# Study of the Corrosion Inhibition of Zinc by Benzotriazole with an Electrochemical Quartz Crystal Microbalance

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The inhibiting effect of BTA on the corrosion of electroplated zinc coatings in acidic sodium sulfate solutions was studied by use of an electrochemical quartz crystal microbalance. Experiments showed that BTA is mainly inhibiting the anodic reaction of the zinc dissolution reaction. In quiescent solution, the rate-determining step of the corrosion process is mass transport of dissolved oxygen to the electrode surface so that BTA does not significantly decrease the corrosion rate. When the solution is deaerated by nitrogen bubbling, the corrosion rate is controlled by the charge transfer process and the corrosion rate of zinc is greatly reduced by BTA. When the solution is bubbled with air, the corrosion rate increases significantly. The rate of the hydrogen evolution reaction is charge-transfer-controlled and the oxygen reduction is controlled by mass transport.

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## Introduction

An electroplated zinc coating is widely used in the industry for providing cathodic protection to steel substrates. Zinc is a very active metal so that it corrodes quickly in aqueous solutions. Therefore, thick zinc coatings are usually required for long-lasting protection. Recently, many zinc-alloy coatings were developed to meet different industrial requirements. These alloys, including Zn-Ni, Zn-Fe, Zn-Co and Sn-Zn usually are superior to pure zinc coatings in corrosion resistance, mechanical properties, appearance and electrical properties.[1-5] However, the zinc dissolution reaction still plays an important role in the corrosion of these alloys. Therefore, inhibitors that decrease the corrosion rate of zinc may also be beneficial to these zinc alloy coatings. The dissolution of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen- and sulfur- containing organic compounds.[6-8] These compounds have electron donating groups and form donor-acceptor bonds with metal atoms on the surface. As such, they decrease the corrosion rate by inhibiting the hydrogen evolution reaction. Benzotriazole (BTA) has been widely used as a corrosion inhibitor for copper, its alloys, and for mild steels.[9,10] However, little is known about the manner in which BTA decreases the corrosion of zinc. In this paper we present some results using an electrochemical quartz crystal microbalance (EQCM) that help elucidate the effect of BTA on inhibiting the corrosion of zinc coatings.

## Experiment

An electrochemical quartz crystal microbalance (EQCM) was used for in-situ measurement of the mass loss rates during corrosion of zinc coatings. The operation of the EQCM is based on the vibration feature of a quartz crystal. Over a wide mass range, the relationship between changes of the the resonant frequency ($\Delta f$) of a quartz crystal and changes of the mass that is rigidly attached to the crystal surface ($\Delta m$) is linear:

$$\Delta f = -\boldsymbol{K}\Delta m \qquad (1)$$

where $\boldsymbol{K}$ is a positive constant. So, when measuring changes in the vibration frequency of the crystal, the EQCM monitor automatically converts the changes in the frequency into the mass changes that the sample undergoes. The sensitivity of the EQCM can be 1 ng cm$^{-2}$, which makes it an ideal instrument to study electroplating and corrosion.[11,12]

The EQCM equipment used in the experiment was a Maxtek PM-710 plating monitor with 5 MHz quartz crystals of 26 mm diameter. The plating substrate was a gold film coated on the crystal surface. The exposed area of the gold film was 1.4 cm$^2$. A personal computer with a data-acquisition software was used to record the mass changes.

The zinc electroplating bath was an alkaline solution. Its composition was: ZnO 12 g L$^{-1}$, NaOH 120 g L$^{-1}$, additive 8 mL L$^{-1}$. The plating was performed on the gold surface at ambient temperature and the plating current density was 5~10 mA cm$^{-2}$. Voltammetric measurements were taken with a PAR 273 potentiostat connected to a personal computer. A saturated calomel electrode (SCE) was used as the reference and a carbon rod as the counter electrodes.

