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Investigation on inhibition of CrO_4^{2-} and MoO_4^{2-} ions on carbon steel pitting corrosion by electrochemical noise analysis

Z.H. DONG*, X.P. GUO, J.X. ZHENG and L.M. XU
Department of Chemistry, Huazhong University of Science and Technology, Wuhan, China 430074
*(*author for correspondence, e-mail: corrtest@mail.hust.edu.cn)*

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Abstract

The inhibition effect of chromate (CrO_4^{2-}) and molybdate (MoO_4^{2-}) anions on the pitting corrosion of 16Mn carbon steel in 0.1 M NaCl containing bicarbonate solution was studied based on electrochemical noise analysis (ENA) and the potentiodynamic polarization method. The experimental results indicated that, once the pits occur on the surface of the carbon steel after 4–6 h of immersion, increasing the concentration of CrO_4^{2-} and MoO_4^{2-} ions accelerate the repassivation process, and attenuate the duration and the nucleation rate of metastable pits. Further analysis demonstrated that noise resistance R_n might not be suitable for the evaluation of the inhibition efficiency of CrO_4^{2-} and MoO_4^{2-} anions on pitting corrosion in the present system. However, the transient charge q_{pit}, which is an integral of all current transients during a certain period, can characterize the inhibition performance on pitting corrosion. A new definition of inhibition efficiency based on q_{pit} is given.

1. Introduction

Pitting corrosion occurs when passive films break down at local points on surfaces exposed to corrosive environments containing aggressive anions. This causes potential and current fluctuation; such transients are known as electrochemical noise.

It is well known that CrO_4^{2-} and MoO_4^{2-} ions are good inhibitors to the pitting corrosion of steel. Chromates can passivate steel by forming a monatomic or polyatomic oxide film due to their strong oxidizing abilities. It has been shown that chromium is incorporated into the passive film as Cr^{3+} [1]. The effectiveness of molybedate as inhibitor for steel may be ascribed to its ability to provide additional oxygen anions that interfere with the Cl^- adsorption on the metal surface [2]. In addition, a competitive adsorption model has been put forward to describe the inhibition of pitting corrosion, in which aggressive ions (Cl^-) and inhibitive species compete for some active sites on the metal surface. When the ratio of the surface coverage of inhibitive species to Cl^- ions exceeds a certain critical value, pitting nucleation may be inhibited [3].

One of the most attractive aspects of the electrochemical noise (EN) measurement method is its ability to identify the type of corrosion, which is difficult with alternative electrochemical methods. EN has also been shown to be an effective approach to studying pitting processes [4]. It can provide fundamental information about the nucleation, propagation and repassivation process of pitting. It is believed that metastable pits can occur over a wide potential range, well below the pitting potential, and can be observed by the random occurrence of fast potential drops and a small rise in current transients which may vary in magnitude and duration [5].

The current transient pattern corresponding to metastable pits typically consists of a slow rise followed by a sharp recovery (for stainless steel) or a quick rise followed by a slow recovery (for carbon steel and aluminium alloys) [6]. The duration of the current transients mainly depends on the rates of the initiation and death of metastable pits. The potential fluctuation is ascribed to the recharge and discharge of the capacitance of the passive film [7]. It is suggested that potential noise may not be directly related to the pitting process [8].

Noise resistance (introduced by Eden et al. [9]) and spectral noise impedance (introduced by Bertocci et al. [10]) were shown to be the parameters suitable for monitoring many types of corrosion and inhibitor evaluation [11]. In addition, characteristic charge and frequency appear to provide information about the nature and intension of the corrosion process [6].

The present work has investigated the effects of CrO_4^{2-}, MoO_4^{2-} on the noise resistance, the pit nucleation rate, and the integral charge of current transients by the analysis of potential and current fluctuations generated during pitting corrosion. An inhibition efficiency of pitting corrosion was defined based on the integral of the current transients.

2. Experimental details

2.1. *Materials and solutions*

Two cylindrical specimens of 15 mm (dia.) × 5 mm were made from a sheet of 16Mn carbon steel with the chemical composition (wt %): C 0.26, Mn 0.56, P 0.009, Si 0.063 and S 0.031, the remainder was Fe. The two specimens were then embedded in PTFE cuneate rings leaving an area of 0.5 cm^2 exposed to solution, and used as working electrodes (WEs). The surfaces of the WEs were ground with emery paper to 800 grit, cleaned in distilled water and degreased in methanol in sequence. To prevent crevice corrosion, the edge between the specimen and the PTFE ring was coated with a layer of masking lacquer. After the lacquer became dry, the two WEs were immersed into the test solution, facing each other vertically at a distance of 4.0 cm.

