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** Electrochemical Society Active Member.

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Fig. 2. Effect of rotation rate on anodic polarization of Fe in 3M NaCl + 20 mM BTA.

20 mM BTA. For both uninhibited and inhibited Fe, a thick black porous film formed on the disk surface as the peak current was approached. Previous experimental studies indicated that the black porous film formed during electrodissolution of uninhibited Fe consisted of FeCl₂.²⁵,²⁶

Figure 2 shows that anodic dissolution of inhibited Fe in 3M NaCl was significantly affected by the rotation rate; above 600 rpm, an anodic film was not observed, and the current increased monotonically with increase in potential. Limiting current vs. the square root of rotation rate plots are linear through the origin (Fig. 3), indicating that electrodissolution of Fe was mass-transfer controlled in this region up to 600 rpm. For 20 mM BTA and <600 rpm, a rapid increase in current was observed at about 3.5 V. At potentials above this transition region, which was not observed in the absence of BTA, Fe dissolution was not as strongly dependent on the rotation rate.

Potential oscillations.—Potential oscillations were observed within and above the limiting diffusion current region for both uninhibited and inhibited Fe. Figure 4 shows waveforms of potential oscillations at 200 rpm, 2.20 A/cm², and various concentrations of BTA. Irregular potential oscillation waveforms were observed for all BTA concentrations with higher BTA concentrations exhibiting higher mean potentials but smaller amplitudes.

Potential oscillations for both uninhibited¹⁸ and inhibited Fe were strongly dependent on current density (Fig. 5). Immediately below the limiting current density, where the Fe surface was fully covered with a black film, oscillatory behavior of inhibited Fe was not evident. As the applied
current density was increased further, the surface coverage of the black film started to decrease, at which point oscillations were observed. In contrast to uninhibited Fe, oscillations of inhibited Fe (20 mM) appeared, disappeared, and then reappeared again with increasing current density (Fig. 5). At both 200 and 400 rpm, oscillations of inhibited Fe in the post-limiting current region had different behavior at potentials below and in the vicinity of the transition region, where the current sharply increased. Below this transition region, waveforms were uniform, the oscillation frequency increased, but the amplitude decreased with increasing current density.

At 0.63 A/cm², as shown in Fig. 6, the relatively uniform oscillations with a mean oscillation potential of about 1.5 V abruptly ceased at 300 s and dropped down to a steady-state potential of about 0.25 V. Our previous rotating-ring-disk studies indicated that Fe(III) was detected at about 1.5 V; the solubility of FeCl₃ is considerably greater than FeCl₂. When the applied current density was increased to 0.94 A/cm² (Fig. 5), the steady-state potential increased to about 0.6 V, and oscillations were not observed. At higher current densities/potentials within and above the transition region, sustained oscillations were again observed. However, the wave forms were quite irregular with higher mean oscillation potentials.

As shown in Fig. 7, the frequency and amplitude of the potential oscillations of inhibited Fe, as observed previously for uninhibited Fe, decreased with increasing rotation rate, indicating the effect of the increased rate of mass transport of dissolved FeCl₂ species on the stability of the anodic film. At sufficiently high rotation rates, oscillations were completely suppressed due presumably to the complete disappearance of the visible surface film.

Characterization of the potential oscillations by nonlinear dynamic analysis.—In the presence of BTA, Fe exhibited aperiodic potential oscillations, as observed previously for uninhibited Fe. Power spectra, phase portraits, Poincaré sections, correlation dimensions, and Lyapunov exponents have been determined from the experimental time series in order to characterize the temporal behavior of these oscillations.

Figures 8 and 9 show power spectra of the time series in Fig. 4 and 5, respectively, following the calculation procedures described in the previous paper. The power spectra for the potential oscillations of both uninhibited and inhibited Fe exhibited dominant frequency components (Fig. 8). The general spectra, however, had broad bands, indicating
Fig. 10. Two-dimensional projection of the phase space plot constructed from the time series in Fig. 4 for inhibitor concentration and time delay (a) 0 mM BTA: \( T = 0.13 \) s, (b) 3.5 mM BTA: \( T = 0.14 \) s, (c) 20 mM BTA: \( T = 0.17 \) s; from the time series in Fig. 5 for current density and time delay (d) 1.89 A/cm²: \( T = 0.11 \) s, (e) 0.63 A/cm²: \( T = 0.07 \) s, (f) 0.31 A/cm²: \( T = 0.09 \) s. (T is one-fifth to one-tenth of the mean orbital period.)
chaotic oscillations. For uninhibited Fe, the power spectrum consisted of several major frequency components at \( v = 2.0 \) Hz and a dominant frequency at \( v = 3.8 \) Hz. With the addition of 3.5 mM BTA, the dominant frequency occurred at 0.5 Hz. With further increase in concentration to 20 mM, the dominant frequency component shifted to 1.2 Hz. For both 3.5 mM and 20 mM BTA, the sharp peak at 3.8 Hz, as for uninhibited Fe, was observed. At the higher BTA concentration of 35 mM, however, broader spectral lines were observed.

