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Synergistic corrosion inhibition mechanism of Calcium lignosulfonate (CLS) and inorganic inhibitors in alkaline environment containing Cl^-

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New Abstract

In order to reduce and retard corrosion reactions on carbon steel in alkaline environment, the synergistic corrosion inhibition mechanism of calcium lignosulfonate (CLS) and three kinds inorganic inhibitor (Na_2MoO_4, Na_2SnO_3, and $NaWO_4$) with various molar ratio was investigated by electrochemical measurements and surface analysis in alkaline solution (pH 11.5) with 0.02 mol/L NaCl. Molybdate and stannate in hybrid inhibitor could promote the passivation of steel and form a complex film, which could suppress the corrosion effectively. And the insoluble metal oxides in the complex film formed by three kinds of inorganic inhibitor could help the adsorption of CLS onto steel surface. The CLS molecules could adsorption onto steel surface and metal oxides to form an adsorption film to protect the steel from corrosion. A three-layer protection film formed by hybrid inhibitor, including passivation film, deposition film and adsorption film, would effectively inhibits the corrosion reactions on steel surface. CLS compound with molybdate with the ratio of 2:3 shows the best inhibition effect on both general corrosion and localized corrosion.

Keywords: Compound corrosion inhibitor, Synergistic effect, Electrochemical measurements

Introduction

Alkaline environment is a common corrosion condition in reinforced concrete system, marine environment and industrial desulfurization installation. Developing new kinds of environmental-friendly inhibitors with high inhibition efficiency for concrete rebar becomes a necessary research subject. As an effective corrosion inhibitor, calcium lignosulfonate (CLS) has been proved to be a good corrosion inhibitor in alkaline corrosion envrionment for carbon steel [1,2]. As environmental-friendly inorganic corrosion inhbitor, many authors published their results for inhibiting effect of tungstate [3], molybdate [4] or stannate [5]. However, tungstate, molybdate and stannate are usually not used as corrosion inhibitor alone, which is due to thier low inhibition efficiency at low concentration, high cost and low oxidizing ability. Therefore, using co-inhibitors is useful to increases the inhibition effect of this kind inorganic inhibitors, and there are several investigations of combine inorganic and organic inhibitors to improve the corrosion protection effect [6,7]. Combined inorganic inhibitor with organic compounds for protection of metallic matrix is supposed to have a good synergistic inhibition

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effect. In order to further figure out the synergistic inhibition effect between CLS and inorganic inhibitors in pH 11.5 corroison medium , the corrosion inhibition mechanism of CLS compound with different inorganic inhibitors (Na_2MoO_4, Na_2SnO_3 and $NaWO_4$) was investigated by cyclic potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), linear polarization, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

Methodology and Results

Q235 carbon steel was set in epoxy resin and leaving a 0.64 cm^2 area exposed to the test solution. The working surface were prepared and abrade by emery paper from 240 to 1000 grade, then washed with de-ionized water and ethanol and finally dried by hot air. The corrosion medium was composed of 0.0021 mol/L NaOH, 0.0042 mol/L KOH, and 0.02 mol/L NaCl, and the pH value was adjusted to 11.5 by NaOH or HCl. All electrochemical tests were performed in a standard three-electrode cell by using CS350 electrochemical workstation (Corrtest Company, Wuhan, China), and the saturated calomel electrode and a platinum foil used as the reference and counter electrode, respectively. Surface analysis including SEM, EDS and XPS were performed on inhibited steel surface to study the micromorphology, chemical composition and protection film.

