The P values before t_{bd} were extremely high, more than 99.9% mostly, indicating complete protection of Fe against corrosion before breakdown. These high values are considered to be attributed to the high protective abilities of both healed passive film and polymer coating.

Preparation of the polymer coating on the passivated electrode and healing treatment in 0.1 M NaNO₃ needed many hours; an example of the total time, Σt was 193 h. An improvement of Σt can be achieved by substitution of octyltriethoxysilane C₈H₁₇Si(OC₂H₅)₃ (C₈TES) for C₁₈TES⁸⁾.

The time for modification with C₁₈TES, 93 h is reduced to 2 h using C₈TES. Because the thickness of the C₁₈TES-modified coating, 5.4 nm is decreased to 4.1 nm of the

C₈TES-modified one, however, the protective abilities of the polymer coating against breakdown and corrosion must be lowered⁸⁾. The present investigation deals with preparation of the two-dimensional polymer coating modified with C₈TES on the passivated Fe electrode and healing treatment in 0.1 M NaNO₃. The E_{oc} monitoring and repeated polarization measurements of the electrode are carried out in oxygenated 0.1 M KClO₄, 0.1 M NaNO₃, 0.1 M Na₂SO₄ and 0.1 M NaCl. The values of t_{bd} and P measured in these solutions are compared with those of the electrode passivated, covered with the C₁₈TES-modified polymer coating and healed in 0.1 M NaNO₃.

2. Experimental

2.1 Materials

Sodium 16-hydroxyhexadecanoate was prepared by neutralization of 16-hydroxyhexadecanoic acid HO(CH₂)₁₅CO₂H with NaOH in ethanol and purified by recrystallization from ethanol. Reagent grade chemicals of BTESE and C₈TES were used without further purification. Reagent grade chemicals of methanol, ethanol, acetone and acetonitrile were utilized as solvents. A borate buffer solution at 8.49 of pH was prepared by diluting analytical reagents, 0.150 M of H₃BO₃ and 0.0357 M of Na₂B₄O₇ with Millipore water. Reagent grade KClO₄, NaNO₃, Na₂SO₄ and NaCl were dissolved into Millipore water to prepare the respective solutions at 0.1 M of the concentration.

A rod of 99.99% Fe (5 mm diameter) was embedded in a Teflon holder and a circular cross section of the rod was adopted as an electrode for electrochemical measurements. The electrode surface was abraded with emery papers and then with 1.0 and 0.3 μm alumina abrasives on a wet felt cloth. The electrode was sonicated in water and then in ethanol and rinsed with water immediately before use.

2.2 Passivation of the Fe electrode and derivatization with NaHOC₁₆A

The Fe electrode was immersed in the borate buffer solution at 30°C for 1 h and passivated in the solution at 0.50 V vs. SCE potentiostatically. Passivation was continued until the passive current density was decreased below 0.50 μAcm⁻² for providing a similar passive film on the electrode in each experiment. It took 2 to 3 h to prepare the passive film on the electrode, depending on surface conditions⁹⁾. After passivation, the electrode was rinsed with water thoroughly.

The passivated electrode was immersed in a methanol-water solution (1:2 in volume) of 1 × 10⁻⁴ M NaHOC₁₆A at 30°C for 44 h, rinsed with water sufficiently and dried in vacuo. The HOC₁₆A⁻ SAM was thus prepared on passivated Fe.

2.3 Modification of the $\text{HOC}_{16}\text{A}^-$ SAM with BTESE and C_8TES

The Fe electrode passivated and covered with the SAM was modified in an acetone solution of 5×10^{-2} M BTESE at 40°C for 2 h under an anhydrous atmosphere and rinsed with acetone. The electrode was then treated in an acetone solution of 1×10^{-2} M H_2O at 40°C for 1.5 h, rinsed with acetonitrile and dried in vacuo. Subsequently, the electrode was immersed in an acetone solution of 5×10^{-2} M C_8TES at 40°C for 2 h, treated in the acetone solution of H_2O at 40°C for 10 min, rinsed with acetonitrile and dried in vacuo. The two-dimensional polymer coating, called BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM, was thus prepared on the passivated Fe electrode.

