

# Features of electrochemical noise generated during pitting of inhibited A516-70 carbon steel in chloride solutions

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The features of electrochemical noise generated during pitting of A516-70 carbon steel in chloride solutions containing  $\text{Na}_2\text{CrO}_4$  were investigated. Polarization curves showed that the threshold  $\text{Cl}^-$  concentration in 0.01 M  $\text{Na}_2\text{CrO}_4$  solution to initiate pitting and the threshold  $\text{CrO}_4^{2-}$  concentration in 0.1 M NaCl solution to maintain passivation for A516-70 carbon steel were approximately 0.1 M and 0.01 M, respectively. Noise measurements indicated that above the critical  $\text{Cl}^-$  concentration, the stochastic current fluctuations appeared after 5 h of immersion, which was an indication of pit initiation. Increasing  $\text{CrO}_4^{2-}$  concentration to 0.05 M led to the production of symmetrical current spikes at the start of immersion. The noise pattern changed to frequent fluctuations with small amplitude during immersion. Noise analysis in the frequency domain showed that pitting initiation was characterized by the slope of the PSD plot approaching -2. Extending the immersion time decreased the pitting initiation rate, as indicated by the decreased PSD slope and increased PSD frequency.

Keywords: *carbon steel, electrochemical noise, inhibition, pitting*

## 1. Introduction

Electrochemical noise (EN) may be caused by the spontaneous fluctuation of corrosion potential and current generated by the corrosion reaction. The EN technique has been used to study the onset of localized corrosion events involving pitting, crevice corrosion and stress corrosion cracking [1–3].

It is well known that steel can be passivated in chromate solution of sufficient concentration due to the strong oxidizing ability of  $\text{CrO}_4^{2-}$  [4]. The presence of aggressive ions, such as chloride ions, and their preferential attack on some 'active' points on the passive film can lead to local thinning and breakdown of the passive film, and the consequent initiation of pits [5]. It was reported [4] that the inhibition of pitting can be described by a competitive adsorption model in which aggressive ions ( $\text{Cl}^-$ ) and inhibitive ions ( $\text{CrO}_4^{2-}$ ) compete for sites on the metal surface. If the surface coverage ratio of aggressive ions to inhibitive ions exceeds a certain critical value, breakdown of passivity occurs, and pitting is initiated.

EN analysis has been proven to be an effective method to study the pitting process [6–12]. It also gives information about the critical concentrations of aggressive ions and inhibitive ions which initiate pits on the carbon steel. The present work was aimed at investigating the features of EN generated by A516-70 carbon steel immersed in solutions containing  $\text{Cl}^-$

and  $\text{Na}_2\text{CrO}_4$  in various concentrations and how these critical concentrations of  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  influenced the noise features. The polarization curves were also measured for confirmation of the noise analysis and the effect of immersion time on pitting activity was considered.

## 2. Experimental procedures

Electrodes were made of a sheet of A516-70 carbon steel of composition (wt %): C 0.31, Mn 1.0, P 0.035, S 0.04 and Si 0.25. Each sample was cut to 6 mm × 6 mm × 5 mm and ground to 600 grit on all faces. The unexposed edges were coated with a masking paint to prevent crevice corrosion between the epoxy mount and the electrode. The specimens were embedded in epofix resin manufactured by LECO resulting in an exposed steel area of 0.4 cm<sup>2</sup>. The working surface was ground with emery paper to 1000 grit, then cleaned by distilled water and methanol prior to testing.

Two series of testing solutions were used in the measurements of polarization curves in order to assess the critical concentrations of  $\text{CrO}_4^{2-}$  and  $\text{Cl}^-$  needed to maintain the passivation of A516-70 carbon steel in the given system. In the first series, the base solution was 0.01 M  $\text{Na}_2\text{CrO}_4$ . NaCl was added to produce the  $\text{Cl}^-$  concentrations of 0.005, 0.05, 0.1 and 0.5 M, respectively. The base solution in the second series was 0.1 M NaCl. Changing the amount of

$\text{Na}_2\text{CrO}_4$  produced  $\text{CrO}_4^{2-}$  concentrations of 0.005, 0.01 and 0.05 M, respectively.