After electroplating, the EQCM probe with the Zn-coated crystal was immersed into a corrosive solution for the corrosion testing. The blank solution for the corrosion experiments was 0.1 M $Na_2SO_4$ with the pH value adjusted to 3.6 by adding sulfuric acid. The blank solution and a solution containing 100 mM BTA were tested separately. Potentiodynamic curves were measured in both solutions. To study the effect of BTA on the corrosion rate of zinc under different conditions, corrosion measurements at open circuit potential (OCP) were divided into three periods. During the first period the solution was quiescent and air-saturated. During the second period, purified nitrogen gas was bubbled through the corrosive solution to remove the oxygen and to cause some agitation. In the third period compressed air was bubbled through the solution. The open circuit potential of the zinc specimen and the rates of mass change during the entire process were recorded continuously.

Because gas bubbling changes the agitation condition of the solution as well as the oxygen concentration in the solution, additional experiments were carried out with a magnetic stirrer in order to study the effects of agitation and of oxygen content separately. The mass loss rates of zinc deposits were measured again in the corrosive solution either with or without BTA, under aerated and deaerated conditions, respectively.

## Results and Discussion

### *1. The effect of BTA on polarization curves in deaerated solution.*

Figure 1 shows the polarization curves of zinc in the blank $Na_2SO_4$ solution and in the blank solution containing 100 mM BTA. Nitrogen gas was bubbled into both solutions before and during the polarization. It can be clearly seen that under these conditions BTA shifts the open circuit potential more than 100 mV in the more positive direction. Also the anodic current density was effectively decreased. This is an indication that BTA is inhibiting the zinc dissolution reaction:

$$Zn = Zn^{2+} + 2e^- \tag{2}$$

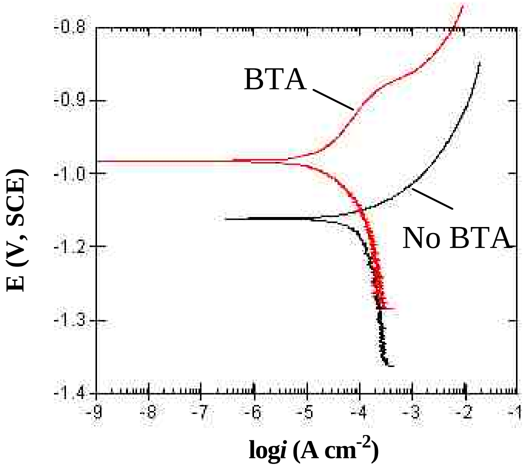

*Fig. 1. Polarization curves of Zn in the deaerated ($N_2$ bubbling) 0.1 M $Na_2SO_4$ (pH 3.6) solutions with and without BTA.*

However, the mechanism of corrosion inhibition by BTA can not be determined solely from polarization curves. The corrosion process may be determined not only by the charge transfer steps of the anodic and cathodic reactions but also by mass transport. Therefore, it is important to know what is the rate-determining step of the corroding system at the OCP. By use of the EQCM, the corrosion mechanism of zinc and the effect of BTA can be demonstrated more clearly.

*2. The effect of BTA in deaerated solutions.*

Fig. 2 shows the changes of the mass loss rate of zinc as a result of stirring by a magnetic stirrer in the deaerated ($N_2$ bubbled) 0.1 M $Na_2SO_4$ solution (pH 3.6) with and without BTA. During the mass loss rate measurement, the open circuit potentials were also recorded and shown in Fig. 3. In the deaerated solutions, only the hydrogen evolution reaction is the cathodic reaction. Fig. 2 and 3 show that, in the solution containing 100 mM BTA, magnetic stirring does not have evident effects on either the mass loss rate or the OCP. However, in the deaerated blank solution, the mass loss rate of the zinc deposit increases substantially, with some variation over time, when the magnetic stirrer is turned on (at 120 min in Fig. 2), and the OCP also shifts (modestly) to more positive values (at 120 min in Fig. 3). This indicates that in the absence of BTA, mass transport of $H^+$ ions is a rate-determining step so that stirring increases the corrosion rate while shifting the OCP in the positive direction. On the other hand, in the presence of BTA, when stirring was turned on at 120 minutes there was no change in either the corrosion rate (Fig. 2) or the OCP (Fig. 3). This indicates that the corrosion reaction in the presence of BTA is charge transfer controlled. Thus, compared to the blank solution the anodic polarization curve would be expected to shift to more positive values and the hydrogen evolution reaction to smaller overpotentials, which is what is observed in Fig. 1.