2.4 Healing treatment of the passivated and polymer-coated electrode in 0.1M NaNO_3

The passivated and polymer-coated Fe electrode was treated in 0.1 M NaNO_3 at 30°C for 48 h to heal the passive film at defects of the polymer coating. The E_{oc} value of the electrode was followed using SCE during the treatment. The electrode was then rinsed with water and dried in vacuo.

2.5 Polarization measurements of the passivated, polymer-coated and healed electrode in various solutions

The values of E_{oc} for the passivated and polymer-coated electrode were monitored with SCE in oxygenated 0.1M KClO_4 and 0.1 M NaNO_3 at 30°C as a function of the immersion time, t for many hours. Changes of the E_{oc} values for the passivated, polymer-coated and healed electrode were followed in 0.1M KClO_4 , 0.1 M Na_2SO_4 and 0.1 M NaCl at 30°C . Passive film breakdown, which is generally realized by an abrupt decrease in E_{oc} , occurred in most cases and hence, t_{bd} was determined in the $E_{\text{oc}}-t$ curve.

Polarization measurements of the electrodes were carried out in aerated 0.1 M KClO_4 , 0.1 M NaNO_3 , 0.1 M Na_2SO_4 and 0.1 M NaCl at 30°C by scanning the potential, E at 20 and 10 mVmin^{-1} of the scan rates in the negative and positive directions from E_{oc} , respectively, using SCE reference and Pt counter electrodes connected to a potentiostat. The measurements were repeatedly conducted after immersion in those solutions for 1.5, 4.0, 10 and 24 h and further, every day up to 10 d.

3. Results and Discussion

3.1 Polarization measurements of the passivated and polymer-coated electrode in 0.1 M KClO_4

Fig. 1 shows an example of E_{oc} change for the Fe electrode passivated and covered with the two-dimensional polymer coating of BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM in aerated 0.1 M KClO_4 as a function of t . The initial value of E_{oc} was -0.118 V vs. SCE, a little lower than the

Fig. 1 Open-circuit potential, E_{oc} of an Fe electrode passivated in a borate buffer solution and covered with a two-dimensional polymer coating of BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM in 0.1 M KClO_4 as a function of the immersion time, t .

values of the electrode covered with the C_{18}TES -modified coating, shown in the previous study⁵⁾⁻⁷⁾. However, E_{oc} was maintained around -0.050 V vs. SCE for 21 h thereafter, implying the presence of a passive film on the surface. Many abrupt downward shifts and recoveries of E_{oc} , called potential spikes, appeared in the $E_{\text{oc}}-t$ curve, revealing precursory phenomena of passive film breakdown. The E_{oc} value decreased abruptly at 21.6 h of t_{bd} , the time for passive film breakdown and a pit appeared on the surface. The E_{oc} value was lowered below -0.40 V vs. SCE in a short range of t . After that, E_{oc} diminished with increasing t gradually and localized corrosion changed to generalized one. Since t_{bd} of the passivated Fe electrode in 0.1M KClO_4 was 10.2 h⁵⁾, the polymer coating protected the passive film from breakdown evidently. Because the t_{bd} value for the electrode passivated and covered with BTESE + C_{18}TES -modified $\text{HOC}_{16}\text{A}^-$ SAM in this solution was 45.2 h⁵⁾, however, the effect of the C_8TES -modified coating on passive film breakdown was inferior to the C_{18}TES -modified one. Incorporation of ClO_4^- through the polymer coating with small C_8 alkyl tails is believed to occur more easily than the one with large C_{18} alkyl tails. There is a substantial difference in the protective ability of the polymer coatings against passive film breakdown between C_8TES - and C_{18}TES -modified ones.

Polarization curves of the bare Fe electrode in oxygenated 0.1 M KClO_4 at $t = 24$ h and the electrode covered with the C_8TES -modified polymer coating at the various immersion times are exhibited in Fig. 2. The anodic process of Fe corrosion in oxygenated neutral electrolytic solutions is dissolution of Fe as Eq. (5).