The test solutions chosen for EN measurements contained a constant  $\text{CrO}_4^{2-}$  concentration (0.01 and 0.05 M, respectively) with changing  $\text{Cl}^-$  amounts of 0.05, 0.1, 0.2 and 0.5 M. This arrangement was aimed at determining critical  $\text{Cl}^-$  concentration for the initiation of pits in the inhibitive system based on the noise analysis.

All the solutions in this work were prepared with analytical grade chemicals and distilled water. All tests were conducted at room temperature (22 °C). During testing, each solution was exposed in air.

The measurements of polarization curves were conducted using an EG&G 273 potentiostat. The cell consisted of the sample, used as the working electrode (WE), a Ag/AgCl reference electrode (RE) and a platinum counter electrode (CE). Each sample was immersed in the test solution for 60 min prior to the polarization measurements. The scan rate was  $0.2 \text{ mV s}^{-1}$ .

To obtain EN measurements, a pair of nominally identical A516-70 electrodes were immersed in the testing solution. An Ag/AgCl electrode was employed as the reference electrode (RE). During experiments, simultaneous potential and current data were recorded using an ACM AutoZRA measurement system with a sampling of one point per second. The sampling period for each noise measurement was 1024 s. The noise data collected in the time domain were transformed into the power spectrum density (PSD) plots in the frequency domain by the maximum entropy method (MEM) [13]. The direct current (DC) component was filtered from the noise data by subtracting a fitted parabola from the data before calculating PSD.

In this work, only current noise data were analysed because potential fluctuations during metastable pitting resulted from the dominant effect of the electrode capacitance [14–18]. The potential transients were controlled by the recharging and discharging of capacitance of passive film and were not, therefore, directly related to the pitting process. Only the current transients corresponded to the initiation, growth and repassivation processes of pitting.

### 3. Results and discussion

#### 3.1. Polarization characteristics of A516-70 carbon steel

Figure 1 shows the polarization curves for the experimental series involving constant 0.01 M  $\text{CrO}_4^{2-}$  and variant  $\text{Cl}^-$  concentrations. Increasing the  $\text{Cl}^-$  amount had a substantial negative effect on the passivity of A516-70 carbon steel. The critical  $\text{Cl}^-$  concentration to initiate pits in 0.01 M  $\text{CrO}_4^{2-}$  solution was approximately 0.1 M.

The polarization curves measured in 0.1 M  $\text{Cl}^-$  solution with different  $\text{CrO}_4^{2-}$  concentrations are

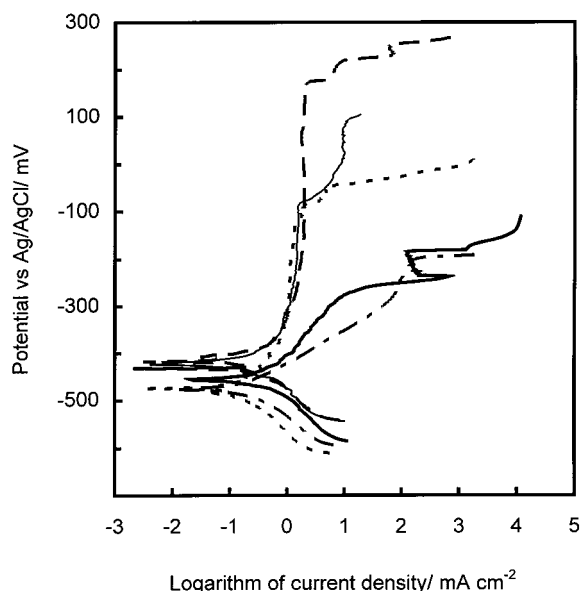


Fig. 1. Polarization curves of A516-70 carbon steel in 0.01 M  $\text{Na}_2\text{CrO}_4$  solution containing different concentrations of  $\text{Cl}^-$ : (—) 0, (—) 0.005, (----) 0.05, (—) 0.1 and (—) 0.5 M.

shown in Fig. 2. A concentration of 0.005 M showed no significant passivation occurring on the sample. The critical value of  $\text{CrO}_4^{2-}$  concentration to maintain passivation was about 0.01 M.