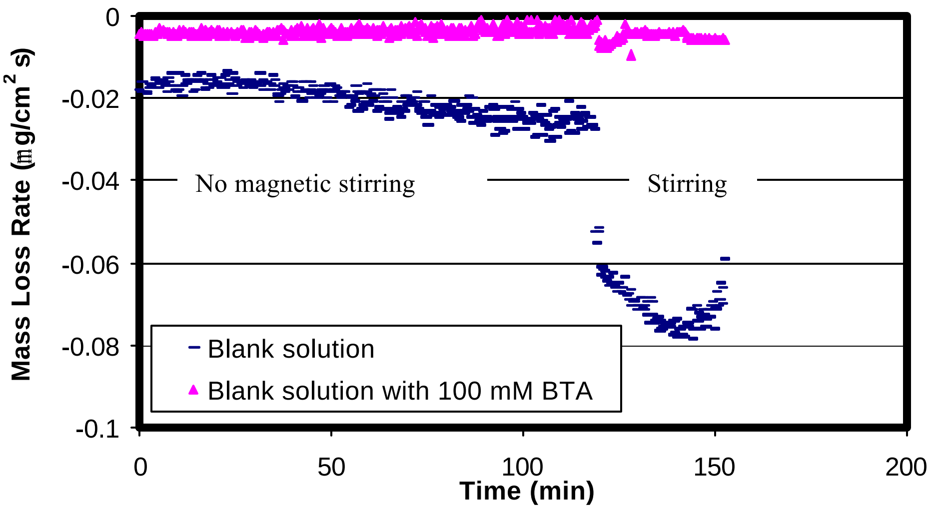

*Fig. 2. The effect of magnetic stirring (off from 0 to 120 min and on at a constant value from 120 to 150 min) on the corrosion rate of Zn in the deaerated 0.1 M $Na_2SO_4$ corrosive solution with and without BTA. During the first 120 minutes the solution was slightly agitated by nitrogen bubbles.*

Since zinc dissolution is the only anodic reaction, the mass loss rate of zinc during the zinc dissolution reaction is proportional to the corrosion current density. If one plots the mass loss rates (as positive quantities) vs. the OCP in each solution, these curves should be similar to the anodic polarization curves of zinc in the respective solutions. From the above discussion, a schematic plot of the polarization curves of the partial corrosion reactions is shown in Fig. 4. The presence of BTA shifts the anodic polarization curve in the positive direction. The hydrogen evolution reaction at the more positive corrosion potential (B in Fig. 4) in the presence of BTA is charge transfer controlled, while mass transport controlled at A where stirring increased the limiting current in the absence of BTA.

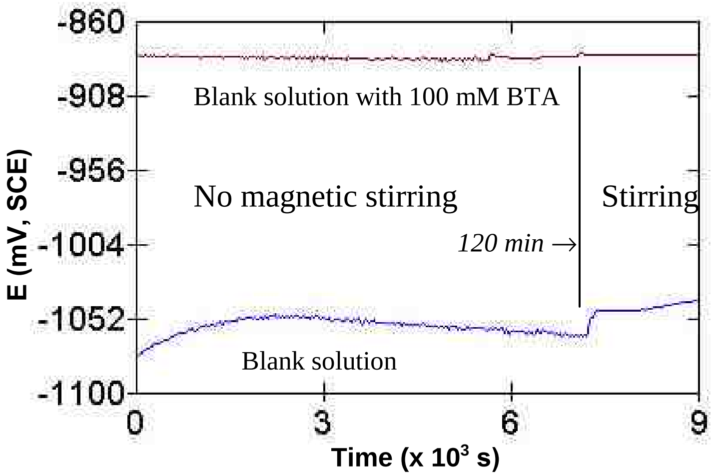

*Fig. 3. The effect of magnetic stirring on the OCP of Zn in the deaerated 0.1 M $Na_2SO_4$ solutions (pH 3.6) with and without BTA.*