The cathodic process is reduction of molecular oxygen as Eq. (6).

Marked suppression of the anodic process was presumed at $t = 1.5, 10$ and 24 h due to the presence of the passive

Fig. 2 Polarization curves of a bare Fe electrode at $t = 24$ h (—) and the passivated and polymer-coated one at 1.5 h (---), 10 h (— · —), 24 h (— — —) and 48 h (— · · —) in 0.1 M KClO_4 . The E_{oc} values of the latter electrode at 1.5 and 10 h are indicated with E_{oc}^1 and E_{oc}^2 , respectively.

film on the surface. Inhibition of the cathodic process at $t = 48$ h is attributable to covering the surface with the polymer coating acting as a barrier layer to oxygen diffusion.

The corrosion current density was determined by extrapolation of the cathodic and anodic Tafel lines. The anodic polarization curves for the polymer-coated electrode were not measured in some cases because marked fluctuations of the anodic current density appeared and pit initiation on the passive surface might occur by anodic polarization. Hence, the corrosion current density was approximately obtained by extrapolating the cathodic Tafel line to E_{oc} indicated in the figure.

The protective efficiency, P (%) is expressed by Eq. (7).

$$P (\%) = 100 (1 - i_{cor}/i_{cor}^0) \quad (7)$$

where i_{cor}^0 and i_{cor} denote the corrosion current density of bare and polymer-coated electrodes, respectively. The P values for the electrode with polymer coating of BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM are plotted against t in Fig. 3. The three values before 10 h were extremely high, 99.9%, indicating complete protection of substrate Fe

Fig. 3 Protective efficiency, P for the passivated and polymer-coated electrode in 0.1 M KClO_4 as a function of the immersion time, t .

against corrosion in 0.1 M KClO_4 before $t_{bd} = 21.6$ h. No pitting corrosion appeared on the surface before t_{bd} . The P value decreased with increasing t after t_{bd} and localized corrosion was initiated on the surface at $t = 24$ h. Generalized corrosion was observed around the pit at 36 and 48 h. A part of the surface was not corroded even at 48 h, implying that the polymer coating remained there and prevented Fe corrosion in 0.1 M KClO_4 . Hence, 59.0% of P was kept at 48 h.

3.2 Polarization measurements of the passivated, polymer-coated and healed electrode in 0.1 M KClO_4

The passivated Fe electrode covered with the polymer coating of BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM was treated in 0.1 M NaNO_3 at 30°C for 48 h to repair defects of the passive film. The E_{oc} value of the coated electrode in aerated 0.1 M NaNO_3 was monitored with the immersion time, t . A typical example of E_{oc} change for the coated electrode in 0.1 M NaNO_3 is depicted as a function of t in Fig. 4. The initial value of E_{oc} was -0.140 V vs. SCE, fairly low. However, the value increased slowly and was maintained around -0.10 V vs. SCE during immersion for 48 h. Many small fluctuations appeared before 30 h but the value was stabilized thereafter.

As has been described in the previous paper⁷⁾, NO_3^- acts as an oxidizing inhibitor for Fe corrosion. The cathodic processes Eqs. (8) and (9) and the anodic process, Eq. (5) occur at the surface, and hence, ferrous and ferric hydroxides precipitate and change to their oxyhydroxide or oxides, as Eqs. (10) and (11), resulting in repairing defects within the passive film.

Thus, a defect-free passive film covered with the polymer coating can be prepared on the Fe electrode. In fact, the healing treatment of the passivated electrode covered with the polymer coating of BTESE + C_{18}TES -modified $\text{HOC}_{16}\text{A}^-$

Fig. 4 E_{oc} change for the passivated and polymer-coated electrode during healing treatment in 0.1 M NaNO_3 as a function of the immersion time, t .