The effect of applied current density on oscillation frequencies for inhibited Fe (20 mM BTA) is shown in Fig. 9. A narrow range of frequencies was evident at the lower current densities of 0.31 and 0.63 A/cm², while the sharp peak at 3.6 Hz and several frequency components between 0.5 and 1.2 Hz were observed at the higher current densities of 1.89 and 2.20 A/cm².

The 2-D projections of phase-space portraits, as shown in Fig. 10 and 11, were constructed from the time series of uninhibited (a) and 3.5 mM BTA-inhibited (b) Fe had similar chaotic appearances, while those of 20 mM (c) and 35 mM BTA-inhibited (data not shown) Fe had more ordered structures. Figure 10 also shows the effect of applied current densities on the phase portraits of inhibited Fe (20 mM BTA). A decrease in current density from 2.20 to 1.89 A/cm² (both within the transition region, Fig. 2) resulted in a more complex appearance with much higher divergence rates of the nearby trajectories. As the current density was decreased further, simpler and more ordered phase-portrait structures were obtained.

Figure 11 shows the effect of rotation rate on the phase portraits. At 200 rpm and 2.50 A/cm², there was a dense constricted region at lower potentials. When the rotation rate was increased to 400 rpm, the chaotic attractor assumed a more contracted form.

The Poincare sections of the attractors in Fig. 10 are given in Fig. 12. Poincare sections for the attractors in Fig. 11 were also obtained but are not shown. The deterministic nature of the potential oscillations rather than random noise is indicated by the structured set of points for both inhibited and uninhibited Fe.

The dimensions of the attractors for both uninhibited and inhibited Fe were estimated following the procedure by Grassberger and Procaccia and applied to the oscillatory behavior of Fe in H₂SO₄ by Diem and Hudson. Further details are also given in Part VIII of this series. By utilizing the power law form of Grassberger and Procaccia's correlation integral, \( C(r) = A r^n \), the correlation dimension, \( n \), can be determined by linear regression of \( \log C(r) \) vs. \( \log r \) plots. The correlation dimension gives the lower bound for attractor dimensions. For chaotic oscillations, the slope of log-log plots of \( C(r) \) vs. \( r \) would become independent of the embedding dimension, \( m \), this limiting value of the slope is the estimated correlation dimension. On the other hand, irregular oscillatory behavior due to random noise would lead to continuously increasing slopes of the log-log plots with increasing \( m \).

The attractor dimensions for the time series shown in Fig. 4, 5, and 7 were determined from the log-log plots of \( C(r) \) vs. \( r \) for Fe dissolution in 20 mM BTA at 200 rpm and 2.20 A/cm² (Fig. 13). Linear behavior over a relatively wide range of \( r \) was obtained. Similar linear regions were also obtained for such plots at other BTA concentrations, current densities, and rotation rates. The slopes (0 to 35 mM BTA), obtained by linear regression, were plotted against the embedding dimensions \( m \), as shown in Fig. 14. For both uninhibited and inhibited Fe, convergence to a constant slope was approached with increasing \( m \), indicating deterministic chaotic oscillatory behavior. The correlation dimensions were estimated by extrapolation of \( n \) to \( m^{-1} = 0 \) (\( n_r \)). These values are presented in Table I. For current densities below the transition region, the correlation dimension has a value of 2.20, while above the transition region, the correlation dimensions are between 2.62 and 2.89. The correlation dimensions are less than three, indicating that the chaotic attractors should be embeddable in a three-dimensional phase space with a minimum of three first-order ordinary differential equations required to describe the dynamical behavior, consistent with the results of Poincare sections.