The critical concentrations of aggressive ions and inhibitive ions are illustrated by the competitive adsorption model [4]. If chromate adsorption predominates on the open surface, a passive film of  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}(\text{OH})_3$  is formed. However, if the adsorption of chloride ions predominates, a complete passive film will not form and pitting then ensues on the electrode surface. Therefore, there should be threshold concentration values of  $\text{CrO}_4^{2-}$  and  $\text{Cl}^-$  for the initiation of pits.

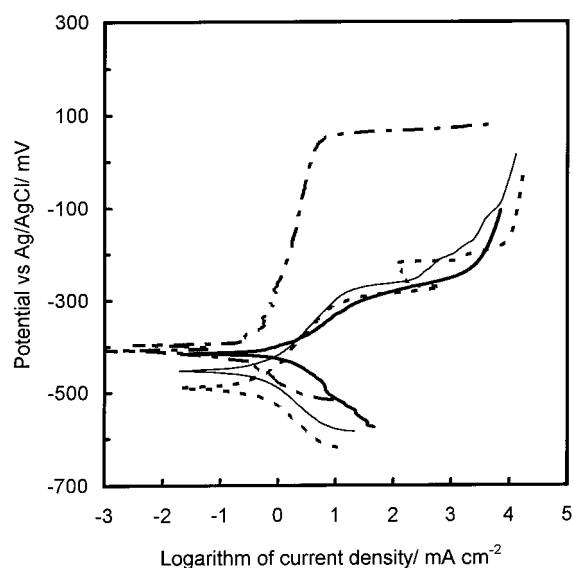


Fig. 2. Polarization curves of A516-70 carbon steel in 0.1 M NaCl solution containing different concentrations of  $\text{CrO}_4^{2-}$ : (—) 0, (----) 0.005, (—) 0.01 and (—) 0.05 M.

### 3.2. Noise analysis in the time domain

The steady passive state was reached when A516-70 carbon steel was immersed in 0.01 M  $\text{CrO}_4^{2-}$  solution. Previous noise measurements [10, 19, 20] for passivated steel consisted of very frequent current transients with amplitudes less than 2 nA. There were no detectable noise fluctuation peaks.

Figure 3 shows the current noise recorded after 5 h of immersion of A516-70 carbon steel in 0.01 M  $\text{CrO}_4^{2-}$  + 0.05 M NaCl solution. The noise pattern measured in the chloride containing solution was the same as that measured in the solution without  $\text{Cl}^-$ , except that the amplitude of current fluctuations increased to 4 nA. There were also no visible fluctuation peaks. When the  $\text{Cl}^-$  concentration reached 0.1 M, stochastic and sharp current noise peaks appeared (Fig. 4). In 0.05 M  $\text{CrO}_4^{2-}$  + 0.1 M NaCl solution, a repeating pattern of a current spike in the positive direction, followed by a quick drop below its original value (around  $2.5 \times 10^{-8}$  A) and then a return to the original value, was observed at short immersion time. Monticelli *et al.* [21] also observed this kind of fluctuations for AA 6365 aluminium alloy in nitrate solution and termed the results as 'symmetrical' spikes. Figure 5 shows the shape of the symmetrical spikes obtained after 0.5 h of immersion of A516-70 carbon steel in the solution. During continuous immersion,

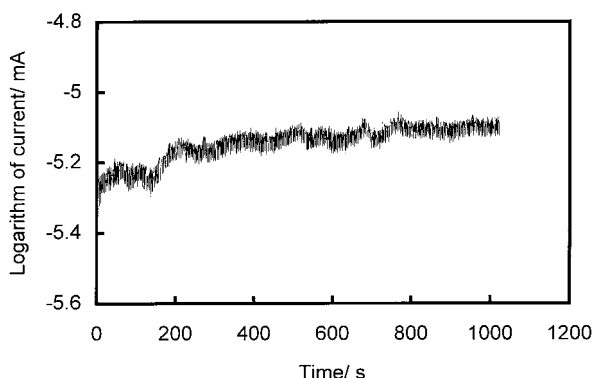


Fig. 3. The current fluctuations of A516-70 carbon steel after 5 h of immersion in 0.01 M  $\text{Na}_2\text{CrO}_4$  + 0.05 M NaCl solution.

