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Inhibition behavior for copper corrosion by photoelectrochemical methods①

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Abstract: The application of photoelectrochemical methods in the inhibition effects for copper corrosion was described. The methods include cyclic voltammetry photocurrent measurements, intensity modulated photocurrent spectrum(IMPS) and laser-scanning photoelectrochemical microscopic method(PEM) which have been applied to the evaluation of inhibitors and inhibition behavior. The inhibition effect of BTA for copper corrosion is better than that of 4CBTA, 5CBTA, CBT-1, PTD, BT-250, CBTME and CBTBE at the same concentration. The inhibition mechanism of the derivatives of BTA with —COOH group(4CBTA, 5CBTA, CBT-1) is different from those with estergroup(CBTME, CBTBE).

Key words: copper; corrosion; inhibitors; inhibition mechanism; photoelectrochemical method
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1 INTRODUCTION

Oxides, sulfides, halides and various passive films produced on the surface of metal electrodes by electrochemical reaction usually have semi-conductive properties and there exist photoelectric effects at the interface of electrode and electrolyte solution during illumination. The origin of photoelectric effect is that electron-hole pairs created by light in the depletion layer are separated. Usually we can obtain some information about the composition and structure of the electrode surface layer by means of the measurement of photoelectric effect, so called photoelectrochemical method. The photoelectrochemical method is an in-situ method, which is effective for characterizing optical and electronic properties of passive films, analyzing the composition and surface structure of metal and alloy and studying the process of metal corrosion and inhibition. Some important information can not be obtained by usual electrochemical methods and surface analysis techniques, but can be gotten by photoelectrochemical method[1-7]. We can study not only the corrosion and passivation behavior for metal by photoelectrochemical method but also the inhibition mechanism for metal corrosion[8-11]. This paper is to introduce some experiments with the inhibition behavior for copper corrosion by using photoelectrochemical techniques, such as cycle voltammetry photocurrent response method, intensity modulated photocurrent spectrum (IMPS) and laser-scanning photoelectrochemical microscopic method(PEM).

2 EXPERIMENTAL

A three-electrode cell with a flat optical window was used. The reference electrode was a saturated calomel electrode (SCE), whereas the counter electrode was a Pt electrode. The working electrode was prepared from 99.9% copper plates embedded in epoxy resin, and was gradually polished with different grades of emery paper. All experiments were performed using the copper electrodes with freshly prepared surfaces. The electrolyte was a borax buffer solution, which consisted of 0.075 mol/L $Na_2B_4O_7$ and 0.150 mol/L H_3BO_3 and its pH was maintained at pH9.2. To prevent chloride ion interference from the reference electrode, the reference electrode and working electrode were connected using a 0.1 mol/L KNO_3-3% agar salt bridge. Immediately prior to each experiment the copper electrode was cathodically treated at a potential of $-1.1V_{vs\ SCE}$ in the borax buffer solution for 5 min.

The potential control was provided by a PARC M273 potentiostat. The irradiation wavelength of a 1 kW Xe lamp was selected by using a WDG-1A monochromator(Siping Optical Instruments), with spectral bandwidth smaller than 30 nm. An ND-4 chopper(Nanjing University of China) was used to modulate the light intensity, whereas a PARC M 5208EC lock-in analyzer was used to detect the signals. For spectral measurements, the light intensity was measured by a calibrated silicon photodiode, and the light flux never exceeded 20 $mW \cdot cm^{-2}$. The modulation frequency of chopper was 39 Hz. The