The base solution was 0.5 M $NaHCO_3$ with addition of 0.1 M Cl^-. All the solutions were prepared from analytical grade reagents and distilled water.

2.2. *Experimental procedures*

The noise was measured by an in-house built zero resistance ammeter (ZRA) and a voltage follower. The ZRA was employed to measure the current noise between the above two nominally identical WEs. At the same time, with a saturated calomel electrode (SCE) as reference electrode (RE), the voltage follower was employed to measure the voltage noise between the coupled WEs and RE. The current noise and voltage noise were recorded simultaneously.

To increase the accuracies of the ZRA and the voltage follower, a high input impedance ($>10^{12}$ Ω) and low drift (<10 pA/week) chopper-stabilized operational amplifier ICL7650 and a high accuracy Σ–δ 20 bit A/D converter AD7703 were used in the data acquisition system. A minimum voltage resolution of 10 μV and a maximum sampling rate of 8 Hz was achieved. In addition, an analogue anti-aliasing low pass filter was employed before the A/D conversion [12]. Data analysis was accomplished by OriginLab Origin 6.1.

The potentiodynamic measurements were carried out using a PC controlled Solartron 1286 electrochemical interface, with a Pt coil as counter electrode and SCE as reference electrode. The potential scanning rate was 0.3 mV s^{-1}.

All tests were carried out in a thermotank at constant temperature of 38 °C, with an additional shield against electromagnetic interference.

3. Results and discussion

3.1. *Pitting potential of 16Mn carbon steel*

Figure 1 shows the pitting potential and its error measured at various concentrations of CrO_4^{2-} and MoO_4^{2-} ions in the basic solution by potentiodynamic scanning after the test electrodes had been immersed in the solution for 30 min.

As shown in Figure 1, both the chromate and the molybdate move the pitting potential E_{pit} in the more positive direction. However, the CrO_4^{2-} ions have a more positive shift than the molybedate at the same concentration. The action of CrO_4^{2-} and MoO_4^{2-} ions can be explained by the competitive adsorption between Cl^- ions and these inhibitive species [3]. With increase in inhibitor concentration, the adsorption of CrO_4^{2-} or MoO_4^{2-} rather than Cl^- ions predominates, and most pit-sensitive sites on the surface are covered by $Cr(OH)_3$ or MoO_2, which leads to a more positive E_{pit} [2].

3.2. *Features of electrochemical noises*

After 6 h of immersion of the 16Mn steel in 0.1 M Cl^- + 0.5 M $NaHCO_3$ solution, a steady growth state of pits was reached, and a pit of diameter about 0.6 mm appeared on the surface of one of the coupled WEs.

Figure 2(a) shows the potential and current fluctuations measured in the base solution in the absence of CrO_4^{2-} ions. Then a calculated quantity of chromate solution was added to the base solution to yield 0.005 M CrO_4^{2-} concentration in the base solution, and a large potential drift was subsequently observed. When the potential drift became negligible after approximate 20 min, the noise was recorded again, as shown in Figure 2(b). In the same manner, the chromate solution was added to yield 0.01 M and 0.02 M CrO_4^{2-} concentrations in sequence in the above base solution. The corresponding noise records are shown in Figure 2(c) and (d).

As shown in Figure 2, the features of rapid rise and slow recovery of the potential and the current noises were observed. In addition, all the noise spikes are in the

