

Electrochemical research on corrosion behavior of A3 steel in compound sodium molybdate and organic inhibitor solution

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Abstract. The electrochemical corrosion behavior of A3 in compound sodium molybdate and organic inhibitor solution was tested by the electrochemical workstation method. The concentration of the compound inhibitor set to range 250 mg/L to 3000 mg/L. The polarization curve results of A3 in different concentration inhibitor solutions show that the inhibitor markedly represses the anodic processes. The EIS has two time constant. The extreme concentration is 1500 mg/L.

1. Introduction

Inhibitors play an important part in preventing metal used in recycling cooling water from corroding. Sodium molybdate has low toxicity to environment and biological as a kind of inorganic inhibitor that can influence electrochemical corrosion reaction [1, 2].

ATA as an organic inhibitors can form a SMS (self-assembled monolayers) on the surface of metal matrix through the chemical bond. ASM technology has the advantage of higher inhibition efficiency at the low dosage compared with the traditional method [3-6].

This study mainly used organic inhibitors ATA formed a SMS on the surface, meanwhile with the help of inorganic inhibitors sodium molybdate and ZnSO₄ fill the void of the SMS, by the two methods cooperating with each other the compound inhibitors can form an impact and uniform membrane on the surface of the A3.

2. Experimental

2.1. Materials

Sodium Molybdate 10 mg/L, ATA (3-Amino-1, 2, 4-triazole) 1 mg/L, POCA (Copolymer of Phosphono and Carboxylic Acid) 2.5 mg/L, ZnSO₄ 8 mg/L, PESA (Sodium of Polyepoxysuccinic Acid) 10 mg/L. The concentration set to range from 250 mg/L to 3000 mg/L.

2.2. Inhibitors preparations

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Firstly, dilute the ATA at 60°C and then cool it to room temperature; secondly add molybdate POCA and PESA to the molybdate solution waiting for them dissolved, and then stir it well; Thirdly, add ZnSO₄ to the compound solution and stir well for use.

2.3. Instrument

Potentiostat/galvanostat CS 2305, JSM-6510 scanning electron microscopy (SEM), BT224s Electronic Balance. Magix Pro PW2440 X-ray photoelectron spectroscopy (XPS).

2.4. Experimental procedure

2.4.1. Electrochemical test of A3. A3 electrode was sealed in epoxy resin except the exposed cross-section as working surface. The A3 electrode was embedded in epoxy resin with an exposed cross-sectional area of 1 cm². The counter electrode in electrochemical test was platinum while saturated calomel electrode (SCE) was used as the reference electrode. The electrochemical studies were operated on the Potentiostat/galvanostat CS2305. Linear polarization measurement were carried out with a potential perturbation of ±100 mV around the open circuit potential (OCP), Electrolyte was prepared by adding compound sodium molybdate and organic inhibitor solution with the concentration ranging between 250 mg/L~3000 mg/L in tap water. The electrochemical impedance spectra (EIS) of the A3 electrode system were measured at 10mV disturbing sinusoidal wave and the frequency was 0.1 Hz to 10 kHz.

2.4.2. SEM test. The A3 plate with size of 50 mm x 25 mm x 2 mm were immersed in the compound inhibitor solutions after 72 h at 45°C, then washing it by water and alcohol in turn. The operation parameters were at 25 kV acceleration voltage.

2.4.3. XPS test. The A3 The A3 plate with size of 50 mm x 25 mm x 2 mm were immersed in the compound inhibitor solutions after 72 h at 45°C, then then washing it by water and alcohol in turn. The operation parameters were at 3 kV focus voltage, 3 kV energy voltage. The XPS use magnesium as target and operated at 0.1 mpa vacuum degree.