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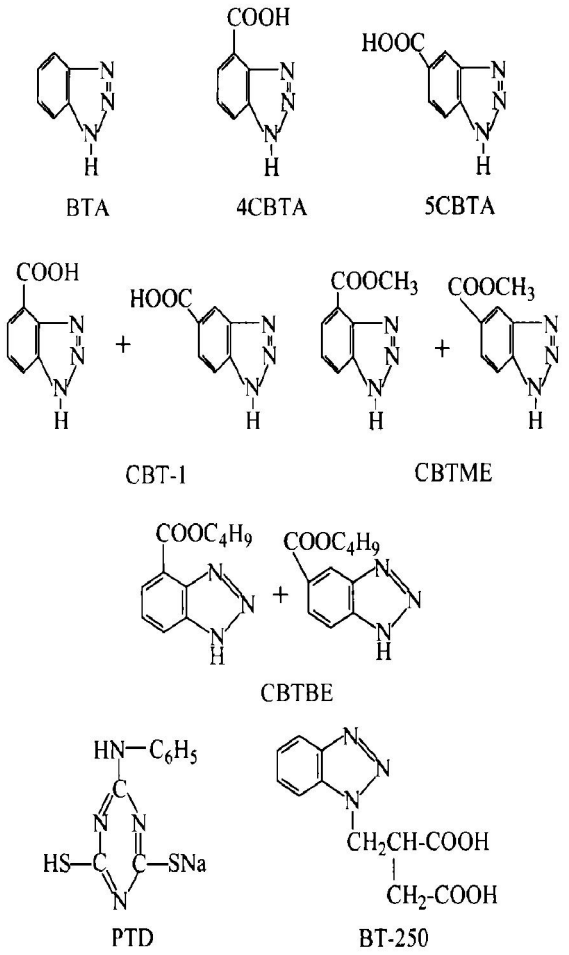
wavelength of monochromate light was 420 nm.

3 RESULTS AND DISCUSSION

3.1 Application of photoelectrochemical method to evaluate the effects of inhibitors for copper corrosion

The structures of the inhibitors for copper corrosion shown in text are as follows:



The inhibition effects of different inhibitors for copper corrosion can be evaluated by photoelectrochemical method. As shown in Ref.[12], on a negative potential scan, the potential corresponding to the cathodic photocurrent $J_{ph}= 0$ is defined as Φ_V, at which Cu_2O on the electrode surface is completely reduced to Cu, and is used to characterize the interaction of Cu_2O layer with the surface film caused by inhibitor. The more negative the Φ_V, the more efficient the inhibitor. Ref.[12] points out that J_{ph} at a certain negative potential can also be used to evaluate the inhibition effect of copper corrosion inhibitors, and the larger the J_{ph} at such a potential, the more efficient the inhibitor. These results could apply to the evaluation of inhibitors for copper corrosion such as 4CBTA, 5CBTA, CBT-1, CBTME, CBTBE and BT-250. In the buffer borax solution the inhibition effect of BTA for copper corrosion is better than that of 4CBTA, 5CBTA, CBT-1, PTD, BT-250, CBTME and CBTBE at the same inhibitor concentration[12-15].

In addition, two parameters, the value of anodic photocurrent on positive potential scan and the value of cathodic photocurrent on negative potential scan, are also used to evaluate the effectiveness of copper corrosion inhibitors. The former could apply to the evaluation of the inhibitors like BTA, CBTME, CBTBE, PTD and BT-250, because the photoresponse could shift from p-type to n-type at a certain amount of inhibitor on the positive scan. The larger the anodic photocurrent, the better the inhibition effects[12, 13]. The latter could apply to the evaluation of the inhibitors like 4CBTA, 5CBTA, CBT-1 and Na_2WO_4. As the photocurrent type does not change from p-type to n-type on the positive scan, the inhibition effect could be evaluated by the cathodic photocurrent on the negative scan. The larger the cathodic photocurrent, the better the inhibition effects[13, 15].

3.2 Application of photoelectrochemical method to the mechanism of inhibitors for copper corrosion

Fig. 1 shows the Intensity Modulated Photocurrent Spectra (IMPS) of a Cu electrode at different electrode potentials in the borax buffer solution