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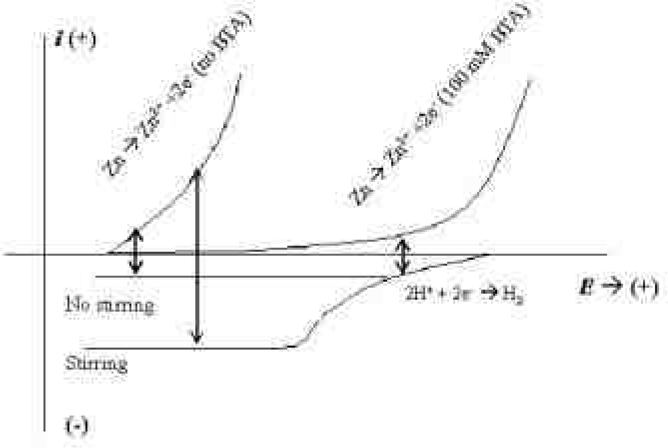

*Fig. 4. A schematic diagram of the anodic and cathodic polarization curves in the deaerated, corrosive solutions. A possible inhibitive effect of BTA on the hydrogen evolution reaction is neglected in this schematic figure.*

## *3. The effect of BTA in the presence of oxygen.*

Fig. 5 shows the mass loss rate of the zinc coating in the $Na_2SO_4$ solution without BTA in the bubbling experiment. The differences of the corrosion rates in the three stages can be easily distinguished. The mass loss rate in the first stage of corrosion (without bubbling) was about 0.014 µg cm$^{-2}$ s$^{-1}$. When the solution was agitated by nitrogen gas bubbles, the mass loss rate increased to about 0.045 µg cm$^{-2}$ s$^{-1}$. $N_2$ bubbling showed the same effect of stirring, albeit weaker, as magnetic stirring caused for the deaerated blank solution (Fig. 2). When the nitrogen gas bubbling was replaced by air bubbling, the mass loss rate increased further to about 0.06-0.08 µg cm$^{-2}$ s$^{-1}$.

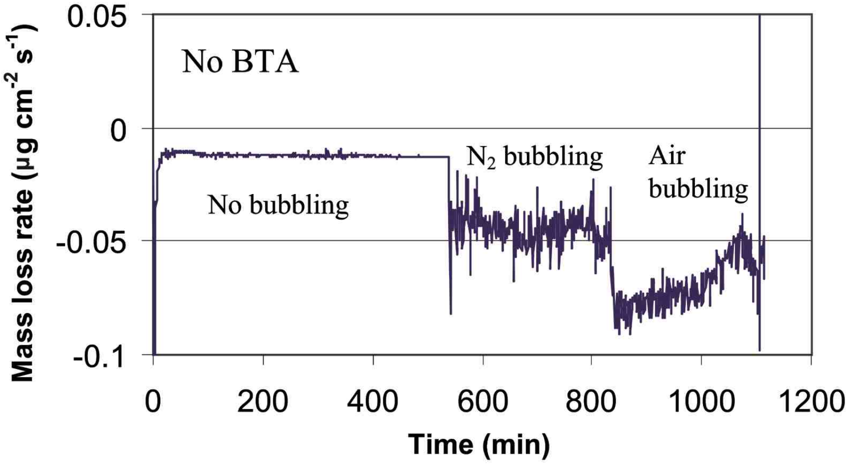

*Fig. 5. Mass loss rate of the Zn coating in the 0.1 M $Na_2SO_4$ solution (pH 3.6) without BTA.*

Fig. 6 shows the mass loss rate of the zinc coating in the $Na_2SO_4$ solution containing 100 mM BTA. When the solution was not bubbled by any gas, the corrosion rate is almost the same as in the solution without BTA (Fig. 5 and for weak $N_2$ bubbling in Fig. 2). When nitrogen gas was bubbled into the solution, unlike the previous case, the corrosion rate dropped to 0.003 µg cm$^{-2}$ s$^{-1}$, which is about the same value as reported for BTA in Fig. 2 during the initial 120 minutes when the only stirring was provided by weak $N_2$ bubbling. When air bubbling was substrated for the nitrogen, the mass loss rate increased to 0.04-0.05 µg cm$^{-2}$ s$^{-1}$, which was smaller than for the air-bubbled blank solution (Fig. 5).