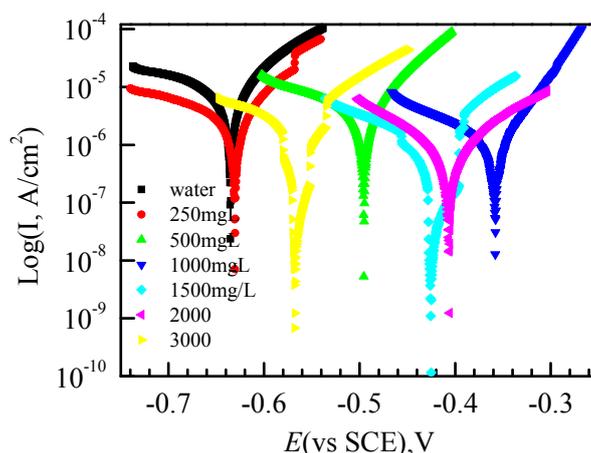


Figure 1. Polarization curves of A3 electrode in different concentration inhibitor solutions.

3. Results and discussions

3.1. Electrochemical test results

3.1.1. Effect of concentration on the polarization curves of A3 electrode. Figure 1 shows the polarization curves of A3 electrode in different concentration sodium molybdate and organic inhibitor

solutions. From figure 1 a markedly represses on anodic processes and a positive shift of the corrosion potential E_{corr} can be found. Furthermore the anodic branch of the polarization curves is noted that have a higher slope than that in blank solution (without additive). The electrochemical parameters of A3 derived from polarization measurement were given in table 1. From table 1 that the R_p and I_0 value decrease with the concentration of the compound sodium molybdate and organic inhibitor increase when it below 1500 mg/L. The R_p and I_0 value increase with the concentration of the compound sodium molybdate and organic inhibitor increase when it above 1500 mg/L. From the change of R_p and I_0 that the film formed on the A3 by the compound sodium molybdate and organic inhibitor become wore thicker with the increase of inhibitors. The change of I_0 also indicate that the compound inhibitors has composite effect on the anode and cathode reaction.

Table 1. Electrochemical parameters of A3 derived from polarizational measurement.

	$R_p (\Omega \cdot \text{cm}^2)$	B_a (mV)	B_c (mV)	$I_0 (\mu\text{a}/\text{cm}^2)$	EI (%)
0mg/L	2422.0	61.27	110.38	6.60	
250mg/L	5725.5	57.22	119.95	2.99	55.05
500mg/L	15273.0	54.88	131.70	1.31	83.03
1000mg/L	13041.0	52.67	146.43	1.32	85.18
1500mg/L	100129.0	69.30	105.26	0.34	94.70
2000mg/L	58288.0	61.30	87.77	0.73	89.04
3000mg/L	23543.0	34.37	-	1.09	83.60

3.1.2. Effect of concentration of inhibitor on electrochemical impedance spectra. Figure 2 shows the Nyquist plots of A3 electrode in different concentration compound sodium molybdate and organic inhibitor concentration solutions. From figure 2 the radius of the nyquist plots of A3 change bigger with the increase of the inhibitor concentrations below 1500 mg/L while it change smaller with the increase of the inhibitor concentration above 1500 mg/L. The Nyquist curve of the compound sodium molybdate and organic inhibitor resume a single capacitive with no sign of inductive impedance when the concentration set below 1000 mg/L which meaning that the adsorption layer on the A3 electrode surface is stable.

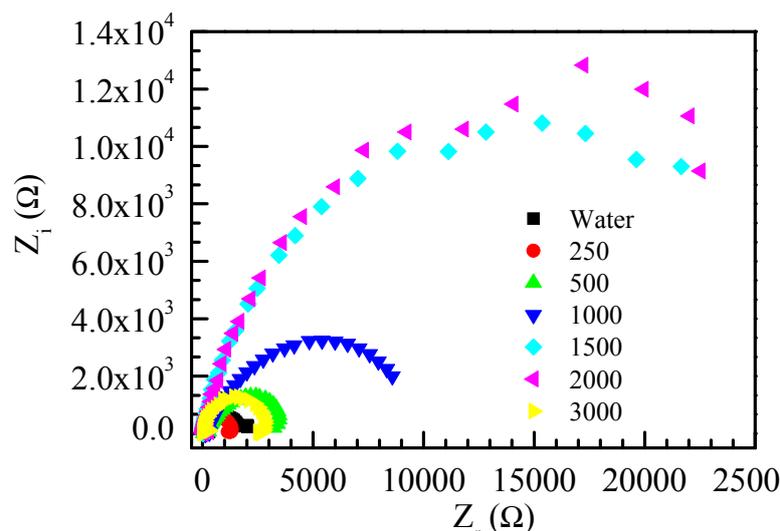


Figure 2. Nyquist spectra of electrode in different concentration inhibitor solutions.