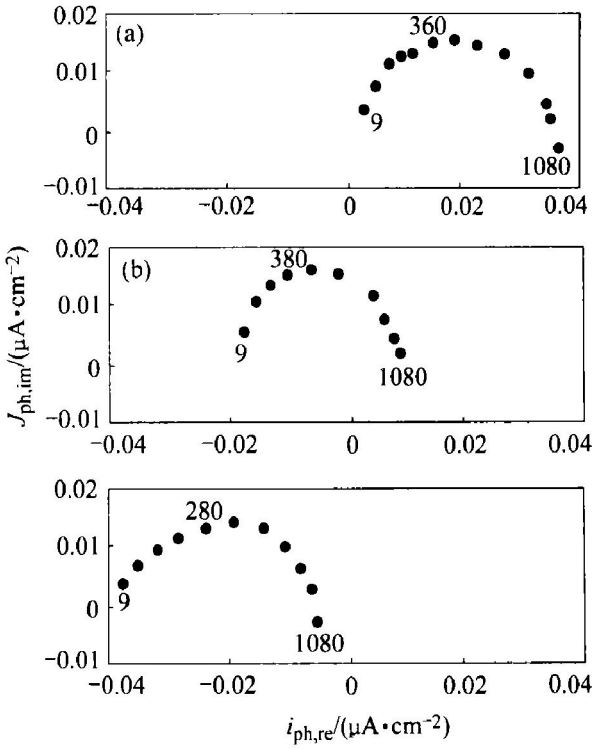


Fig. 1 Intensity modulated spectra of Cu electrode in borax buffer solution containing 40 mg/dm^3 BTA at different potentials
(a) —0.2 V, (b) —0.4 V, (c) —0.6 V
(The numbers beside solid circles indicate modulation frequencies in Hz; irradiation wavelength: 420 nm)

with 40 mg/dm^3 BTA. According to the theoretical treatments[16-18], the spectra of an n-type semiconductor should occupy the first quadrant of the complex coordinate plane, and the possible ohmic drops could move the high frequency part to the fourth quadrant. In contrast, the spectra of a p-type semiconductor should occupy the third quadrant of the complex coordinate plane, and the ohmic drops could move the high frequency part to the second quadrant. Therefore, the IMPS obtained on the Cu electrode at 0.2 V(Fig. 1(a)) and at − 0.6 V(Fig. 1(c)) show the photoresponse of n-type and p-type, respectively. However, the IMPS of the Cu electrode at − 0.4 V (Fig. 1(b)) covers both the first and the second quadrants, the high frequency part and the low frequency part display n-type photoresponse and p-type photoresponse, respectively. Hence the n-type region and the p-type region coexist in BTA-stabilized Cu_2O underlayers on the surface of the Cu electrode[11, 14].

By studying two types of photocurrent curves it is found that the inhibition mechanism of the derivatives of BTA with —COOH group(4CBTA, 5CBTA, CBT-1) is different from those with ester group (CBTME, CBTBE). In the former case the inhibitors promote thickening of Cu_2O film on Cu electrode surface, thus the cathodic photocurrent caused by Cu_2O film increases. Therefore the effectiveness of copper corrosion inhibitors could be evaluated by cathodic photocurrent. The larger the cathodic photocurrent, the better the inhibition effect[13]. In the latter case the Cu-inhibitor film, such as Cu-BTA film, acting as a barrier, hinders oxygen ions from entering into underlying Cu_2O film. As a result, O^{2-} ions deficient Cu_2O regions of n-type are formed. The photocurrent type changes from p- to n-type on the positive scan at a certain concentration of inhibitor. The value of anodic photocurrent could also evaluate inhibition effect. The larger the anodic photocurrent, the better the inhibition effect[13, 14].

3.3 Application of photoelectrochemical method to synergistic effect of inhibitors for copper corrosion

BTA and CBTME belong to the same kind of inhibitors. The inhibition effect of BTA for copper corrosion is better than that of CBTME at the same concentration of inhibitors. A combination of BTA and CBTME at some ratios shows a good synergistic effect for inhibition of copper corrosion. The anodic photocurrents for a Cu electrode in the borax buffer solution (pH 9.2) at 2 mg/dm^3 BTA + 3 mg/dm^3 CBTME, 5 mg/dm^3 BTA and 5 mg/dm^3 CBTME are 0.090, 0.060 and 0.025 μA/cm^2 on the positive scan at the potential of 0.2 V at the scan rate of 1 mV/s, respectively. It is shown that the inhibition effect of the combination of BTA and CBTME (2 mg/dm^3 BTA+ 3 mg/dm^3 CBTME) is better than that of either 5 mg/dm^3 BTA or 5 mg/CBTME alone[13, 19].

BTA and Na_2WO_4 belong to different kinds of inhibitors for copper corrosion. Photoelectrochemical experiments exhibit that the complexes of BTA and Na_2WO_4 show synergistic effect, which is in good agreement with the results by SERS[15].

