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Corrosion prevention of passivated iron in 0.1 M NaCl by coverage with an ultrathin polymer coating and healing treatment in 0.1 M $NaNO_3$

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ABSTRACT

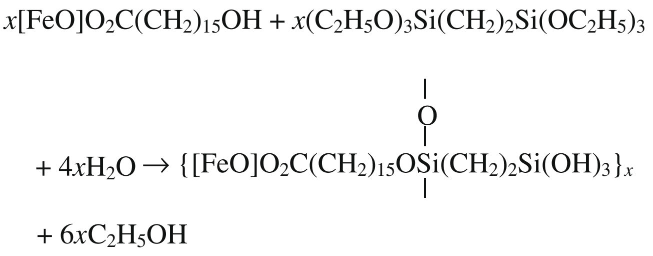
An ultrathin, ordered and two-dimensional polymer coating was prepared on a passivated iron electrode by modification of 16-hydroxyhexadecanoate ion $HO(CH_2)_{15}CO_2^-$ self-assembled monolayer with 1,2-bis(triethoxysilyl)ethane $(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3$ and octadecyltriethoxysilane $C_{18}H_{37}Si(OC_2H_5)_3$. Subsequently, the electrode was healed in 0.1 M $NaNO_3$. Protection of passivated iron against passive film breakdown and corrosion of iron was examined by monitoring of the open-circuit potential and repeated polarization measurements of the polymer-coated and healed electrode in an aerated 0.1 M NaCl solution during immersion for many hours. Localized corrosion was markedly prevented by coverage with the polymer coating and the healing treatment in 0.1 M $NaNO_3$. Prominent protection of iron from corrosion in 0.1 M NaCl was observed before the breakdown occurred. The electrode surface covered with the healed passive film and polymer coating was analyzed by contact angle measurement, X-ray photoelectron spectroscopy and electron-probe microanalysis.

1. Introduction

In our previous study [1,2], breakdown of a passive film in a borate buffer solution (pH 8.49) containing 0.1 M of Cl^- was completely protected by coverage of passivated iron with an ultrathin (less than 5.4 nm in thickness), ordered (self-assembly) and interconnected (two-dimensional polymer) coating. An iron electrode was passivated in the borate buffer and derivatized in a solution of sodium 16-hydroxyhexadecanoate $NaHO(CH_2)_{15}CO_2$ ($NaHOC_{16}A^-$) to form a self-assembled monolayer (SAM) of 16-hydroxyhexadecanoate ion $HO(CH_2)_{15}CO_2$ ($HOC_{16}A^-$) on a passive film surface of iron [FeO]OH, as

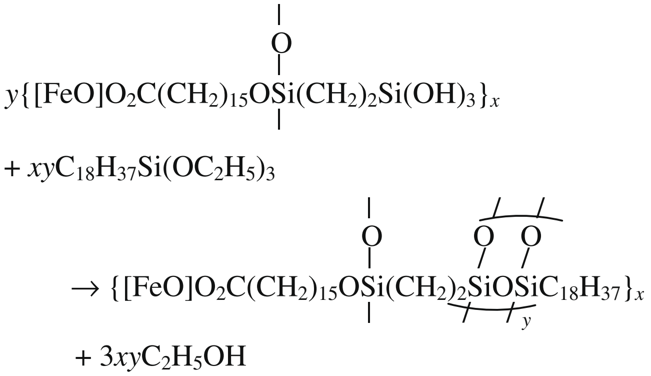
$$[FeO]OH + HO(CH_2)_{15}CO_2^- \rightarrow [FeO]O_2C(CH_2)_{15}OH + OH^- \quad (1)$$

The SAM was modified in a solution of 1,2-bis(triethoxysilyl)ethane $(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3$ (BTESE) followed by hydrolysis with water, as



$$x[FeO]O_2C(CH_2)_{15}OH + x(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3 + 4xH_2O \rightarrow \{[FeO]O_2C(CH_2)_{15}O\underset{|}{\overset{\overset{|}{O}}{\overset{|}{Si}}}(CH_2)_2Si(OH)_3\}_x + 6xC_2H_5OH \quad (2)$$