The values of the OCP of zinc in both solutions during the different gas bubbling corrosion periods are shown in Figures 7 and 8. The open circuit potential of zinc in the 0.1 M $Na_2SO_4$ solution containing BTA (Fig. 8) was always more positive than in the blank solution (Fig. 7). In the BTA solution, as well as the mass loss rate (Fig. 6), the OCP also shifted when the corrosion condition was changed (Fig. 8); the higher the corrosion rate, the more positive was the open circuit potential. In the solution without BTA, the same trend of the OCP was observed (Fig. 7), although to a lesser degree than in the BTA solution (Fig. 8).

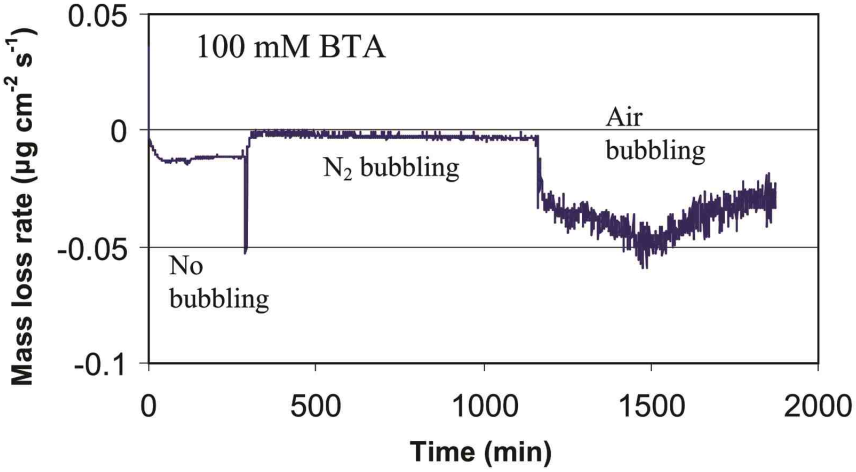

*Fig. 6. Mass loss rate of the Zn coating in the $Na_2SO_4$ corrosive solution (pH 3.6) with 100 mM BTA.*

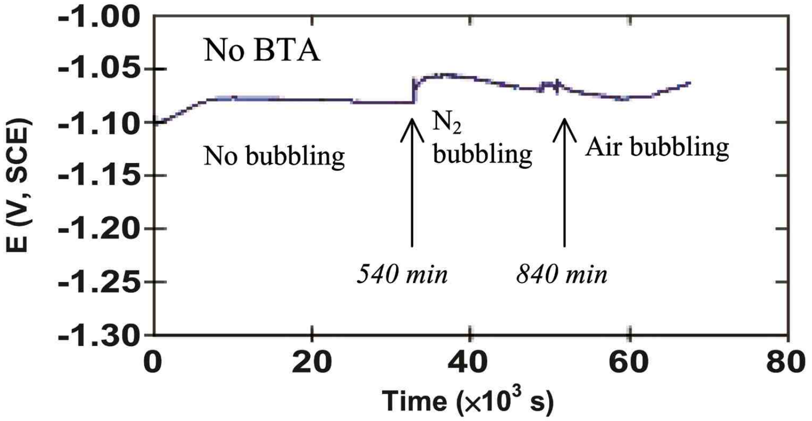

*Fig. 7. Open circuit potential of the Zn coating in the 0.1 M $Na_2SO_4$ solution (pH 3.6) without BTA.*

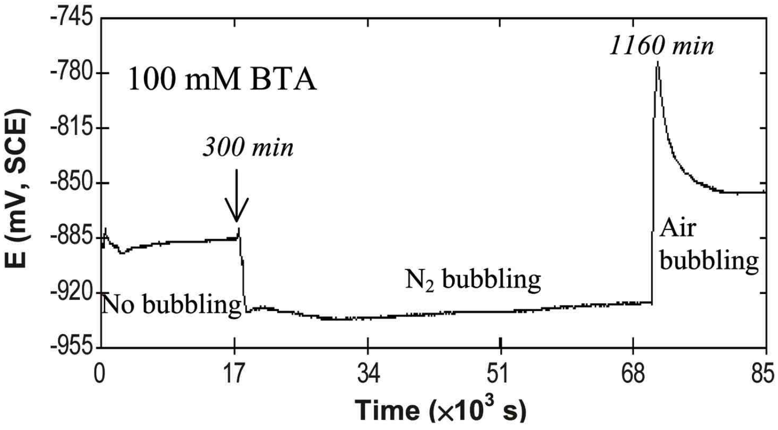

*Fig. 8. Open circuit potential of the Zn coating in the 0.1 M $Na_2SO_4$ solution (pH 3.6) with 100 mM BTA.*