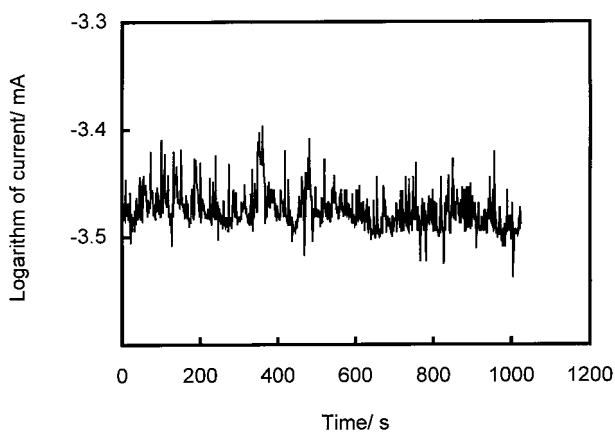


Fig. 4. Current fluctuations of A516-70 carbon steel after 5 h of immersion in 0.01 M  $\text{Na}_2\text{CrO}_4$  + 0.1 M NaCl solution.

these kinds of spikes became less apparent. The current noise after 5 h of immersion is shown in Fig. 6. Compared with the current noise obtained in the solution containing 0.01 M  $\text{CrO}_4^{2-}$  (Fig. 4), the amplitude of current fluctuations was much lower although both current noise signals were recorded at the same immersion time of 5 h. Therefore, the current noise features were strongly dependent on the  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  concentrations.

It was believed [1–3, 7–11] that the sharp, stochastic current fluctuations were an indication of the initiation of pitting. When chloride ions were added into the passive solution, the interactions between the passive film and the chloride ions led to the local absorption of chloride ions on the surface of passive film and the degradation of passivation. If the critical coverage of  $\text{Cl}^-$  was not reached, that is, the  $\text{CrO}_4^{2-}$  adsorption predominated, the carbon steel was remained in passive state. No apparent noise transients are observed, just as in the case shown in Fig. 3. When the  $\text{Cl}^-$  concentration reached a critical value, the local breakdown of the passive film caused the increase of current. The following repassivation process was responsible for the slow recovery of the current to its original value. It was the breakdown and repair of the passive film that caused the stochastic fluctuations of the current, which indicated the onset of pitting.

In the presence of large amounts of  $\text{CrO}_4^{2-}$ , the formation of an anodic site, caused by the local attack of  $\text{Cl}^-$ , led to the quick increase in current. The decrease in current can be achieved either by (1) passivation of anodic sites by chromate adsorption, or (2) inhibition of the cathodic sites by reductive deposition of  $\text{Cr}_2\text{O}_3$ . This produced a quick heal of the active zone and a sudden drop towards less positive values of the current that often exceeded its original value and generated symmetrical current spikes. After a certain immersion time, the stable passive film was formed due to the adsorption predominance of  $\text{CrO}_4^{2-}$  on the steel surface. The typical current noise of the passivation system was observed (Fig. 6).

In the present system, the critical  $\text{Cl}^-$  concentration to initiate pitting on the passivated A516-70 carbon steel in 0.01 M  $\text{CrO}_4^{2-}$  solution was approximately 0.1 M according to the analysis of noise features in different solutions. This value was consistent with the critical  $\text{Cl}^-$  concentration assessed by polarization curves. Therefore, analysis of EN can provide the critical concentration of aggressive ions to initiate pitting.

### 3.3. Noise analysis in the frequency domain

The current PSD plots of A516-70 carbon steel after 5 and 10 h of immersion in 0.1 M NaCl solution containing 0.01 M and 0.05 M  $\text{CrO}_4^{2-}$ , respectively, are shown in Fig. 7. A common feature of these plots was that the 'white noise', which was independent of the frequency, appeared in the lower frequency region; in