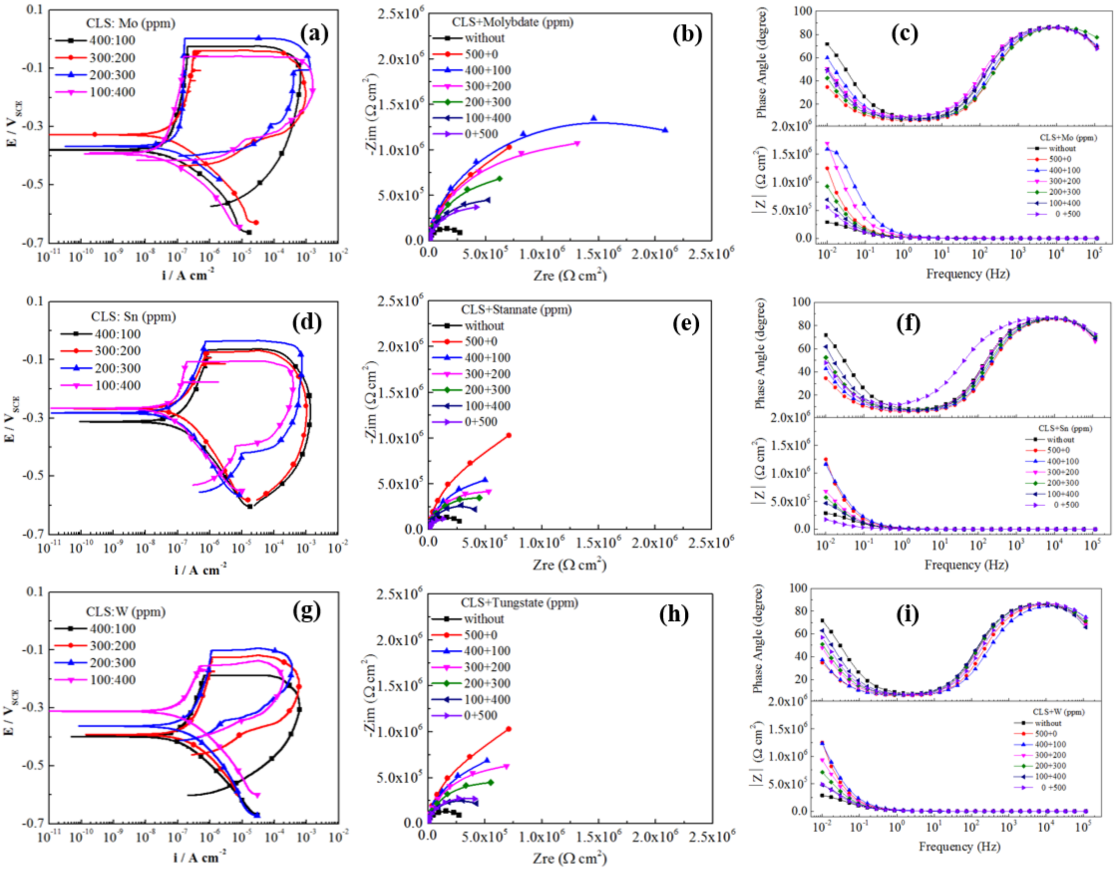

Figure 1 - Electrochemical measurement results for Q235 carbon steel in pH 11.5 solution containing 0.02 mol/L Cl^- with different ratio compound inhibitor,
(a) polarization curves, (b) Nyquist polts, (c) Bode polts for CLS compound with molybdate.
(d) polarization curves, (e) Nyquist polts, (f) Bode polts for CLS compound with stannate.
(g) polarization curves, (h) Nyquist polts, (i) Bode polts for CLS compound with tungstate.

500 ppm hybrid inhibitor with various ratio of CLS and inorganic inhibitor were added into test solution to understand the synergist inhibition effect of inhibitors. The ratio of CLS to inorganic inhibitor is 400:100, 300: 200, 200:300, 100:400, respectively. The electrochemical measurement resutls are shown in Figure 1. Hybrid inhibitors could not change the corrosion behavior of Q235 steel in test environment. CLS compound with three kind of inorganic inhibitors could inhibit both general corrosion and localized corrosion. CLS compound with molybdate have the best inhibition effect, while CLS compound with tungstate have better effect on localized corrosion, and compound with stannate have better effect on general corrosion. The inhibition effect of hybrid inhibitor increases as the inorganic ratio increases, and the inhibition effect for both general corrosion and localized corrosion is best when the CLS and inorganic inhibitor ratio is 2:3. As the inorganic inhibitor ratio further increases, the inhibition effect slightly decreases.

