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Phytic acid adsorption on the copper surface: Observation of electrochemistry and Raman spectroscopy

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ABSTRACT

The adsorption of phytic acid (PA) on copper was investigated using electrochemical impedance spectroscopy (EIS), electrochemical polarization measurement and surface-enhanced Raman scattering (SERS) spectroscopy. Electrochemical results indicated that inhibition efficiency of PA film for copper from corrosion in 3 wt% NaCl solution was beyond 80% at an optimum self-assembly concentration of 0.1 mM for 6 h. Electrochemical polarization indicated that PA functioned as a cathodic inhibitor. In addition, Raman studies showed that PA adsorbed on the copper surface formed via P–O groups. Finally, the value of ΔG_{ads} ($-39.96\,kJ\,mol^{-1}$) was close to $-40\,kJ\,mol^{-1}$, suggesting that the adsorption of PA on the copper surface was the chemical adsorption.

1. Introduction

Phytic acid (PA) and its salts, naturally derived materials, have been used as environmentally benign chemical additives. The most attractive advantages of PA include its low-cost and availability as a typically polyphosphorylated carbohydrate (Scheme 1) widely occurring in beans, brown rice, corn, sesame seeds, and wheat bran. PA, used as cleansing agent, water treatment agent, food additives and cosmetic additive, has been proved that it is non-toxic to human and "green" to environment. Due to its structure containing 12 acid groups, PA and its salts are liable to interact with metal ions as a result of formation of complexes at the metal surface for antirust and anticorrosion [1–7].

Copper and its alloys have been widely used in the world because of its excellent chemical properties [8,9]. Nevertheless, they are susceptible to corrosion problems in the aggressive media, especially in the chloride-containing aqueous solution, which can considerably accelerate the dissolution of metal [10]. One of the important methods for the protection of metal is to use the inhibitors [11–16]. Many of the well-known inhibitors are organic compounds typically containing nitrogen, sulfur, and oxygen atoms, which create a barrier to the corroded attack. Unfortunately, these inhibitors are mostly toxic to the environment and relatively expensive.

Among the widely used inhibitors, the better choice of the appropriate inhibitor for a particular application is PA or its salts. The corrosion inhibition of PA and its salts for the copper and silver have been studied. Yang et al. [2] used sodium of phytic acid to study its corrosion inhibition possibility for the copper surface. Hao et al. [5] utilized electrochemical and photocurrent response methods to study anticorrosion and inhibiting mechanism of PA at Cu-based alloy. In this work, in order to gain an insight into the self-organization mechanism of a molecule at the interface, we introduce the surface-enhanced Raman scattering (SERS) spectroscopy [17–19] to probe the adsorption behavior of the assembled adsorption of PA on the copper surface, which can provide abundant molecular vibration information to clarify the configuration of molecular adsorption and the interaction mechanism on the supporting substrate.

Further observation of the PA adsorption on the copper surface has been performed by electrochemical impedance spectroscopy (EIS) [20]. EIS technique, a nondestructive, sensitive, and informative method, has been extensively used for the evaluation of coatings for corrosion inhibition, especially for analyzing the electrode with assembled organic layers. The electrochemical polarization in the form of Tafel plot can provide the corrosion rates from linear polarization and determine the efficiency of the corrosion inhibitor [21,22]. Additionally, the adsorption behavior of PA is investigated by Langmuir adsorption isotherm.

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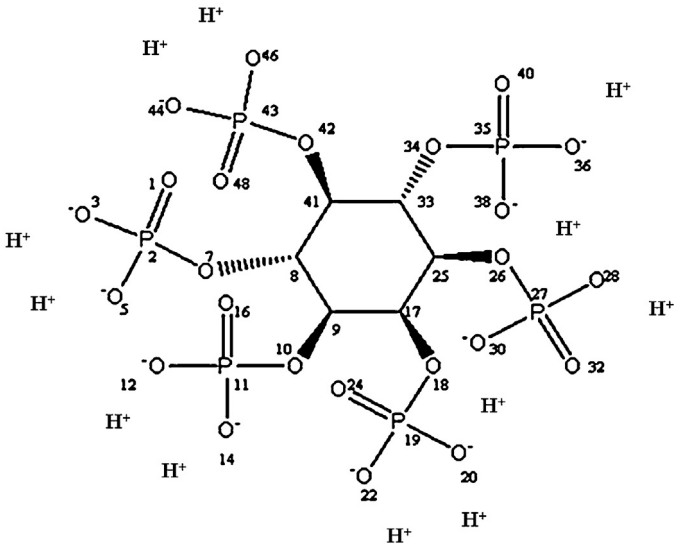

Scheme 1. Structure of phytic acid.

The aim of present work is to investigate the corrosion inhibition behavior in 3 wt% NaCl solution of PA films adsorbed at the copper surfaces in different concentrations of PA solutions and time by electrochemical methods. Meanwhile, SERS spectroscopy is used to elucidate the structure of PA adsorbed on the copper surface.