SAM is remarkably effective for increasing the t_{bd} value in 0.1 M Na_2SO_4 ⁶⁾, 0.1 M NaCl ¹⁰⁾ and 0.1 M KClO_4 with and without Cl^- ¹¹⁾.

Fig. 5 shows the E_{oc} value of the Fe electrode passivated, covered with BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM and healed in 0.1 M NaNO_3 for 48 h as a function of t in 0.1 M KClO_4 . The protective efficiencies, P_1 and P_2 , of which the former is indicated with a magnified scale corresponding to an extremely high value before t_{bd} and the latter is a usual one, are also shown as a function of t in the figure. The E_{oc} value was high, 0.007 V vs. SCE at the initial stage but decreased and remained between -0.050 and -0.080 V vs. SCE before 57 h. A large downward potential spike appeared at $t = 50$ h. An abrupt decrease of E_{oc} , indicating passive film breakdown, was observed at 57.4 h of t_{bd} . Two pits appeared on the surface, in fact. This increase in t_{bd} from 21.6 to 57.4 h indicated enhanced prevention of passive film breakdown by healing treatment of the passivated electrode. The t_{bd} value, 57.4 h was higher than 45.2 h for the polymer coating prepared using C_{18}TES without healing treatment but lower by far than $t_{bd} > 360$ h for the coating with the treatment. It was concluded that the passive film covered with the polymer coatings was protected against breakdown by the healing treatment. However, the difference in the protective effect on the breakdown between polymer coatings prepared using C_{18}TES and C_8TES was not improved by the treatment.

As indicated with P_1 , the protective efficiencies of the passivated, polymer-coated and healed electrode in 0.1 M KClO_4 were extremely high, more than 99.9% before t_{bd} . However, the efficiency markedly decreased to 40.9% at $t = 72$ h, as shown with P_2 . Complete protection of Fe from corrosion was achieved by coverage with the healed passive film and polymer coating unless the passive film was broken down.

Fig. 5 Values of E_{oc} ($\triangle$), P_1 (magnified scale, $\circ$) and P_2 (usual one, $\square$) for the passivated, polymer-coated and healed electrode in 0.1 M KClO_4 as a function of the immersion time, t . The time for passive film breakdown is indicated with t_{bd} .

3.3 Polarization measurements of the passivated and polymer-coated electrode in 0.1 M NaNO_3

The E_{oc} and P values of the passivated and polymer-coated electrode in aerated 0.1 M NaNO_3 are exhibited as a function of t in Fig. 6. The healing treatment was not adopted in this experiment. The initial value of E_{oc} was -0.087 V vs. SCE and a potential spike appeared immediately after immersion. Thereafter, E_{oc} was maintained around -0.050 V vs. SCE until the end of the test (240 h). A broad potential spike was observed in the range of t between 42 and 44 h, suggesting that pit initiation at a defect of the passive film and healing action of NO_3^- occurred repeatedly. Because NO_3^- in the solution acts as an oxidizing inhibitor for the passivated Fe electrode, the anodic dissolution of Fe, Eq. (5) and the cathodic processes of NO_3^- reduction, Eqs. (8) and (9) took place at the defect, resulting in prevention of pit initiation by the formation of ferrous and ferric oxides, Eqs. (10) and (11). In fact, a tiny localized anodic dissolution feature was detected on the surface but breakdown was prevented completely due to high E_{oc} after 44 h. Thus, no breakdown occurred for the passivated and polymer-coated electrode during immersion in 0.1 M NaNO_3 for 240 h.

The P values of the electrode covered with the passive film and polymer-coating were very high, between 99.91 and 99.94%. It was concluded that protection of Fe from corrosion was completely achieved during immersion of the electrode passivated and covered with the C_8TES -modified polymer coating in 0.1 M NaNO_3 for 240 h. The t_{bd} value of the electrode passivated and covered with the C_{18}TES -modified polymer coating in 0.1 M NaNO_3 was reported to be more than 480 h⁷⁾. A t_{bd} value of the electrode passivated and covered with the C_8TES -modified polymer coating in 0.1 M NaNO_3 is presumed to be > 480 h because NO_3^- markedly inhibited pit initiation and growth on the passive film of Fe¹²⁾.