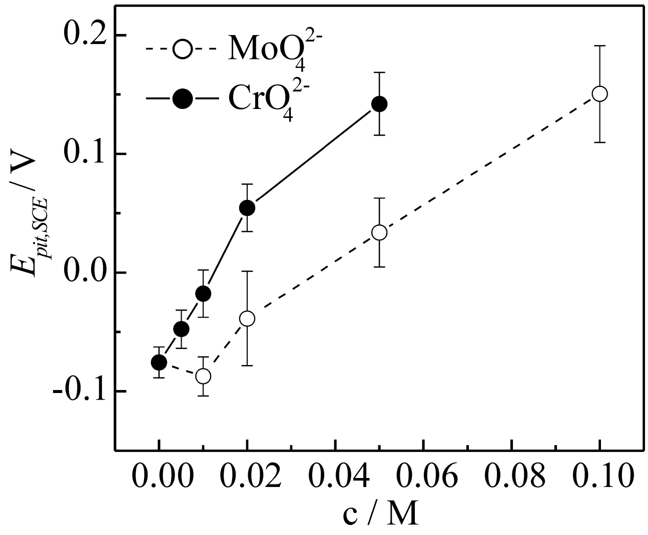

Fig. 1. Pitting potential as a function of chromate and molybdate concentration for 16Mn carbon steel in base solution.

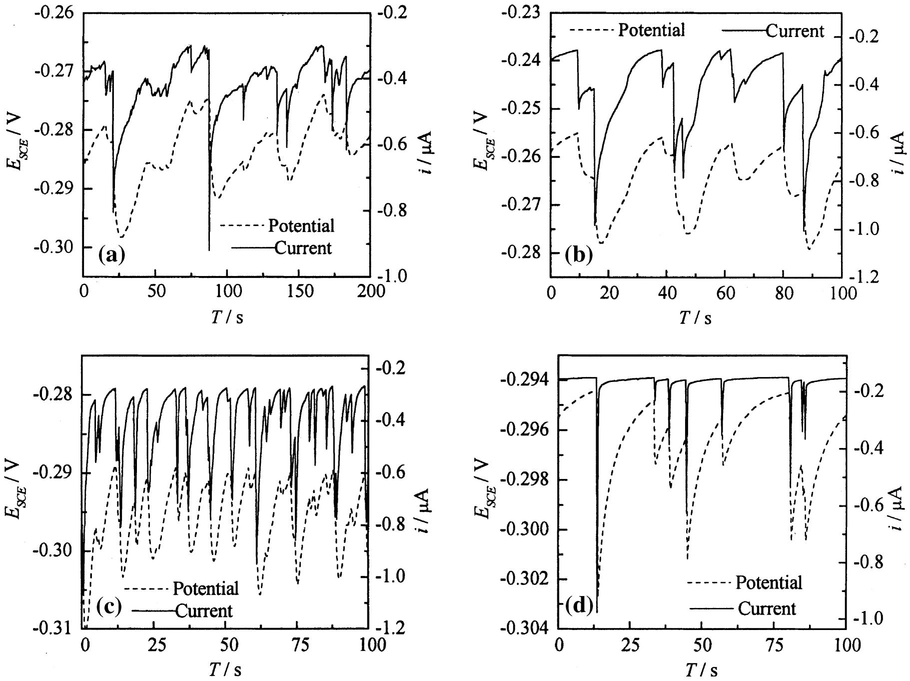

Fig. 2. Potential and current noises of 16Mn carbon steel in base solution in the presence of different chromate concentration. (a) without CrO_4^{2-}, (b) 0.005 M CrO_4^{2-}, (c) 0.01 M CrO_4^{2-} and (d) 0.02 M CrO_4^{2-}.

same direction. Considering the measurement was conducted using a true RE, metastable pits only occurred on the WEs. This resulted in the negative-going potential transients. On the other hand, the two WEs were nominally identical, and pits should occur stochastically in any one of the two WEs, but most current transients occur asymmetrically in only one direction, as shown in Figure 2.

The above asymmetry is not a mere coincidence, and was often observed in this work. According to Cottis [5], it may be ascribed to the slight pH changes that occur as a result of the net current between the two WEs. The nonpitting electrode will be a net cathode, and the neighbouring solution will become more alkaline, which will inhibit pit nucleation. Meanwhile, the pitting electrode will be a net anode, and the solution will get more acidic, which will facilitate pit nucleation, and lead to a large asymmetry between the two WEs.

From Figure 2(a) to (d), the shape and duration of the observed noise transients varied with increasing CrO_4^{2-} concentration. In the absence of CrO_4^{2-} ions, a typical potential or current transient lasted about 25–35 s approximately, and the current and potential transients had almost identical duration. With increase in CrO_4^{2-} concentration, it was found that the amplitude of the potential noise other than the current noise decreased gradually. However, the duration of the current transient declined rapidly from 35 s to 4 s. Meanwhile, there was no obvious decrease in the duration of the potential transient. In addition, a sharp spike in the potential noise was observed in high CrO_4^{2-} concentration.