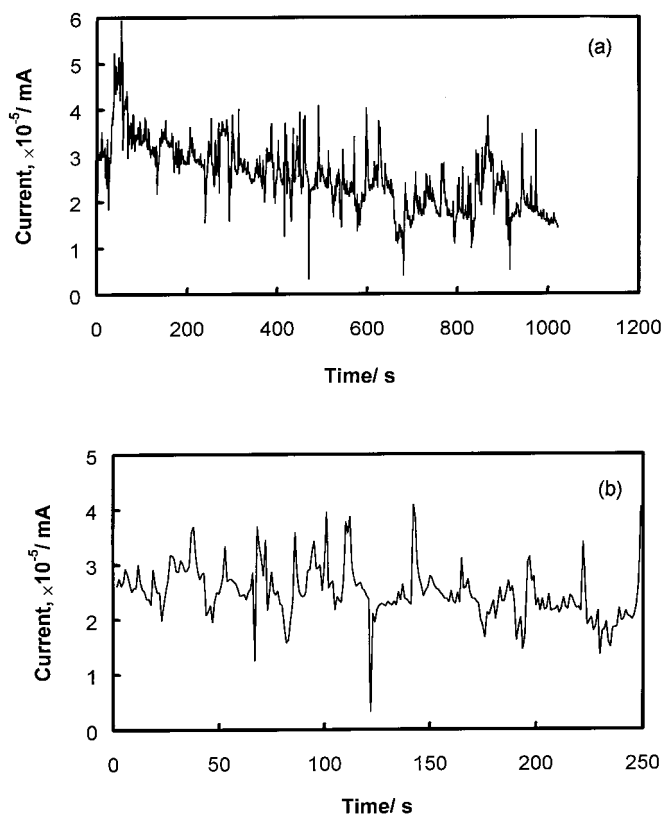


Fig. 5. Current fluctuations of A516-70 carbon steel after 0.5 h of immersion in 0.05 M  $\text{Na}_2\text{CrO}_4$  + 0.1 M NaCl solution at different time scales: (a) within 1000 s, and (b) within 250 s.

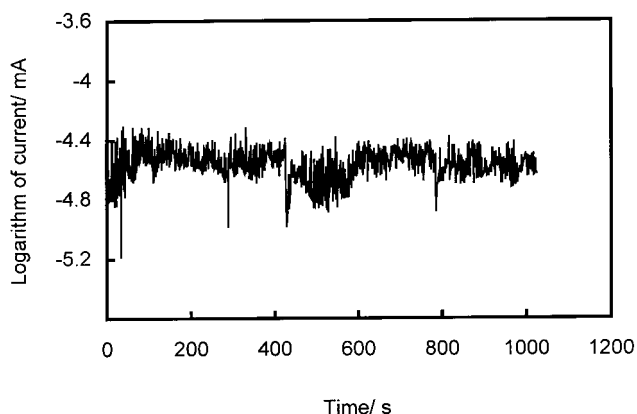


Fig. 6. Current fluctuations of A516-70 carbon steel after 5 h of immersion in 0.05 M  $\text{Na}_2\text{CrO}_4$  + 0.1 M NaCl solution.

the higher frequency region, it was  $1/f^n$  noise. The slope of the  $1/f^n$  noise is defined as the roll-off slope ( $n$ ) with the frequency at the cross point between white noise and  $1/f^n$  noise being defined as the roll-off frequency ( $f_c$ ).

It has been suggested [1, 7, 20, 22] that the PSD roll-off slope is related to the type of corrosion attack, however, some points are still controversial. For example, Dawson *et al.* [10, 22] thought that pitting corrosion generally results in a small slope with about  $n = -2$  or less, while general corrosion exhibits spectra with slopes of  $n = -4$ . Other work [23, 24] showed the opposite conclusion, that the roll-off slope of PSD curve would be steeper ( $n = -2$ ) when pitting corrosion initiated, as compared to the passive

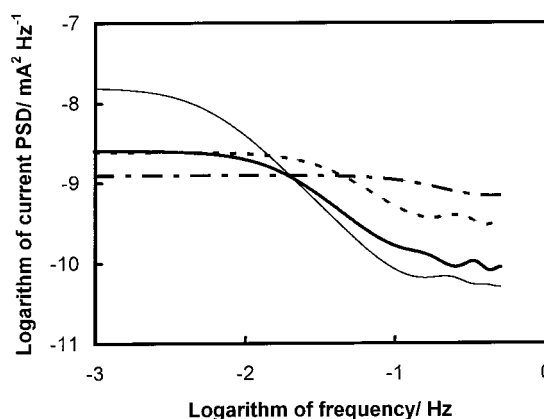


Fig. 7. Current PSDs of A516-70 carbon steel after 5 and 10 h of immersion in 0.1 M NaCl solution containing 0.01 M and 0.05 M  $\text{Na}_2\text{CrO}_4$ , respectively. Key: (—) 5 h, 0.01 M, (---) 5 h, 0.05 M, (—) 10 h, 0.01 M and (---) 10 h, 0.05 M.