2. Experimental

2.1. Chemicals and materials

PA in 50 wt% solution was purchased from the Sigma–Aldrich Corporation. Sulphuric acid, sodium chloride, and ethanol were of analytical grade and purchased from Sinopharm Chemical Reagents Company. All solutions were prepared with Milli-Q water (18 MΩ cm).

2.2. Apparatus

Raman spectroscopic measurements were performed by using a confocal microprobe Raman system (LabRam II, Dilor, France). A liquid nitrogen-cooled 1024 × 800 pixels charge-coupled device was utilized as a detector, and an exciting line of 632.8 nm was supplied by a He–Ne laser with power of ca. 5 mW. A 50× long-working-length objective was used for focusing the laser spot on the electrode surface. The slit and pinhole were set at 100 and 1000 μm, respectively. Each spectrum was measured 3 times, and the acquisition time was 20 s. Calibration was done referring to the 519 cm^{-1} line of silicon.

The electrochemical measurements were carried out by a CHI750c electrochemistry workstation (CH Instruments, Inc.).

2.3. Pretreatment for electrode

The copper electrode was made from the polycrystalline copper rod (99.999%, Sigma–Aldrich) and the geometric area of surface was ca. 0.0314 cm^2 (embedded in a Teflon sheath). Before the experiment, the copper electrode was sequentially polished with Emery paper and 0.3 μm alumina/water slurries until a shiny, mirror-like surface was obtained, and then was washed with Milli-Q water and pure ethanol ultrasonically to remove any existed alumina particles. For SERS detection, to obtain the necessary roughness of the copper surface, an oxidation reduction cycle treatment (ORC) [23] was performed in a conventional three-electrode cell. The bare copper specimen or the PA film modified copper specimen was used as the working electrode. A platinum electrode was used as the counter electrode. All potentials cited in this paper were converted to saturated calomel electrode (SCE).

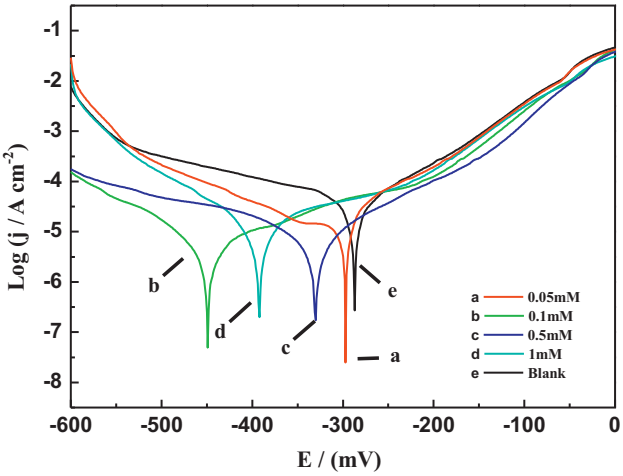

Fig. 1. Potentiodynamic polarization curves in 3 wt% NaCl solution for blank copper and the copper electrode with PA film formed in different concentrations of PA solutions for 6 h.

2.4. Formation of PA film

Before the formation of PA film, the polished copper electrode was underwent ORC in 2 M H_2SO_4 by switching between −550 mV and +450 mV vs. SCE to achieve a fresh surface, then rinsed with Milli-Q water and absolute ethanol as soon as possible. And then the treated copper electrode was immersed immediately into the deoxygenated PA solution with different concentrations for different times at room temperature. After that the modified electrode was taken out of the solution and rinsed carefully with ethanol and Milli-Q water, and subsequently dried by flowing nitrogen gas prior to further investigations.

2.5. Electrochemical measurements

Electrochemical measurements studies were firstly carried out in order to establish the optimum conditions for the formation of protective film on the copper surface. The electrochemical studies were carried out in a three-electrode cell. EIS measurements were performed at the open circuit potentials with the AC voltage amplitude of 5 mV in the frequency range from 0.01 Hz to 100 kHz. The polarization curves were obtained from 0 to −600 mV vs. SCE with a scan rate of 10 mV s^{-1}.

3. Results and discussions

3.1. Electrochemical polarization studies

Figs. 1 and 2 show the electrochemical polarization curves in 3 wt% NaCl solution for the naked and PA-covered copper electrodes with different concentrations and time. The corresponding electrochemical parameters such as the corrosion potential (E_{corr}) and corrosion current densities (j_{corr}) along with the inhibition efficiency (η) are listed in Tables 1 and 2. Both the anodic and cathodic Tafel regions are used to determine the j_{corr} and E_{corr} [24].

In 3 wt% NaCl solution, compared with bare copper, it is easy to find that the presence of PA film results in more negative potential as well as decreasing the both anodic and cathodic current densities, while it seems that the cathodic current densities decrease is