The largest Lyapunov exponent, which provides a measure of the exponential divergence of nearby trajectories in phase space, is positive valued for a chaotic state. Calculations of the Lyapunov exponents for the time series in Fig. 4, 5, and 7 were performed with the algorithm of Wolf et al. The largest Lyapunov exponents and the parameters (embedding dimension, delay time, propagation time, upper and lower limits of the magnitude of a vector's transverse component) chosen for determining these Lyapunov exponents are also given in Table I. For uninhibited and inhibited Fe, the positive values are a further indication of chaotic behavior. A comparison of the attractors shows the
Fig. 12. Poincaré sections of Fig. 10 with the planes (a) 0 mM BTA: $E(t) = 2.7 \, \text{V}$, (b) 3.5 mM BTA: $E(t) = 2.8 \, \text{V}$, (c) 20 mM BTA: $E(t) = 4.3 \, \text{V}$; (d) 1.89 A/cm²: $E(t) = 2.7 \, \text{V}$, (e) 0.61 A/cm²: $E(t) = 1.8 \, \text{V}$, (f) 0.31 A/cm²: $E(t) = 1.4 \, \text{V}$.
smallest exponential divergence rate of the nearby trajectories for 20 mM BTA. It is also noted that increasing rotation rate increases the exponential divergence rate.

Discussion

Anodic film formation in the absence and presence of BTA.—Anodic film formation was clearly observed during linear potential sweep experiments for both uninhibited and inhibited iron; a thick and porous black film formed on the iron surface at potentials just below the peak current. Previous experimental studies indicated that the black porous film in the absence of BTA is a ferrous chloride precipitate. Under forced convection conditions film formation is initiated when the Fe-electrolyte interface reaches saturation concentrations of FeCl₂. At limiting diffusion currents, the rotating Fe disk is completely covered with a FeCl₂ film; film dissolution is controlled by mass transport of the diffusion-limiting species, FeCl₂. For uninhibited Fe beyond the limiting diffusion current region, the salt film consisted of Fe(II)-Fe(III)-Cl, as indicated by the cyclic growth and breakdown of the salt film was observed by the reappearance of the film. It was at this point that the disk, then it extended to the center and completely covered the disk. When the current density was increased, the anodic film started to disappear at the disk perimeter with the disappearance of the film extending to the center of the disk until it was film-free; this was followed immediately by the reappearance of the film. It was at this point that the surface film was observed accompanied by the potential oscillations, as shown in Fig. 4 and 5. Disk edges were more highly etched than at the center indicating higher Fe dissolution at the perimeter. Analysis of similar behavior had been performed by Newman and co-workers.

Anodic film formation was also observed under steady-state galvanostatic conditions for both uninhibited and inhibited Fe. Black film first formed at the outer perimeter of the disk, then it extended to the center and completely covered the disk. When the current density was increased, the anodic film started to disappear at the disk perimeter with the disappearance of the film extending to the center of the disk until it was film-free; this was followed immediately by the reappearance of the film. It was at this point that the cyclic growth and breakdown of the salt film was observed accompanied by the potential oscillations, as shown in Fig. 4 and 5. Disk edges were more highly etched than at the center indicating higher Fe dissolution at the perimeter. Analysis of similar behavior had been performed by Newman and co-workers.

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Table I. Correlation dimensions, Lyapunov exponents, and parameters used to compute Lyapunov exponents for potential oscillations of Fe in 3 M NaCl.

<table>
<thead>
<tr>
<th>Embedding dimension</th>
<th>200 rpm and 2.20 A/cm²</th>
<th>20 mM BTA, 200 rpm</th>
<th>20 mM BTA and 2.50 A/cm²</th>
<th>Rotation rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BTA concentration (mM)</td>
<td>Current density (A/cm²)</td>
<td>2.20</td>
<td>200</td>
</tr>
<tr>
<td>Log (r)</td>
<td>2.3</td>
<td>4.3</td>
<td>6.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Log (C(r))</td>
<td>2.3</td>
<td>4.3</td>
<td>6.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Delay time (s)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Evolution time (s)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Max. vector length</td>
<td>1.44</td>
<td>1.31</td>
<td>0.76</td>
<td>1.06</td>
</tr>
<tr>
<td>Min. vector length</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Lyapunov exponent (λ)</td>
<td>1.44</td>
<td>1.31</td>
<td>0.76</td>
<td>1.06</td>
</tr>
<tr>
<td>Correlation dimension (κ)</td>
<td>2.41</td>
<td>2.26</td>
<td>2.89</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Fig. 13. Correlation function vs. distance between points for potential oscillations of Fe in 3 M NaCl + 20 mM BTA, 200 rpm, and 2.20 A/cm².