Subsequently, the electrode surface was modified with octadecyltriethoxysilane $C_{18}H_{37}Si(OC_2H_5)_3$ ($C_{18}TES$),



$$y\{[FeO]O_2C(CH_2)_{15}O\underset{|}{\overset{\overset{|}{O}}{\overset{|}{Si}}}(CH_2)_2Si(OH)_3\}_x + xyC_{18}H_{37}Si(OC_2H_5)_3 \rightarrow \{[FeO]O_2C(CH_2)_{15}O\underset{|}{\overset{\overset{|}{O}}{\overset{|}{Si}}}(CH_2)_2(\overset{\overset{/}{O}}{\overset{/}{Si}}O\overset{\overset{/}{O}}{\overset{/}{Si}})_yC_{18}H_{37}\}_x + 3xyC_2H_5OH \quad (3)$$

to form a two-dimensional polymer [1–3]. The structure of the polymer coating has been illustrated in the preceding paper schematically [4].

Anodic polarization curves of the passivated and polymer-coated iron electrodes were measured in the borate buffer containing 0.1 M of Cl^-. The protective ability of the coating against passive film breakdown was evaluated from the pitting potential, E_{pit}. Disappearances of E_{pit} and current spikes were observed in the passive and transpassive regions of the polarization curve for the polymer-coated electrode, leading to a conclusion that the breakdown in the borate buffer containing 0.1 M Cl^- was protected

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by coverage with the two-dimensional polymer coating completely [1,2].

Because a borate ion can act as an inhibitor for breakdown of the passive film on iron, the polymer-coated electrode was examined by monitoring of the open-circuit potential, E_{oc} and repeated polarization measurements of the coated electrode in an aerated 0.1 M NaCl solution. The coating also prevented the breakdown in 0.1 M NaCl, indicating that the breakdown occurred at 8.5 h after immersion in the solution, whereas the bare passivated electrode was broken down at less than 5 min [3]. Cooperation of the passive film and polymer coating resulted in an extremely high value of the protective efficiency, P (See Eq. (9)), more than 99.9% unless the breakdown took place, indicating complete protection of iron against corrosion in 0.1 M NaCl [3].

Effects of some anions other than Cl^- in their solutions on breakdown of the passivated iron electrode covered with the polymer coating and corrosion of iron at the coated electrode before breakdown were investigated in the previous study [4–6]. On the basis of anion effects on localized corrosion kinetics, anions are classified into three groups [7,8],

(1) aggressive anions which cause localized corrosion, for example, Cl^-, Br^-, I^-, ClO_4^-, SO_4^{2-} and NO_3^-,
(2) anions which accelerate localized corrosion induced by aggressive anions but do not themselves cause localized corrosion, for example, NO_3^- and SO_4^{2-},
(3) anions which inhibit the localized corrosion rate and increase E_{pit}, for example, NO_3^-, SO_4^{2-}, ClO_4^-, CrO_4^{2-}, PO_4^{3-} and OH^-.

In our previous study [9], Cl^-, Br^- and I^- were classified into aggressive anions for passive film breakdown on iron in the borate buffer solution at pH 8.49 but ClO_4^- and SO_4^{2-} into non-aggressive anions. Because a borate ion acts as an oxidizing inhibitor in the presence of O_2, it is not clear whether ClO_4^-, SO_4^{2-} and NO_3^- belong to aggressive or inhibitive anions for passive film breakdown of iron in their solutions. Hence, effects of the passive film and polymer coating on breakdown and corrosion of passivated iron were investigated by E_{oc} monitoring and repeated polarization measurements in aerated 0.1 M $KClO_4$ [5], 0.1 M $NaNO_3$ [6] and 0.1 M Na_2SO_4 [4].

The time required for passive film breakdown, t_{bd} of the passivated electrode in 0.1 M $KClO_4$ was 10.2 h, whereas the value of the passivated and polymer-coated electrode was prolonged to 45.2 h. The P value of the passive film and polymer coating was more than 99.9% before the passive film was broken down [5]. Hence, ClO_4^- was estimated as being a markedly weak aggressive anion.