3.4 Polarization measurements of the passivated, polymer-coated and healed electrode in 0.1 M Na_2SO_4

Sulfate ion is a stronger aggressive anion upon the

Fig. 6 Values of E_{oc} ($\triangle$) and P ($\circ$) for the passivated and polymer-coated electrode in 0.1 M NaNO_3 as a function of t .

passive film of Fe than ClO_4^- but a weaker one than Cl^- ⁶⁾. Fig. 7 demonstrates the E_{oc} , P_1 and P_2 values for the passivated, polymer-coated and healed electrode in oxygenated 0.1 M Na_2SO_4 as a function of t . The E_{oc} value was -0.015 V vs. SCE at the initial stage and many downward potential spikes appeared. However, the value was kept around -0.010 V vs. SCE basically and an abrupt decrease in E_{oc} happened at $t_{\text{bd}} = 19.2$ h. This value is lower than 57.4 h, that of the electrode in 0.1 M KClO_4 ⁵⁾, indicating that SO_4^{2-} is a stronger aggressive anion than ClO_4^- . The t_{bd} value, 19.2 h was lower by far than >240 h, the value of the passivated, C_{18}TES -modified polymer-coated and healed electrode in 0.1 M Na_2SO_4 ⁶⁾. Although the passive film was healed in 0.1 M NaNO_3 , the thicker C_{18}TES -modified coating was superior to the C_8TES -modified one to prevent passive film breakdown in 0.1 M Na_2SO_4 .

The P_1 values for the passivated, polymer-coated and healed electrode in 0.1 M Na_2SO_4 before t_{bd} were extremely high, more than 99.9%, indicating complete prevention of Fe corrosion unless passive film breakdown occurred. After t_{bd} , the protective efficiency rapidly decreased to 41.3% at $t = 48$ h as the P_2 value shows. A pit appeared on the surface and localized corrosion changed with increasing t to generalized one.

3.5 Polarization measurements of the passivated, polymer-coated and healed electrode in 0.1 M NaCl

The values of E_{oc} , P_1 and P_2 for the passivated, C_8TES -modified polymer-coated and healed Fe electrode in aerated 0.1 M NaCl are exhibited as a function of t in Fig. 8. The value of E_{oc} was -0.120 V vs. SCE initially, increased to -0.060 V vs. SCE before 4 h and abruptly diminished to -0.40 V vs. SCE at $t_{\text{bd}} = 9.0$ h. A pit appeared on the surface at $t = 10$ h and generalized corrosion occurred around pit(s) on the surface at 24 h. This t_{bd} value was higher than 5.5 h of t_{bd} for the electrode passivated and covered with the C_8TES -modified polymer

Fig. 7 Values of E_{oc} ($\triangle$), P_1 ($\circ$) and P_2 ($\square$) for the passivated, polymer-coated and healed electrode in 0.1 M Na_2SO_4 as a function of t .

Fig. 8 Values of E_{oc} ($\triangle$), P_1 ($\circ$) and P_2 ($\square$) for the passivated, polymer-coated and healed electrode in 0.1 M NaCl as a function of t .

coating without the healing treatment, measured in the previous experiment²⁾. The healing treatment of the passivated and polymer-coated electrode was effective for preventing passive film breakdown in 0.1 M NaCl evidently. On the other hand, t_{bd} for the passivated, covered with the C_{18}TES -modified polymer coating and healed electrode in 0.1 M NaCl was 24.8 h¹⁰⁾, being higher than t_{bd} in the present investigation. As mentioned above, large C_{18} alkyl tails of the polymer coating are considered to hinder diffusion of Cl^- through the coating without difficulty as compared with small C_8 alkyl tails of the coating and hence, the result is reasonable.