Fig. 14. Change of slope (n) with increase in embedding dimension (m) for time series in Fig. 4.
The present results suggest that addition of BTA reduced the effective porosity of the film, leading to higher mean oscillation potentials, especially at the higher BTA concentrations (Fig. 4). Within the applied current density region where potential oscillations disappeared (Fig. 5), the Fe surface appeared film-free.

Potential oscillations and the growth and breakdown of the anodic film.—The potential oscillations appeared to reflect the cyclic growth and breakdown of the anodic film. The description and analysis of our laboratory's studies of uninhibited Fe electrodissolution in concentrated chloride solutions have been reported previously. Similar mechanisms of film formation and dissolution during high-rate Fe dissolution in chloride media are applicable in the absence and presence of BTA. This is supported by experimental observations as well as by nonlinear dynamic analysis. For example, potential oscillations were directly associated with anodic film growth and dissolution of both uninhibited and inhibited Fe and both completely disappeared at sufficiently high rotation rates. The dynamical analysis demonstrated the existence of low-dimensional chaotic dynamics in the aperiodic oscillations of both uninhibited and inhibited Fe indicating that the observed potential oscillations correspond to deterministic chaos rather than external random noise.

The oscillation characteristics in the presence of BTA indicate that the inhibitor participates in the growth of the anodic film. As shown in Fig. 4, 6, 10, and 12, a significant change in the oscillation characteristics was observed for BTA ≥ 20 mM compared to uninhibited Fe. First, higher average oscillation potentials were obtained reflecting the presence of the inner nonporous Fe-Cl-BTA film. Corresponding phase portraits of inhibited Fe ([BTA] ≥ 20 mM) show a less complicated appearance (Fig. 10) with smaller divergence rates of the trajectories (Lyapunov exponents, Table 1). Underneath the salt film, the surface appeared smoother, indicating that the presence of BTA stabilized the dynamics of film growth and decay. In the lower-current-density region, potential oscillations were relatively uniform (Fig. 5), and the surface beneath the salt film showed fewer pits than in the higher current density region, where the oscillations were irregular. It was also observed that oscillations disappeared and then reappeared as the applied current density increased (Fig. 5); a change in the nature (thickness and/or composition) of the inner nonporous layer in the intermediate current density/potential range may hinder buildup of the outer porous salt film. These phenomena were not observed for uninhibited Fe.

In summary, application of chaos analysis to oscillatory electrodissolution of Fe in concentrated chloride solutions in the absence and presence of BTA shows different dynamical states of anodic film growth and dissolution. The observed chaotic potential oscillations may be ascribed to aperiodic changes in the surface coverage and porosity of the duplex film. Addition of a sufficient amount of BTA ([BTA] ≥ 20 mM) may have reduced the effective porosity of the duplex film resulting in more uniform potential oscillations and a smoother Fe surface.

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Surface Pretreatment for Electrochemical Fabrication of Ultrathin Patterned Conducting Polymers

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ABSTRACT

Polyaniline grows effectively along the glass substrates pretreated with n-alkylsilane reagents in electropolymerization from aqueous solutions, resulting in the formation of an ultrathin polypyrrole film at twin-microband electrodes. However, no effective promotion of lateral growth of polypyrrole was observed when the substrate was pretreated with 3-aminopropyltriethoxysilane or when the electrolysis was conducted in acetonitrile, suggesting that the hydrophobicity of the substrate is essential for promotion of the lateral growth of polypyrrole. The promotion effect is accounted for by adsorption of pyrrole monomers and selective deposition of intermediate oligomers at the hydrophobic surfaces. The polymerization anisotropy (the ratio of lateral growth rate to vertical growth rate) was ca. 25. The partial pretreatment provided a way of micropatterning with polypyrrole on an insulating substrate. Such a promotion effect at hydrophobic polymerization anisotropy (the ratio of lateral growth rate to vertical growth rate) was ca. 25. The partial pretreatment provided a way of micropatterning with polypyrrole on an insulating substrate. Such a promotion effect at hydrophobic surfaces is amplified in the presence of a small amount of an anionic surfactant. Polyaniline also grows effectively along the lateral growth of polyaniline at a twin-microband electrode also was studied.