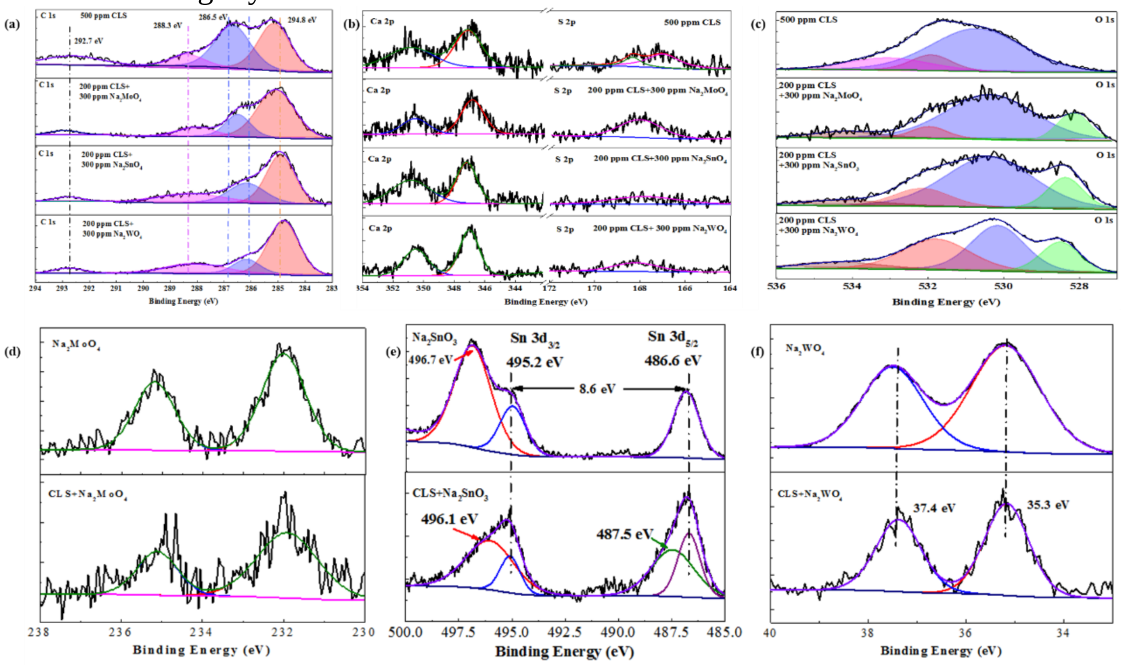

Figure 2 – XPS spectra of hybrid inhibitor treated steel surface,
(a) C 1s, (b) Ca 2p and S 2p, (c) O 1s, (d) Mo 3d, (e) Sn 3d, (f) W 4f.

Figure 2 indicates the protection film formed on steel surface after hybrid inhibitor treated. And the synergistic inhibition mechanism of CLS compound with inorganic inhibitor could be inferred, as shown in Figure 3. The first step is hybrid inhibitor dissociate instantly to lignosulfonate (LS^{2-}), calciumions (Ca^{2+}), and MoO_4^{2-}/WO_4^{-}/SnO_3^{2-}. The adsorbed molybdate or stannate would promote the passivation of steel surface to form Fe oxides and the reduction products of inorganic inhibitors. A deposition film formed by inorganic inhibitors on passivation film could further protect the steel surface. Finally, LS^{2-} would adsorb on the outside film by sharing electrons to metal atoms, forming a hydrophobic layer to protect the steel. The three-layer protection system formed by hybrid inhibitor could prevent both general corrosion and localized corrosion.

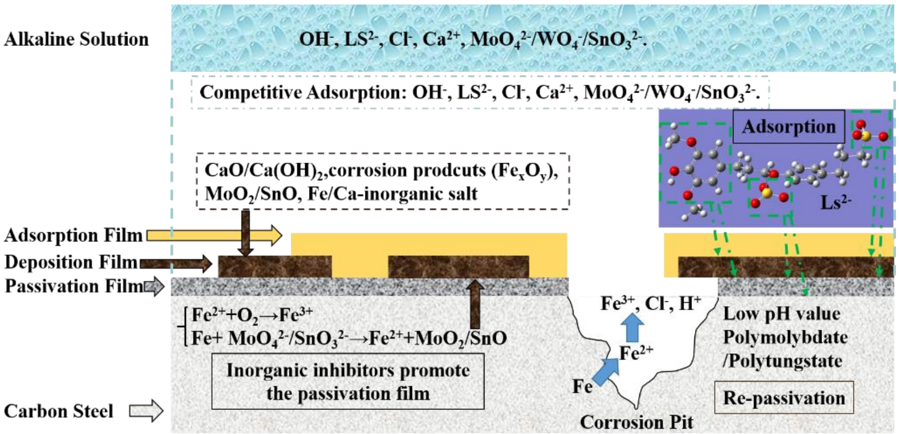

Figure 3 – The schematic illustrations of the inhibition mechanism.

Conclusions

The synergistic inhibition effect and mechanism of CLS compound with molybdate, stannate and tungstate in alkaline environment with 0.02 mol/L Cl^- were studied in this work, and the following conclusions can be drawn: CLS have synergistic inhibition effect with molybdate, tungstate and stannate for carbon steel in test alkaline environment by increasing the pitting potential and decreasing the corrosion current density. Hybrid inhibitor formed by CLS and molybdate shows the best inhibition effect in all hybrid inhibitors, and the best ratio of CLS and inorganic inhibitor is 2:3. The inorganic inhibitor (molybdate and stannate) could enhance the passive film on steel surface. Oxides and hydroxides of Ca, Mo/Sn, and insoluble inorganic inhibitor compounds could deposit on steel surface forming a deposition film. Finally, CLS would adsorb on the outside of steel surface, forming hydrophobic layer to protect the steel. The three layer compounded film effectively inhibits corrosion of the steel surface.

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