The protective efficiencies of the passivated, polymer-coated and healed electrode in 0.1 M NaCl at $t = 1.5$ and 4.0 h were extremely high, both 99.96%. Thus, complete protection of Fe from corrosion in 0.1 M NaCl was achieved by covering the electrode with the healed passive film and polymer coating before breakdown. After t_{bd} , P_2 decreased with an increase in t , to 70.5% at 24 h. Many pits appeared and generalized corrosion occurred on the surface.

4. Conclusions

An ultrathin, two-dimensional polymer coating of BTESE + C_8TES -modified $\text{HOC}_{16}\text{A}^-$ SAM was prepared on the passivated Fe electrode. The passive film on the electrode was then healed in 0.1 M NaNO_3 for 48 h. Since it took about 100 h to modify the $\text{HOC}_{16}\text{A}^-$ SAM adsorbed on the passivated electrode with BTESE and C_{18}TES , modification with C_8TES was adopted instead of C_{18}TES in this study and hence, the time required for modification was markedly shortened to about 6 h. Protection of the passive film against breakdown and Fe against corrosion was examined by monitoring the open-circuit potential, E_{oc} and repeated polarization measurements of the passivated and polymer-coated or passivated, polymer-coated and healed electrode in oxygenated 0.1 M KClO_4 , 0.1 M NaNO_3 , 0.1 M Na_2SO_4 and 0.1 M NaCl. The time for

passive film breakdown, t_{bd} was determined from an abrupt E_{oc} decrease in the $E_{oc}-t$ curve. The t_{bd} value of the passivated and polymer-coated electrode in 0.1 M $KClO_4$ was 21.6 h, whereas the value of the passivated, polymer-coated and healed electrode was 57.4 h, indicating that passive film breakdown was prevented to a more extent by the healing treatment. No breakdown occurred on the passivated and polymer-coated electrode in 0.1 M $NaNO_3$ for 240 h. The t_{bd} values of the healed electrode were 19.2 and 9.0 h in 0.1 M Na_2SO_4 and 0.1 M $NaCl$, respectively, exhibiting enhanced protection of the passive film against breakdown by the treatment. However, these values were lower than those of the passivated, covered with the $C_{18}TES$ -modified coating and healed electrode in the respective solutions.

The values of the protective efficiency, P obtained by polarization measurements of the passivated, polymer-coated and healed electrode were extremely high, more than 99.9% all in the four solutions before t_{bd} . Thus, complete protection of iron from corrosion in these solutions was accomplished by covering the Fe electrode with the healed passive film and the polymer coating of $BTSE + C_8TES$ -modified $HOC_{16}A^-$ SAM unless the

passive film was broken down.

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要 旨

不動態化 Fe 電極上を覆った超薄高分子皮膜の作製に必要な時間を短縮するために、電極に吸着した 16-ヒドロキシヘキサデカン酸イオン $HO(CH_2)_{15}CO_2^-$ の自己組織化膜を 1,2-ビス(トリエトキシシリル)エタン $(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3$ とオクチルトリエトキシシラン $C_8H_{17}Si(OC_2H_5)_3$ を用いて修飾した。さらに、不動態化し、高分子で覆った電極を 0.1 M $NaNO_3$ 中で処理し補修した。不動態皮膜破壊までの時間 t_{bd} と防止率 P (%) を 0.1 M $KClO_4$, 0.1 M $NaNO_3$, 0.1 M Na_2SO_4 および 0.1 M $NaCl$ 中に長時間浸漬した時の開回路電位のモニターと繰り返し分極測定により求めた。 t_{bd} の値はそれぞれ 57.4, >240, 19.2 および 9.0 h であった。不動態皮膜破壊は高分子皮膜の被覆と補修処理によって非常に抑制された。これらの溶液中における P の値は t_{bd} 以前は 99.9% 以上と非常に高く、不動態皮膜破壊が起こらない限り、地金 Fe 腐食の防止は電極を補修した不動態皮膜と高分子皮膜で覆うことで達成できることを示した。

キーワード 不動態化鉄, 自己組織化膜, 二次元重合体, 補修処理, オクチルトリエトキシシラン, 不動態皮膜破壊, 完全防食