state and general corrosion. The present results supported the latter. After 5 h of immersion of A516-70 carbon steel in 0.01 M  $\text{CrO}_4^{2-}$  + 0.1 M NaCl solution, the slope was approaching  $n = -1.9$ , which indicated pitting initiation. When the immersion time extended to 10 h, roll-off slope decreased to  $n = -1.5$ . Noise recordings in the time series showed that the number of current peaks decreased with time. This result was consistent with the statistical analysis of pitting initiation rate in the time domain [24]. This decreased pitting initiation rate may be attributed to the increase in the pitting stabilization tendency or to the growth of passive film [9]. It seemed that the passive film on carbon steel, formed in 0.01 M  $\text{CrO}_4^{2-}$  solution, could

not develop continuously in the  $\text{Cl}^-$ -containing solution in the present system. Surface observation showed that general corrosion occurred. Therefore, the decreased roll-off slope in 0.01 M  $\text{CrO}_4^{2-}$  solution corresponded to the transition from pitting to general corrosion.

For the solution containing 0.05 M  $\text{CrO}_4^{2-}$  + 0.1 M NaCl, the slopes for 5 and 10 h of immersion were  $n = -1.6$  and  $n = -0.5$ , respectively, which also indicated the decreased rate of pitting initiation. A point worth noting is that after 10 h of immersion, the roll-off slope decreased to  $n = -0.5$ , which was close to the slope value in the case of passivity or general corrosion [9, 12, 19]. This may be caused by the growth of passive film in the solution containing 0.05 M  $\text{CrO}_4^{2-}$ . The apparent difference in roll-off slopes obtained from the solutions containing 0.01 M and 0.05 M  $\text{CrO}_4^{2-}$ , respectively, also showed that the critical  $\text{CrO}_4^{2-}$  concentration to passivate the carbon steel should be above 0.01 M. This is consistent with results from the polarization curves shown in Fig. 2.

The increase of repassivation rate of metastable pits with time was indicated by the relative change in roll-off frequency. Previous work [26] had proven that the roll-off frequency was directly related to the repassivation rate of metastable pits. From Fig. 7 was observed that when the immersion time increased from 5 to 10 h, the roll-off frequencies of both solutions increased from 0.004 and 0.03 Hz to 0.01 and 0.1 Hz, respectively. Therefore, the repassivation rate of metastable pits increased during immersion.

Furthermore, the increase in inhibitor concentration also decreased the pitting activity, as indicated by the decreased amplitude of current noise (Figs 4 and 6). Comparing the PSD plots obtained in the solutions containing different  $\text{CrO}_4^{2-}$  concentrations in Fig. 7, the roll-off frequency increased and the roll-off slope decreased when the  $\text{CrO}_4^{2-}$  concentrations increased from 0.01 M to 0.05 M.

#### 4. Conclusions

- (i) Analysis of electrochemical noise features can provide the critical concentrations of  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  to initiate pitting on A516-70 carbon steel. These critical values are proven to be reasonable by the measurements of polarization curves.
- (ii) The threshold  $\text{Cl}^-$  concentration in 0.01 M  $\text{Na}_2\text{CrO}_4$  solution to initiate pits and the threshold  $\text{CrO}_4^{2-}$  concentration in 0.1 M NaCl solution to maintain passivation for A516-70 carbon steel are approximately 0.1 M and 0.01 M, respectively.
- (iii) Above the critical  $\text{Cl}^-$  concentration in 0.01 M  $\text{CrO}_4^{2-}$  solution, stochastic current fluctuations appeared after 5 h of immersion, indicating pitting initiation. Increasing  $\text{CrO}_4^{2-}$  concentration to 0.05 M led to the production of symmetrical current spikes at the start of immersion. By increasing immersion time, the noise pattern

changed to the frequent fluctuations with small amplitude.

- (iv) Pitting initiation was characterized by the roll-off slope approaching  $n = -2$ . During immersion, the pitting tendency decreased as indicated by the decreased roll-off slope and the increased roll-off frequency.

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