Fig. 2 shows the $J-\varphi$ and $J_{ph}-\varphi$ curves for a Cu electrode in the borax buffer solution (pH 9.2) containing BTA and Na_2WO_4 at different ratios. Curves 1, 2, 3, 4 are corresponding to 3 mg/dm^3 BTA, 3 mg/dm^3 Na_2WO_4, the complex of 2.25 mg/dm^3 BTA + 0.75 mg/dm^3 Na_2WO_4 and the complex of 2 mg/dm^3 BTA + 1 mg/dm^3 Na_2WO_4, respectively. It is found that curves 3 and 4 show the photoelectrochemical characteristics of both BTA and Na_2WO_4. The photoelectrochemical characteristic of BTA is different from that of

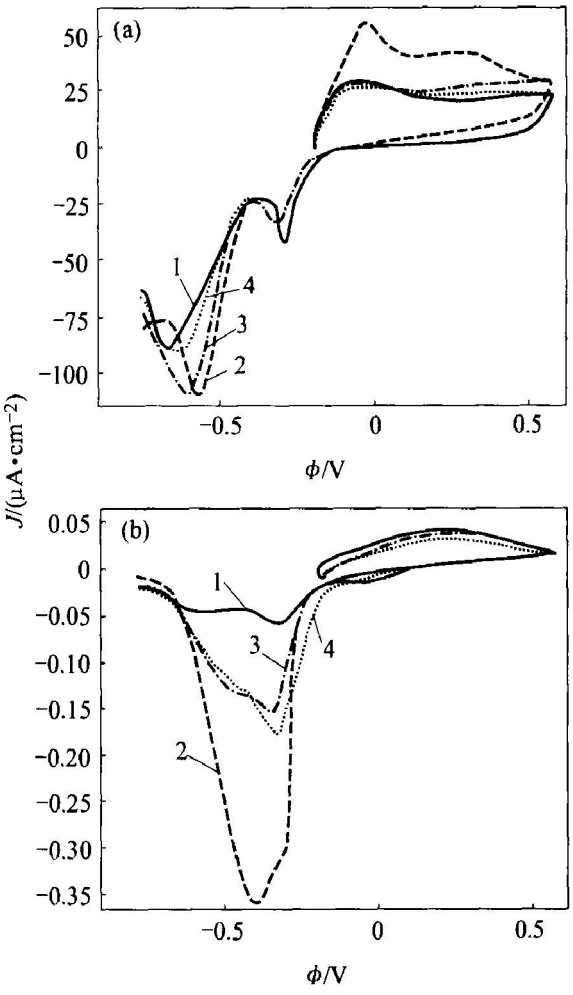


Fig. 2 $J-\Phi$(a) and $J_{ph}-\Phi$(b) curves for copper electrode in borax buffer solution with different concentrations of inhibitors
scan rate: 1 mV/s; modulation frequency: 39 Hz; irradiation wavelength: 420 nm; 1—[BTA] = 3 mg/dm^3; 2—[Na_2WO_4] = 3 mg/dm^3; 3—2.25 mg/dm^3 BTA + 0.75 mg/dm^3 Na_2WO_4; 4—2 mg/dm^3 BTA + 1 mg/dm^3 Na_2WO_4

Na_2WO_4 and the photoresponse of Cu electrode shifts from p-type to n-type at a certain concentration of BTA on the positive scan. The photoresponse of Cu electrode does not show the transition from p-type to n-type at a certain concentration of Na_2WO_4 on the positive scan, but the cathodic photocurrent significantly increases on the negative scan. In the case of BTA-Na_2WO_4 complexes, the photoresponse shifts from p-type to n-type on the positive scan, corresponding to the photoelectrochemistry characteristics of BTA and the cathodic photocurrent significantly increases on the negative scan showing the photoelectrochemistry characteristics of Na_2WO_4. Both BTA and Na_2WO_4 play the role of inhibitor for copper corrosion. The synergistic effect for combined BTA and Na_2WO_4 is also shown by AC impedance spectra[15].

3.4 Application of laser-scanning photoelectrochemical microscopy(PEM) technique to inhibition behavior of inhibitors for copper corrosion

In usual photoelectrochemical measurements, the illuminated area is of the order of a centimeter square, and the measured data reflect the macroscopic and average properties of the object, and the information about local electronic properties and the reaction process on the electrode surface could hardly be obtained. In recent years an in-situ technique with spatial resolution named laser scanning photoelectrochemical microscopy(PEM) was developed[20]. This technique is accomplished by scanning a laser beam which focuses to about several micrometers over the surface and measuring the photoresponse at each scanned point. As the photoresponse is dependent on the local properties of the passive film, we can investigate the heterogeneity of the electron properties of passive films and their susceptibility to pitting corrosion through the PEM images obtained before, during and after pitting corrosion[21].

