



Severe corrosion of copper in a highly alkaline egg white solution due to a biuret corrosion reaction



Xun Liu^{a,b,*}, Wenyuan Hu^a, Shan Yang^a, Zhaoqian Li^a, Chonghua Pei^a, Yong Zhou^c, Guanfu Yin^b

^aState Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China

^bCollege of Materials Science and Engineering, Sichuan University, Chengdu 610065, China

^cDepartment of Materials Science and Engineering, National Lab of Solid State Microstructure, ERERC, Nanjing University, Nanjing 210093, China

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ABSTRACT

Through investigating the interaction between copper metal and egg whites as well as the effects of pH, oxygen and the species of alkalis on copper corrosion rate, an unusual severe corrosion of copper metal in a highly alkaline egg white solution was found. The mechanism was investigated through detailed characterizations using a scanning electron microscope, X-ray diffraction, X-ray photoelectron spectroscopy and UV–visible absorption spectroscopy. The severe corrosion was mainly due to the formation of a hydroxyl–peptide–copper multicomponent stable soluble complex, which the biuret reaction also produces.

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1. Introduction

Because of its desirable physicochemical, mechanical and aesthetic properties, copper metal is widely used in many fields, including electronics, biomedicine, and industrial catalysis, as well as food preparation in daily life [1–4]. However, copper metal is easily corroded in humid air or in liquids, especially in the presence of certain inorganic or organic materials. At present, research mainly focuses on the effects of the presence of inorganic materials [5,6]. In general, the effects of the organic materials having been reported are relatively less except for certain model proteins and some low-molecular-weight organic compounds. Clark and Williams proved that the proteins fibrinogen and serum albumin can accelerate the corrosion of copper [7]. Using bovine serum albumin (BSA) as a model protein, some researchers have reported that it can promote the dissolution of copper in copper-containing intrauterine devices and dental casting alloys [8,9]. Bernardi et al. showed that potential chemical damage to outdoor copper and bronzes from the uric acid in bird urine was significant [10]. Fazal et al. investigated the mechanism of enhanced corrosion of copper in palm biodiesel [11].

As one of the commonest proteins used in the kitchen, egg whites regularly come into contact with copperware or copper-containing devices. The interaction between the egg whites and the copper is

often overlooked. It not only affects the condition and function of copper devices but may also cause dangerous levels of copper ions from copperware to pass into food or drinking water, potentially resulting in copper poisoning [12–14]. In this paper, we investigate the interaction between copper metal and egg whites, describe the resulting severe corrosion at pH values of 12–13, and propose a corrosion mechanism.

2. Experimental

2.1. Reagents

The reagents and chemicals NaOH, Na₃PO₄, Na₂CO₃, HCl, HNO₃, and H₂SO₄, as well as the copper metal (99.99%), glutamic acid (99%) and L-aspartic acid (98%), were all purchased from KeLong Chemical (Chengdu, China). The reagents and chemicals unlabeled purity were of analytical reagent grade. The egg whites were extracted from fresh hen eggs purchased from Wal-Mart (Mianyang, China). The milk came from Mengniu Company (Meishan, China), the glutelin (80%) from Shuoguang Electronic Technology (Shanghai, China), and the BSA (98%) from Shanghai Bio Science & Technology (Shanghai, China). All solutions were made with ultrapure water (Sichuan ULUPURE Ultrapure Technology, Chengdu, China).

2.2. Corrosion

A 1% (v/v) aqueous solution of egg white was pre-prepared, which pH was adjusted using 1 mol/L NaOH or 0.1 mol/L HCl

* Corresponding author at: State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China. Tel.: +86 816 2419280; fax: +86 816 2419280.

E-mail address: liuxun@swust.edu.cn (X. Liu).

solutions to a certain value between 5 and 14 and monitored by pH meter. All experiments were performed in conical flasks under ambient conditions without stirring. Before the reaction, 200 mL of the pre-prepared egg white solution was added, and then the conical flask was put into a thermostat water bath to hold the reaction temperature at 20 °C. When the temperature of the egg white solution was constant, 1 g of copper sheet with a size of 0.5 cm × 0.5 cm was added, and the reaction time started to be counted. After a certain reaction time, 5 mL of reaction solution was sucked up for wet digestion, and then the digested solution was diluted to 50 mL for determining the concentration of copper ion using atomic absorption spectrometry (AAS). The extent of corrosion was measured by comparing the copper ion concentration in the original reaction solution.

2.3. Wet digestion method

In order to eliminate the interference of organic matter, especially insoluble organic matter, on the test of copper ion, wet digestion method was applied to the reaction solutions to decompose the organic matter to CO₂, water and other gases before injection of AAS. Specific details were as follows: 5 mL of reaction solution was sucked up into a pipette and transferred into a Schlenk flask together with 10 mL of distilled water, 15 mL of HNO₃ and 10 mL of H₂SO₄. When the solution turned brown, 5 mL of HNO₃ was added. Once brown gas stopped evolving, the solution was heated quickly until tiny yellow solution formed. Finally, more distilled water was added to increase the volume to 50 mL for the test.