It is believed that these typical current and potential transients indicate the initiation of metastable pitting. After a short time of pit growth, the repassivation of the pitted site causes the transients to return to their original value. Therefore, the abridgment of duration of current transients suggests that the repassivation process of metastable pits is accelerated with the increasing CrO_4^{2-}. In the meantime, the potential fluctuation during pitting corrosion may mainly result from the dominant effect of the double-layer capacitance [7, 8].

Figure 2(d) shows that the decay of the voltage transients is roughly exponentially, with a time constant of about 9–13 s, which corresponds to the product of a double layer capacity and a charge transfer resistance. This is in agreement with the behaviour observed by Cheng and coworkers [8].

Figure 3 shows the noise pattern of 16Mn steel in base solution with different concentrations of MoO_4^{2-} ions. The features in Figure 3 are similar to those in Figure 2, except for a longer duration of the current transients for the latter, which indicates that the MoO_4^{2-} ions exhibit a weaker repassivation on metastable pits compared with CrO_4^{2-} ions at the same concentration.

3.3. *Inhibitor concentration dependence of pitting corrosion*

3.3.1. *Metastable pit nucleation rate*

The number of current transients over a certain time, here defined as metastable pit nucleation rate λ, was counted based on the Pick Peaks tool available in Origin 6.1. The threshold of the current transient peak is 0.1 μA for all current noise records in Figures 2 and 3, which is the 10% of maximum current peak height (about 1.0 μA for all records in Figures 2 and 3). Namely, the transient peaks could be picked out only if its value was over the threshold.

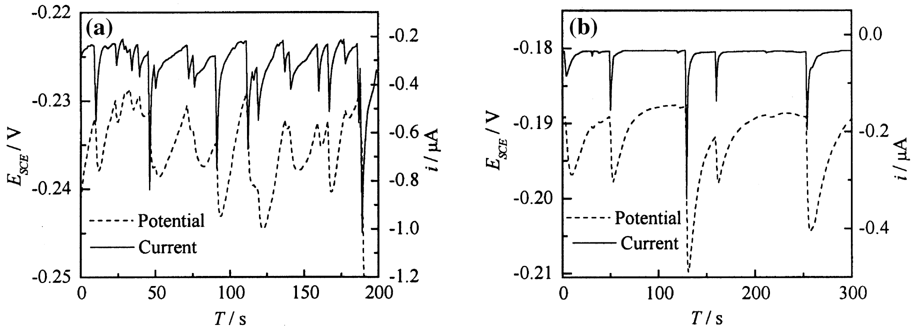

Fig. 3. Potential and current noises of 16Mn carbon steel in base solution in the presence of different molybdate concentration. (a) 0.01 M MoO_4^{2-} and (b) 0.10 M MoO_4^{2-}.

Figure 4 shows the effect of CrO_4^{2-} and MoO_4^{2-} on metastable pit nucleation on 16Mn carbon steel. It is clear that the nucleation rate λ increases with increase in CrO_4^{2-} concentration when below a critical concentration of 0.01 M. However, λ decreases quickly when the CrO_4^{2-} concentration is higher than the critical concentration. It reached a maximum value of 0.188 s^{-1} at 0.01 M CrO_4^{2-} followed by a decline to 0.005 s^{-1} at 0.05 M due to repassivation of existing active sites on the surface of the carbon steel. However, the nucleation rate in the solution containing MoO_4^{2-} decreases less rapidly than in the solution containing CrO_4^{2-}; the nucleation rate in the solution containing 0.1 M MoO_4^{2-} is still about 0.011 s^{-1}.

The nucleation rate mainly correlates to the ratio of the surface coverage of the inhibitive ions to the aggressive Cl^- ions. With increasing CrO_4^{2-} or MoO_4^{2-} anions, more and more adsorbed Cl^- ions are displaced by CrO_4^{2-} or MoO_4^{2-} according to the competitive adsorption model [3], which consequently increases the protectiveness of the passive layer and decreases the nucleation rate.