Figure 3 shows the bode spectra of A3 plate electrode in different concentration compound sodium molybdate and organic inhibitor solutions. From figure 3a the introduction of the compound sodium molybdate and organic inhibitor solutions make the changes increase at high frequency. The change of phase angle at high frequency is discontinuous. The absolute value of Z at low frequency indicates the

polarization resistance [7, 8]. From figure 3b the change of absolute value of Z at low frequency is discontinuous which indicate the introduction of the compound sodium molybdate and organic inhibitor have an extreme value to protect A3 from corrosion.

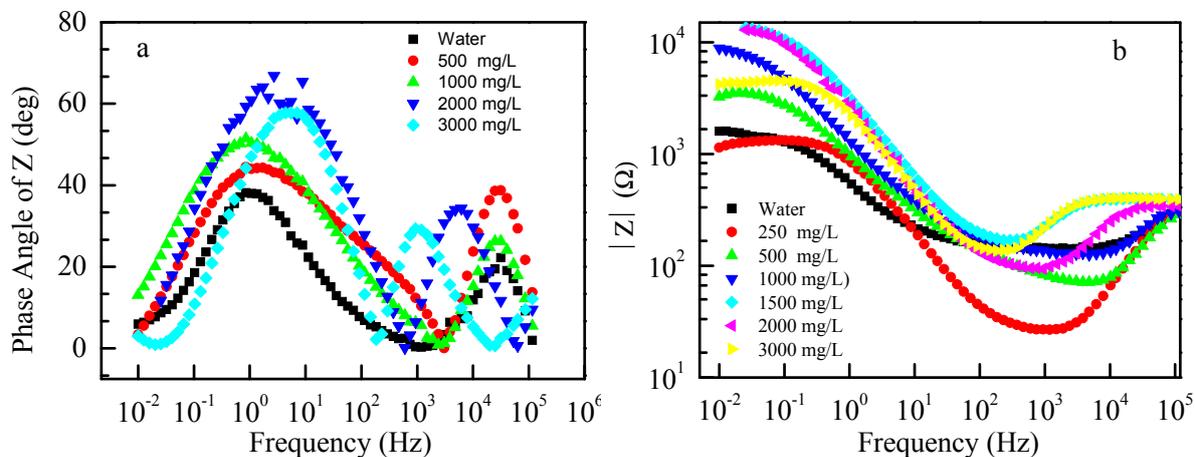


Figure 3. Bode spectra of A3 plate electrode in different concentration compound molybdate inhibitor solutions (a) phase angle plots, (b) absolute value of Z .