Fig. 9 shows the two curves of the OCP vs. mass loss rate (plotted here as a positive quantity) in the two solutions using the data from Figures 5 and 8. As stated before, the two curves represent the polarization curves in the two different solutions. The number beside each point represents the stage of the experiment. The presence of BTA shifts the potential of zinc to the more positive direction by over 100 mV. At the same time, *dE/di*, the inverse of the slope of the curve in Fig. 9, is higher in the BTA solution than in the blank solution. Both of these changes mean that the charge transfer resistance of the zinc dissolution reaction is increased by BTA.

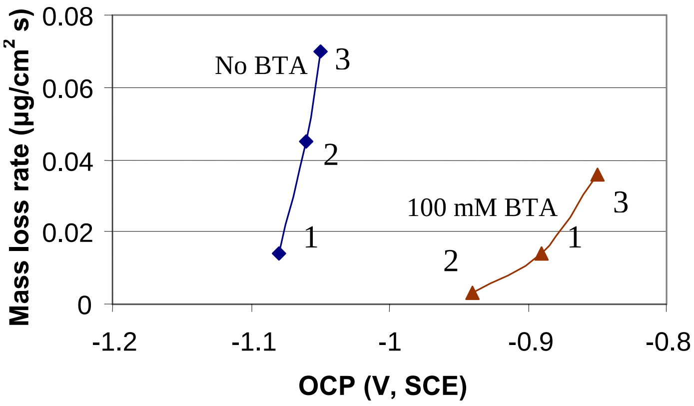

*Fig. 9. Plot of the measured OCP vs. the measured mass loss rate in both solutions.*

Based on the bubbling experiments (Fig. 5 to 8) and Fig. 9, schematic polarization curves of the partial corrosion reactions in the presence of oxygen are plotted in Fig. 10. This plot is similar to Fig. 4 except that the oxygen reduction reaction is one of the cathodic reactions in the presence of oxygen. In the static solution saturated by air (no bubbling), although BTA increased the anodic potential (Fig. 7 and 8), the corrosion rate was not decreased (Fig. 5 and 6). This indicates that the corrosion process is controlled by the mass transport step of the cathodic reactions, which in the schematic of Fig. 10 is considered to be dominated by oxygen reduction for illustrative purposes, i.e., points 1 (no BTA) and 1 (BTA). Therefore, the inhibition effect of BTA is not reflected by the corrosion rate. If the mass transport process of the anodic reaction, i.e., the diffusion away of zinc ions from the electrode surface is the rate-determining step, the mass loss rate also may not be affected by BTA. But it is not considered as a possibility here, because if that was true, when the solution was agitated by bubbling, as the mass loss rate increased, the OCP should have decreased. However, it was shown in the later stages of the experiments that the OCP actually increased with the mass loss rate. So, only the mass transport step of the cathodic reactions can be the rate-determining step.

In the second period of corrosion, the bubbling of nitrogen gas has two effects: it removes the oxygen in the corrosive solution and it enhances the mass transport of hydrogen ions in the solution. In this case, the hydrogen evolution reaction is the main cathodic reaction, and the corrosion process is controlled in the BTA solution by the charge transfer step instead of the mass transport (point 2, BTA in Fig. 10). Under this condition of $N_2$ bubbling, BTA shows an effective inhibition of the corrosion of zinc. The corrosion rate is higher in the blank solution due to the enhanced mass transport of the hydrogen ions by the $N_2$ bubbling while in the solution containing BTA, the corrosion rate decreases due to the smaller overpotential for $H^+$ reduction.

In the oxygen bubbled solution, the mass loss rate increases over that under $N_2$ bubbling in both the blank and BTA solutions because the air bubbling increases both the agitation and the oxygen availability. However, in the presence of BTA the mass loss rate is still smaller than that in the solution without BTA. Under this condition, the cathodic reactions are a combination of the hydrogen evolution reaction and the oxygen reduction reaction. Charge transfer should still be the rate-determining step for the hydrogen evolution reaction with agitation in the solution. However, the oxygen reduction reaction might still be controlled by the mass transportation process, but with a higher limiting current compared to the first step of the experiment where there was no agitation of the solution (point 3, BTA).