However, the increase in the nucleation rate in the solution with CrO_4^{2-} concentration less than 0.01 M, may be ascribed to the insufficient oxidizing ability of low CrO_4^{2-} concentration, the insufficient oxidation causes the prepassive layer on the metal surface to be insufficiently stable to resist the attack of Cl^- ions. In this case, as a 'dangerous' inhibitor [13], CrO_4^{2-} ions even accelerate the nucleation of metastable pits in low concentration. Nevertheless, the inhibition ability of MoO_4^{2-} may be mainly ascribed to the formation of a thin film of insoluble molybdate other than its oxidizing activity [2]. Therefore, an insufficient MoO_4^{2-} concentration may not promote the nucleation of metastable pits.

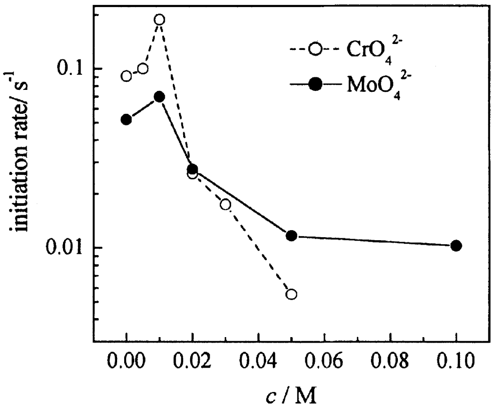

Fig. 4. Effect of chromate and molybdate concentration on metastable pit nucleation rate.

3.3.2. *Noise resistance*

Noise resistance, R_n, was defined by Eden [9] as

$$R_n = \sigma_v(N)/\sigma_i(N) \tag{1}$$

where σ_v and σ_i are the standard deviations of voltage noise and current noise, respectively. N represents the volume of data. In this work, $N = 3072$.

3.3.3. *Transient charge*

The charge of the current transients q_{pit}, which is an integral of all the current transients between the pit initiation (current rise) and the termination of metastable pit growth (current drop) during a certain period, is defined as

$$q_{pit} = \sum_{n=1}^{\lambda T} \int_{t_n}^{t'_n} |i_n(t) - i_b| dt \tag{2}$$

where T is the measurement time of each record (1024 s) and λ is the nucleation rate of a metastable pit. Therefore, the product of λ and T is the total number of current transient events. t_n and t'_n are the initial time and the terminal time of the nth current transient, respectively. i_n(t) is the current as a function of time during the nth current transient, i_b is the baseline of the transients, which is somehow related to the unbalanced corrosion of the coupled WEs. Therefore, i_b must be subtracted from the current transient to yield a net current corresponding to the growth of metastable pits. According to Equation 2, the charge q_{pit} will obviously increase with increase in the amplitude, duration and generation rate of current transients.

Figure 5(a) shows the dependence of R_n and q_{pit} on the CrO_4^{2-} concentration. It is clear that R_n decreases

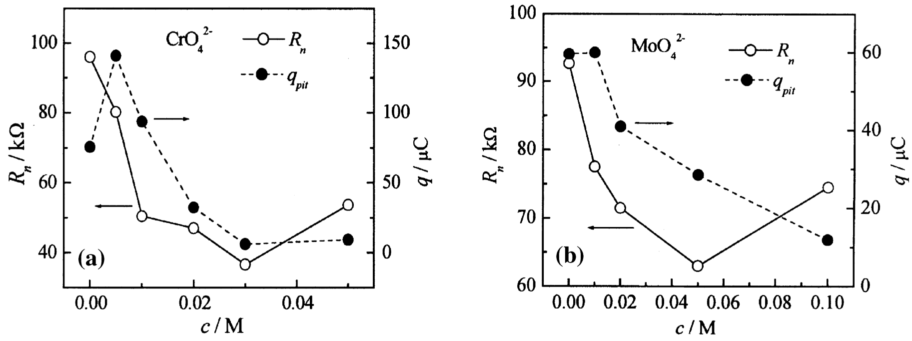

Fig. 5. Change of noise resistance R_n and integral charge q_{pit} with chromate (a) and molybdate (b) concentration.

with the increasing CrO_4^{2-} concentration except for the last data point. The noise resistance has been used to study corrosion rates [14, 15], and it is believed that decreasing R_n is an indication of worsening corrosion. However, the conclusion of increasing corrosion with increase in CrO_4^{2-} concentration apparently disagrees with the experimental results in Figures 1 and 4. The disagreement may be explained by the following analysis. From Figures 2 and 3, it can be seen that the decrease in amplitude of the potential noise is more than that of the current noise with increasing CrO_4^{2-} concentration, which may cause a decrease in the ratio of $\sigma_v(N)$ and $\sigma_i(N)$. In addition, the potential noise is produced by the action of the current noise on the capacitance of the passive film, and the capacitance mainly correlates with the general structure of the passive film, in which general thinning predominates rather than the localized dissolution of the passive film. Therefore, it is questionable if R_n is a criterion of pitting corrosion, and as an index of inhibitor performance on localized corrosion.