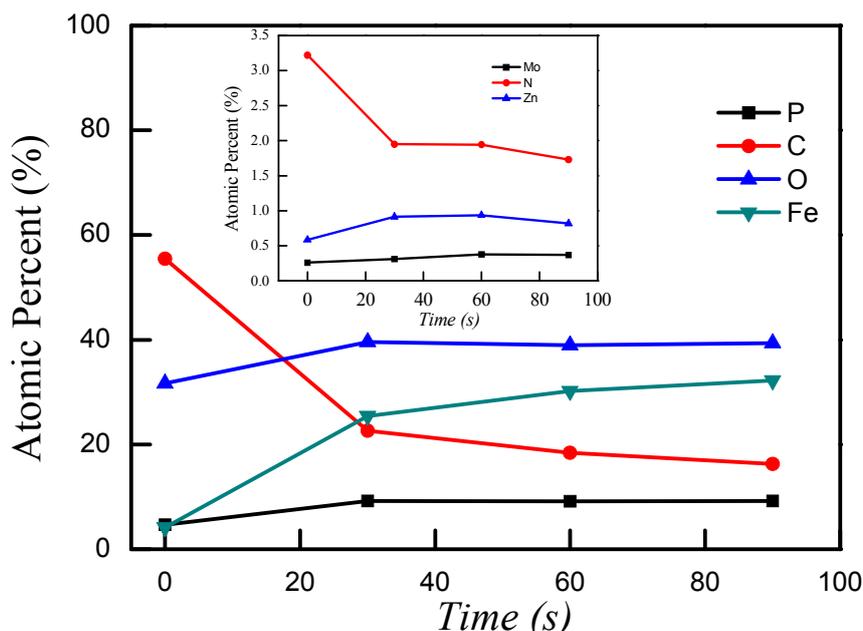


Figure 4. Surface elements results observed by XPS.

3.2. XPS results of A3 plate after test

Figure 4 shows the XPS results of A3 plate which immersed in the compound sodium molybdate and organic inhibitor solutions for 72h. The results show that the surface was composed of C, O, P, Fe, Mo, N, Zn elements. The C contents of A3 plate on the surface were higher than that after sputtering. The reason leading to the C content in surface higher is the C surface adsorption result. The Mo content still can be tested after sputtering 90s which illustrate the compound sodium molybdate and organic inhibitor formed a thin membrane on the A3 plate surface. The membrane formed by the compound sodium molybdate and organic inhibitor solution was comprised of C, O, P, Fe, Mo, N, Zn elements.

3.3. SEM results of A3 plate

Figure 5 shows the SEM results of A3 plate which immersed in the compound sodium molybdate and organic inhibitor solutions for 72 h. From figures 5a and 5b a uniform and compact membrane was formed on the surface of the A3 plate after immersed in the compound sodium molybdate and organic inhibitor solutions. The membrane on the surface can protect A3 used cooling water system from corrosion.

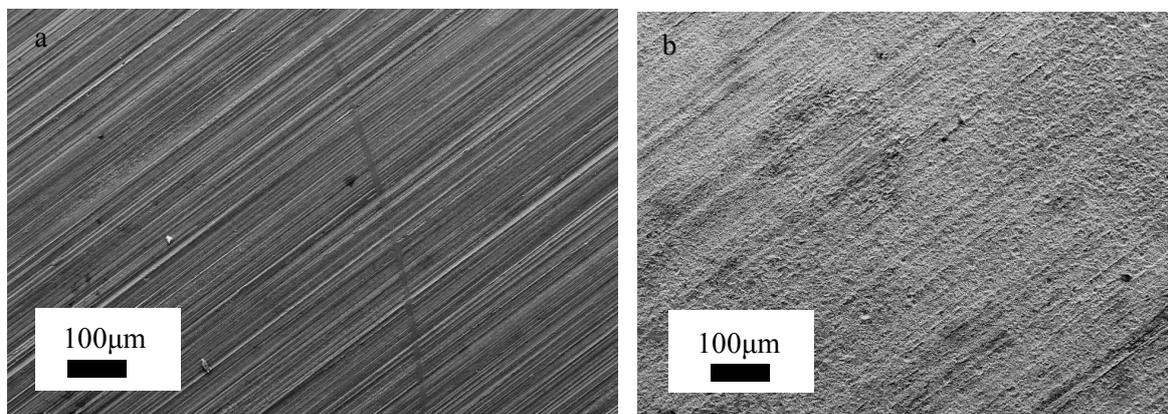


Figure 5. SEM result of A3 plate (a) before test, (b) after test at 45°C.

4. Summary

The researched compound sodium molybdate and organic inhibitor can protect the A3 from corrosion by markedly impact the anode reaction. The electrochemical parameters derived from polarization curves and the EIS result shows the 1500mg/L is an extreme concentration. The bode phase has two time constance.

The XPS results show that the membrane formed on the surface of A3 composed of C/O/P/Fe/Mo/N/Zn elements.

The SEM results show that the membrane formed on the surface of A3 after immersed in the compound sodium molybdate and organic inhibitor solutions is uniform and impact.

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