2.4. Instruments and analytical conditions

The copper ion concentration was measured using flame atomic absorption spectrometry (PerkinElmer Instrument, AA700). X-ray photoelectron spectroscopy (XPS) measurements were performed in a Kratos XSAM 800 instrument with a magnesium anode at 225 W. The surface composition of the copper sheets was analyzed using X-ray diffraction (XRD; Rigaku Dmax-RB) with Cu K α radiation. The pattern was collected with 35 kV of tube voltage and 60 mA of tube current in the angular range 20–80° in a continue scan mode (step width, 0.02°; scanning speed, 8° per minute). A scanning electron microscope (SEM; HITACHI, TM-1000) was used to determine the surface morphology of the copper sheets. UV–visible absorption spectra were taken to confirm the complexing information using a Varian Cary 50 Scan UV–visible spectrophotometer.

2.5. Statistical analyses

The copper ion concentrations were presented as means \pm SE (standard error of mean, $n = 5$), for which the Student's t -value was express at the 95% confidence level.

3. Results

3.1. The influence of reaction conditions

In order to find out the effect of the pH value of egg white solution on copper corrosion rate, experiments of copper corrosion at different pH values were carried out. Fig. 1A shows the relationship between the pH value of the reaction solution and the 10-day copper ion concentration (i.e., a cumulative concentration after 10 days in solution). It can be seen that the copper ion concentrations in the egg white solution are all higher than those for the control groups (without egg-whites) within the experimental pH range. That means that egg whites can accelerate corrosion of copper, but when the pH value is between 5 and 11, the copper

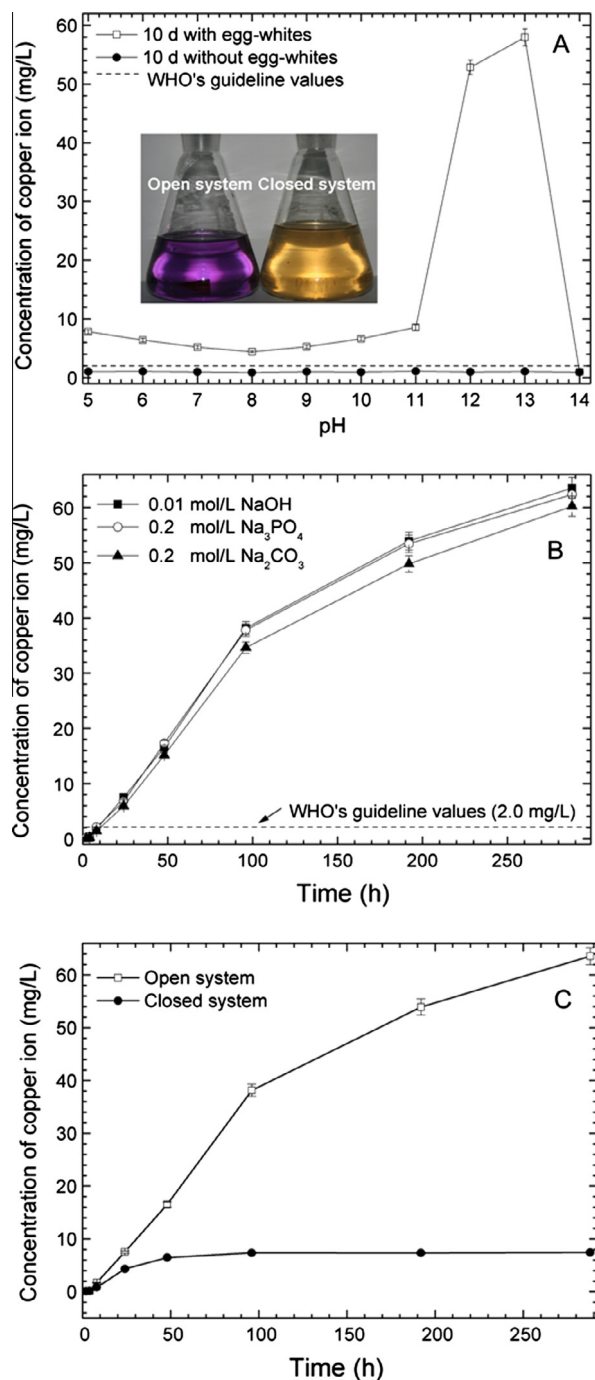


Fig. 1. Experimental data for the following: (A) The relationship between pH and 10-day copper ion concentrations in an open system. The Inset is the photo of 10-day reaction solutions in an open system (left) and in a closed system (right). (B) The relationship between reaction time and copper ion concentrations in different alkaline solutions in an open system. (C) The influence of oxygen at pH 12.

ion concentration shows little change. Remarkable changes, however, occur above pH 11, at which point the solution turns deep burgundy, as shown in Fig. 1. At pH 13, the 10-day maximum concentration reaches the maximum. At pH 14, however, because of coagulation of the egg white, the reaction rate falls to a rate close to the one found in the control groups.

In the above experiment, the NaOH solution was used to adjust the alkalinity of egg white solution. In order to determine the relevance between the severe corrosion reaction and the species of alkalis, Na₃PO₄ and Na₂CO₃ respectively substituted for NaOH in

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