On the other hand, Figure 5(a) also shows that the integral charge q_{pit} decreases with increase in CrO_4^{2-} concentration, except for an increase when the concentration is below 0.01 M. The result is consistent with the variation of the nucleation rate shown in Figure 4. The initial increase in q_{pit} is apparently caused by the increasing nucleation rate. The same result was also obtained in MoO_4^{2-} containing solution, as shown in Figure 5(b). It is believed that the value of q_{pit} essentially provides an indication of the amount of metal lost in metastable pitting events. As a consequence, the decrease in the charge with increasing inhibitor concentration is due to the reduction in the duration of the current transient and of the nucleation rate λ. For this reason, it is reasonable to use the value of q_{pit} as the index of pitting corrosion.

3.4. *Inhibition efficiency of pitting corrosion*

From the preceding analysis, current fluctuations are the primary output of the corrosion reaction while potential fluctuations are an indirect output resulting from the effect of current fluctuations on the metal–solution interface impedance. Therefore, the inhibition of pitting corrosion may be characterized by the integral of all current transients, and the inhibition efficiency (η) of inhibitors can be defined as

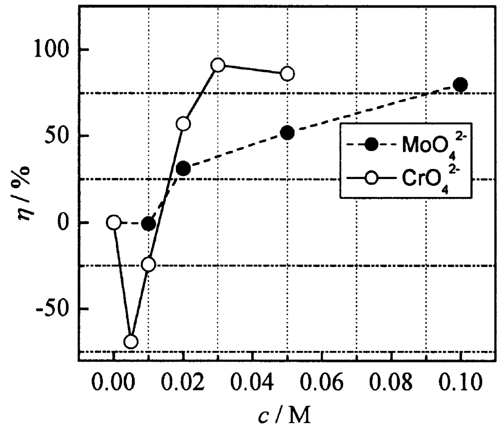

Fig. 6. Change of the inhibition efficiency on pitting corrosion with chromate and molybdate concentration.

$$\eta = \left(\frac{q_b - q_h}{q_b}\right) \times 100\% \quad (3)$$

where q_h and q_b are the transient charges in the presence and absence of inhibitor, respectively. Figure 6 shows the plot of inhibition efficiency against the concentration of CrO_4^{2-} and MoO_4^{2-}.

From Figure 6, it can be seen that η increased with the increasing concentration of CrO_4^{2-} and MoO_4^{2-} ions when the concentrations are above 0.01 M. The inhibition efficiency of CrO_4^{2-} reached 89% at 0.03 M. However, to reach the same inhibition effect of CrO_4^{2-}, the concentration of MoO_4^{2-} must be as five times as that of CrO_4^{2-} at least. The difference may be attributed to the fact that the competitive adsorption ability of CrO_4^{2-} is much stronger than that of MoO_4^{2-}. As a result, the nucleation rate and the duration of metastable pitting will decrease much faster in CrO_4^{2-} containing solution than in MoO_4^{2-} containing solution.

However, Figure 6 also shows that CrO_4^{2-} other than MoO_4^{2-} may promote pitting corrosion when the concentration is below 0.01 M. That is, as a 'dangerous' oxidizing inhibitor, when the concentration of CrO_4^{2-} is insufficient, it accelerates the localized dissolution of carbon steel.

4. Conclusions

(i) In 0.1 M Cl^- containing bicarbonate solution, CrO_4^{2-} and MoO_4^{2-} ions can accelerate the repassivation process of metastable pits. In particular, when the concentration of CrO_4^{2-} increases over the critical concentration of 0.01 M, the nucleation rate, as well as the duration of metastable pits, can be attenuated rapidly.

(ii) The integral charge q_{pit} of the net transient current can be to a certain extent an indicator of pitting corrosion. A more straightforward method to evaluate the inhibition of pitting corrosion is suggested based on the integral charge.

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