No breakdown of the polymer-coated passive film occurred in 0.1 M $NaNO_3$ during immersion for 480 h, indicating that NO_3^- is an inhibitive anion rather than an aggressive one for the breakdown. In fact, NO_3^- acted as an inhibitor for pit initiation and growth in the borate buffer containing Cl^- [10]. More than 98.3% of P was obtained and no localized corrosion was observed on the whole area of surface during immersion in 0.1 M $NaNO_3$ for 480 h, being indicative of complete protection against iron corrosion in this solution [6]. On the other hand, SO_4^{2-} was fairly aggressive since t_{bd} of the polymer-coated electrode in 0.1 M Na_2SO_4 was 12.7 h. After the polymer-coated passive film on the electrode was healed by treatment in 0.1 M $NaNO_3$ for 48 h, the electrode was examined in 0.1 M Na_2SO_4. No breakdown appeared during immersion in 0.1 M Na_2SO_4 for 240 h, implying a significant effect of the healing treatment in 0.1 M $NaNO_3$ on prevention of the breakdown [6]. It was concluded that prominent cooperative protection of iron was accomplished against corrosion in these solutions by coverage with the passive film and polymer coating [4–6].

The present investigation deals with the effects of healing treatment in 0.1 M $NaNO_3$ for the passivated iron electrode covered with the polymer coating on protection of the passive film against breakdown in an oxygenated 0.1 M NaCl solution and prevention of iron corrosion in the solution. Monitoring of E_{oc} and repeated polarization measurements of the electrode were carried out in 0.1 M NaCl after immersion for many hours. The surface of the passivated, polymer-coated and healed electrode was analyzed by contact angle measurement, X-ray photoelectron spectroscopy (XPS) and electron-probe microanalysis (EPMA).

2. Experimental methods

2.1. Materials

A rod of 99.99% iron (5 mm diameter) was embedded in a Teflon holder and a circular cross section was used as an electrode for electrochemical experiments. A disk of 99.99% iron (10 mm diameter) was fixed at the end of a glass tube holder using thermo-shrinkable Teflon tubes and the outside surface of the disk was utilized as an electrode for contact angle measurement, XPS and EPMA. The surfaces of electrodes were abraded with emery papers and then with 1.0 and 0.3 μm alumina abrasives on wet felt cloths. The electrodes were sonicated in water and then in ethanol and rinsed with water immediately before use.

Sodium 16-hydroxyhexadecanoate $NaHO(CH_2)_{15}CO_2$ ($NaHOC_{16}A$) was prepared by neutralization of 16-hydroxyhexadecanoic acid $HO(CH_2)_{15}CO_2H$ with NaOH in ethanol and purified by recrystallization from ethanol. High grade reagents of BTESE and $C_{18}TES$ were adopted as modifiers of the $HOC_{16}A^-$ SAM without further purification. Organic solvents, methanol, ethanol, acetone and acetonitrile (AN) were all high grade chemicals. A borate buffer solution at 8.49 of pH was prepared by diluting analytical reagents, 0.150 M of boric acid H_3BO_3 and 0.0357 M of sodium tetraborate $Na_2B_4O_7$ with Millipore water. For healing treatment of the passivated and polymer-coated electrode, 0.1 M $NaNO_3$ solution was prepared by dissolving an analytical reagent of $NaNO_3$ into Millipore water. An analytical reagent of NaCl was dissolved in Millipore water to prepare a corrosive solution, oxygenated 0.1 M NaCl.

2.2. Passivation of the iron electrode and preparation of the $HOC_{16}A^-$ SAM

The iron electrode was passivated in the borate buffer solution (30 °C) at 0.50 V/SCE using a saturated calomel reference electrode (SCE) and a platinum counter electrode potentiostatically. The passivation was continued until the passive current density decreased below 0.50 $\mu A/cm^2$ for providing a similar passive film on the electrode in each experiment. After passivation, the electrode was rinsed with water thoroughly and dried by a warm air-blow.

The passivated electrode was derivatized in a methanol–water solution (1:2 in volume) of 1×10^{-4} M $NaHOC_{16}A$ at 30 °C for 44 h to prepare the $HOC_{16}A^-$ SAM on the passive film [11]. The electrode was sufficiently rinsed with water and dried in vacuo.

2.3. Preparation of the two-dimensional polymer coating on passivated iron

The passivated iron electrode coated with the $HOC_{16}A^-$ SAM was modified in an acetone solution of 5×10^{-2} M BTESE at 40 °C for 2 h under a dry 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 AN and dried in vacuo. Subsequently, the electrode was immersed in an acetone solution of 5×10^{-4} M $C_{18}TES$ at 40 °C for 93 h and treated in the acetone solu-