Electrochemically conducting organic polymers have been studied extensively over the last decade. Of these polymers, conducting polymers electrochemically synthesized such as polypyrrole and polyaniline have received particular attention due to their high conductivity, chemical stability, and simplicity in synthesis. Electropolymerization evidently is advantageous for fabrication of organic electronic devices since the selective and quantitative growth at the electrode surface enables combination with area-defined microelectrodes. The performance of devices using conducting polymers greatly depends on the characteristics of the polymers; therefore, the control of polymer growth is essential for developing high-performance molecular-based electronic devices. Recently, Martin et al.* reported the preparation of tubular conducting polymers using a microporous membrane as a template upon polymerization. Chemical and electrochemical growth of conducting polymers proceeds along the inner wall of the micropores. This unique morphological characteristic has been used for fabrication of an amperometric biosensor.

Previously we communicated the electrochemical preparation of ultrathin polypyrrole films at a microarray electrode, taking advantage of the promoted lateral growth of polypyrrole along glass surfaces pretreated with an alkylsilane reagent. The array electrodes coated with ultrathin polypyrrole films serve as the electrochemical devices sensitive to redox species, pH of solutions, penicillin, or NADH. Since polypyrrole grows effectively at the pretreated surface, the partial pretreatment of the glass substrate affords a way of micropatterning with polypyrrole. This method for patterning with a conducting polymer on an insulating substrate is useful for future fabrication of molecular devices, which use the unique features of conducting polymers such as the transformation between conducting and insulating states and the incorporation of functional molecules. We report here a detailed study on the lateral growth of polypyrrole along the pretreated surfaces and the applicability to micropatterning with polypyrrole. The lateral growth of polyaniline at a twin-microband electrode also was studied.

Experimental

Chemicals.—Pyrrrole and aniline (Kanto Chemical Co.) were used immediately after being purified by distillation under reduced pressure. n-CH3(CH2)n-SiCl3 (n = 1, 3, 6, 8, 13, 18, Shintetsu Chemical Industries, Ltd.), (NH2CH2CH2CH2)Si(OCH2CH3)3 (Kanto Chemical Co.), and other reagents were used as received. Hexadecane, benzene, and dichloromethane were distilled twice before using for the silanization. All aqueous solutions were prepared with water purified by a Milli-QI (Millipore Co.).

Electrodes.—A twin-microband electrode was used for investigation of anisotropy of polymer growth. The electrode, fabricated by photolithography, has two Pt microbands on a glass substrate; each band is 0.1 μm thick, 10 μm wide, 5 mm long, and separated by 10-100 μm from the adjacent element (Fig. 1). The twin-band electrode was placed at a bottom hole of the electrochemical three-compartment cell with an O-ring (4 mm diam); the total electrode area exposed to the solution was ca. 1 × 10^-3 cm^2. A conventional Pt flag electrode (0.4 cm^2) was used for basic studies. The auxiliary and the reference electrode were a Pt plate and a saturated calomel electrode (SCE), respectively.

Pretreatment of electrode substrates.—The surface pretreatment of the glass part of the electrode was carried out by silanization, i.e., formation of self-assembled alkylsiloxane monolayer films. The substrates were immersed in NaOH-saturated C2H~OH for 12 h, followed by immersion in H2SO4/HNO3 mixture, and rinsing with distilled water. The cleaned substrates were vacuum dried at 70°C for 12 h and then dipped into ca. 20 mM alkyl(trichlorosilane)hexadecane solution under dry Ar. After 3 h, the substrates were removed from the treatment solution and rinsed successively with pure hexadecane, benzene, dichloromethane, and ethanol, and water in an ultrasonic bath. The formation of a monolayer was confirmed by ellipsometric measurements. Judging from the wettability of the treated electrodes, the silanization proceeds mainly at the glass area. The pretreatment with 3-aminopropyltriethoxysilane was prolonged for 6 h because of its comparatively low activity.

Polymerization at twin-microband electrode.—The electropolymerization of pyrrrole at the twin-band electrodes was conducted in a deoxygenated aqueous solution containing 0.1M pyrrrole and 0.1M KNO3 (pH 2 adjusted by adding HNO3) under potentiostatic conditions. The pH of the solution was essential for obtaining reproducible results, because the properties of polypyrrole, especially the conductivity, are highly influenced by pH. The polymerization potential for one of the two bands was set at 650 mV vs. SCE with a bipotentiostat. Figure 2a shows the typical variation of the currents at the two-band electrodes during polymerization. Since the...