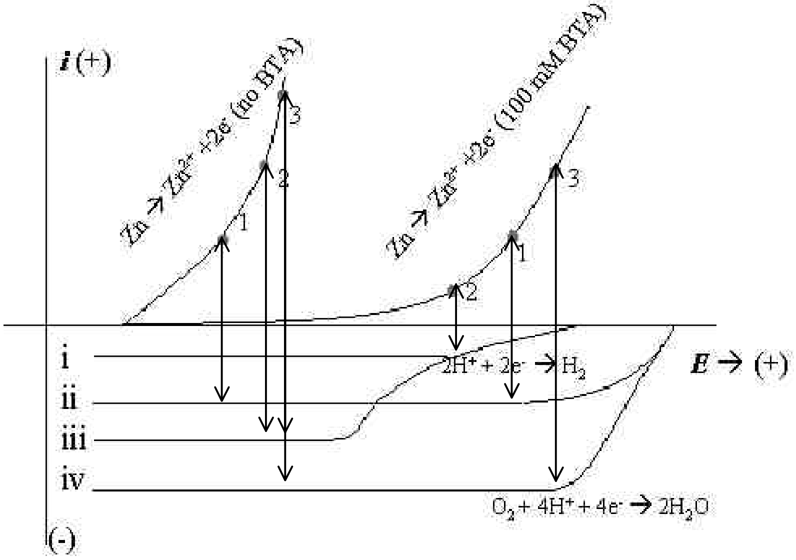

*Fig. 10. A schematic diagram of the anodic and cathodic polarization curves under different bubbling conditions: (i) hydrogen evolution, no bubbling, (ii) oxygen reduction, no bubbling, (iii) hydrogen evolution, bubbling, (iv) oxygen reduction, air bubbling.*

### *4. The effect of BTA in the presence of oxygen and stirring.*

To separate the effects of agitation and the oxygen concentration in the bulk solution, the mass loss rates of zinc deposits were measured again in the naturally aerated solutions either with or without BTA. A magnetic stirrer was used to change the intensity of agitation without varying the oxygen concentration in the bulk solution.

In the blank solution, the effect of agitation is similar to that in the deaerated blank solution. The corrosion rate as well as the OCP increases with increasing agitation. This means in agreement with Fig. 10, that oxygen reduction reaction is diffusion controlled. In the aerated solution containing 100 mM BTA, the corrosion rate also increased as the stirring was increased. However, it was found that the OCP of zinc jumped to a more positive value when the magnetic stirring started and jumped up again when the stirring was stopped. It seems that because of the high flux of oxygen due to the strong agitation by the magnetic stirrer, there must be an irreversible reaction between oxygen, BTA and zinc, which causes the OCP difference before and after stirring. This interaction under the stirring conditions still needs further study.

## Conclusion

In this paper the effect of BTA on the inhibition of zinc in acidic sodium sulfate solutions was studied. The experiments showed that BTA is mainly inhibiting the anodic reaction of the zinc dissolution reaction. BTA increases both the potential of the zinc dissolution reaction and the slope of the zinc polarization curve. This means BTA increases the charge transfer resistance of the zinc dissolution reaction. By use of the EQCM, the partial polarization curves were plotted under different corrosion conditions. Without agitation, the rate determination step is the mass transport of $H^+$ ions and oxygen to the electrode surface. When the solution is agitated by nitrogen bubbling, only the hydrogen evolution reaction is the cathodic reaction and the rate-determining step is the charge transfer process. In this case the corrosion rate of zinc is greatly reduced by BTA. When the solution is bubbled with air, the rate of the hydrogen evolution reaction is controlled by the charge transfer process and the oxygen reduction reaction probably is still controlled by the mass transportation process. Further experiments separating the effects of agitation and the oxygen concentration in the bulk solutions supported this analysis. It is also shown that EQCM is a convenient method to study the corrosion mechanisms of coatings.

## Acknowledgments

This work was supported by the American Electroplaters and Surface Finishers Society (Project 99) and the National Science Foundation (Grant No. DMR-9612303).

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