Detailed descriptions of the theoretical background and technique of PEM have been previously reported[20]. Each experiment was performed in a conventional three-electrode cell under potentiostatic control. The cell was mounted on an X-Y stage (ORIEL Model 18503 Stepper). Photocurrents were generated by a focused chopped Ar^+ laser beam(λ= 458 nm) on the working electrode at a fixed potential at 180 Hz. The diameter of the laser spot was regulated to about 3 μm by using a spatial-filter and corresponding optics. The power was about 10 μW after focusing. The lock-in technique was applied to separate the photocurrents from the passive (dark) currents. The current output of the potentiostat (EG&G, PARC 273) was connected to the signal channel of the lock-in amplifier (EG&G, PARC 5206) and the trigger signal of the chopper (PAR M194A) was fed to the reference input of the lock-in amplifier. The output of the lock-in amplifier which was proportional to the photocurrent was connected to the input of A/D converter of a data acquisition system. The motion of the X-Y stage was controlled by an IBM PC compatible computer. The results could be displayed in a 3-dimensional graph, with X and Y being the spatial coordinates and Z the photocurrent.

PEM technique was used to study the inhibition effects and inhibition mechanism of BTA and CBTME for copper corrosion in the borax buffer solution[19].

PEM technique can be applied to the study of process on microzones of the electrode surface and the observation of the coexistance of the p-type and n-type zones at different positions on the copper electrode surface and the transition from p-type to n-type. Fig. 3(a) is the PEM graph of copper in the borax buffer solution (pH 9.2), showing a p-type photoresponse at some sites. Fig. 3(b) is the PEM graph of copper after adding 5.5 mg/dm^3 CBTME to the borax buffer solution at the poten-

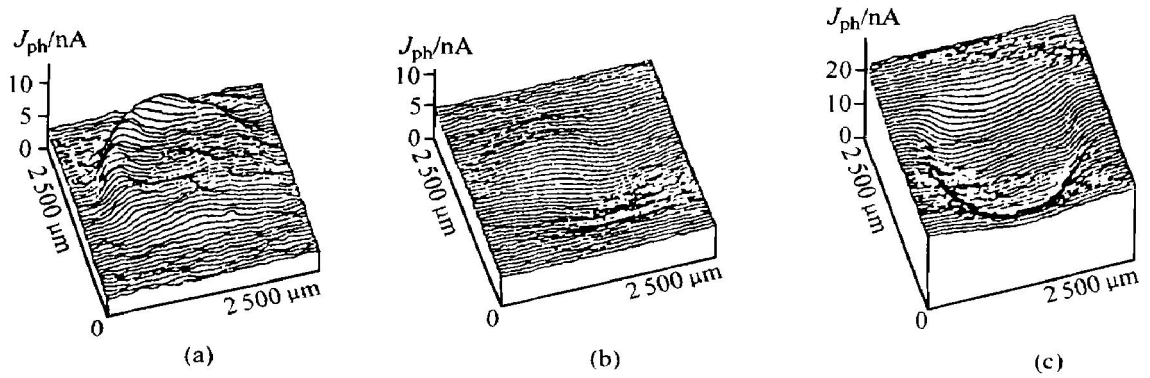


Fig. 3 3D-PEM graphs of copper electrode surface obtained in borax buffer solutions containing CBTME under different conditions

(a) —Blank; (b) —Injecting 5.5×10^{-4}% CBTME at − 0.06 V_{SCE}

(c) —With 5.5×10^{-4}% CBTME after cathodic polarization for seconds at − 0.06 V_{SCE}

tial of − 0.06 V, showing the coexistance of the p-type and n-type photoresponse at different positions on the copper electrode surface. It is suggested that some "active" zones were apt to form film with inhibitor of CBTME and their photoresponse would transfer from p-type to n-type; whereas some non-"active" zones still maintain p-type photoresponse but its photoresponse became smaller due to the action of the inhibitor of CBTME. After a cathodic polarization for seconds at − 0.06 V, the PEM graph with 5.5×10^{-4}% CBTME shows the entire transition of p-type to n-type photoresponse as shown in Fig. 3 (c). Accordingly we can study the electrochemical reaction process at micro-level.

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