

## CORROSION BEHAVIOR OF COPPER IN THE PRESENCE OF PROTEINS

Bianmei Cao<sup>1</sup>, Tingfei Xi<sup>2,3,4\*</sup>, Yudong Zheng<sup>2</sup>, David Hui<sup>5</sup>

<sup>1</sup>Beijing Institute of Medical Device Testing, Beijing 100120, P.R. China

<sup>2</sup>School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China

<sup>3</sup>National Institute for the Control of Pharmaceutical & Biological Products, Beijing 100050, P.R. China

<sup>4</sup>Shenzhen Institute of Peking University, Shenzhen city 518057, Guangdong province, P.R. China

<sup>5</sup>Department of Mechanical Engineering, University of New Orleans, LA 70148, USA

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### Abstract

Copper-bearing intrauterine devices (Cu-IUDs) are being increasingly used all over the world. However, the dissolution of copper in the presence of proteins is not well characterized. Here, with open circuit potential, electrochemical impedance spectroscopy measurements and potentiodynamic polarization test, the corrosion behavior of copper samples in different single-protein simulated uterine solutions was researched. Protein increased the corrosion rate of copper.

*Key words:* Cu-IUD; corrosion; adsorption; electrochemistry; surface characterization

### Introduction

Intrauterine devices (IUDs) are effective, long-term reliable and reversible devices for contraceptive use worldwide [1]. Active copper ions released as a result of copper corrosion in the uterus enhance contraceptive effect greatly. Copper-bearing intrauterine devices (Cu-IUDs) are being increasingly used all over the world [2]. However, side effects, such as pelvic inflammatory disease, pain and bleeding, have been found after the insertion of Cu-IUDs [3, 4].

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\* Corresponding author: Tingfei Xi, [xitingfei@tom.com](mailto:xitingfei@tom.com)

It is important to demonstrate the release of  $\text{Cu}^{2+}$  from Cu-IUDs in human uterine solution for reducing side effects. The pH value in the uterus varies from one individual to another, ranging from 6.0 to 7.9 [5]. The corrosion of copper in uterine solution under different conditions has already been extensively studied [6-9]. After IUDs are inserted into human uterus, the serum proteins may influence the corrosion of IUDs. Jianjun Zhu et al. [10] investigated the influence of proteins on the corrosion resistance of copper tube and found that the proteins always increased the corrosion rate of copper. Clark and Williams [11] found that the corrosion of copper was greatly increased by the presence of serum albumin. However, little work has been done with other proteins, such as  $\gamma$ -globulin and hemoglobin (Hb).

As a practical method, electrochemistry has been widely used in the research of different kinds of metal corrosion. Since the corrosion of Cu-IUD in simulated uterine solution without protein has been studied in our previous studies [12], one of goals of this study is to research the effect of three proteins, human serum albumin (HSA), gamma-globulin ( $\gamma$ -globulin) and hemoglobin (Hb), on the corrosion resistance and electrochemical behavior of copper of Cu IUD, with the potentials ranging around the open-circuit potential (OCP) in simulated uterine solution, at the pH value of 7.0, by the methods of open-circuit potential evolution, potentiodynamic polarization, electrochemical impedance spectroscopy.

## Materials and Methods

### Test materials

The material used is the copper tube of TCu220C IUD product (Tianjin Medical Instrument Factory, China). There are seven copper tubes around high-density polyethylene (HDPE). The outer diameter of copper tube is 2.18mm and the inner is 1.48mm, whereas the length of copper tube is 5.01mm. The purity of copper is 99.99%. And the manufacturing date is about 1 year before the experiments.

For the electrochemical measurements, the copper tube was ultrasonically cleaned in ethanol for 10min, immersed in hydrochloric acid for 30s to remove the external oxide, and then washed with pure water. After dried, the copper tube was coated using insulating gel with a bare surface of  $25\text{mm}^2$  as the working electrode exposed to solution.

### Test solutions

There are many factors that affect the corrosion behavior of copper in the uterine solution. The uterus of human being is a complex environment. It keeps the stability of its compositions and other conditions through metabolism. In order to observe this process more clearly and conveniently, simulated uterine solution (SUS) is usually used to study the corrosion behavior. The compositions of SUS adopted at present are shown in Table 1 [13].

Table 1 Compositions of simulated uterine solution (concentration, g/L)

$\text{NaHCO}_3$	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Glucose	$\text{CaCl}_2$	KCl	NaCl
0.25	0.072	0.50	0.167	0.224	4.97

In addition, three human proteins (Sigma Chemical Co.), serum albumin (Batch 077K7585), gamma-globulin (Batch 027K7535) and hemoglobin (Batch 037K7635), were added into the solution separately to make three single-protein simulated uterine solutions at 0.5g/L. The pH value of 7.0 was established by adding diluted hydrochloric acid or sodium hydroxide solution.

In the electrochemical measurements, all the solutions, prepared from reagent grade agents and distilled water, were maintained at  $37\pm 0.1^\circ\text{C}$  through a controlled-temperature water bath.

#### *Electrochemical measurements*

All the electrochemical measurements were performed with the electrochemical workstation (PGSTAT302N, Netherlands), driven by GPES Version 4.9.007 and FRA Version 4.9.007 softwares used for potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) experiments, respectively. The three-electrode system was adopted. The working electrode was a part of TCu220C IUD: a part of copper tube with the working surface of  $25\text{mm}^2$ , a platinum plate as the counter electrode and an Ag/AgCl reference electrode. Prior to each experiment, the working electrode was ultrasonically cleaned for 5 min in ethanol, and immersed in concentrated hydrochloric acid to remove the oxides on the surface of copper tube, then rinsed in distilled water and dried.

The electrodes were separately immersed into the test solutions and the open circuit potential was monitored until a constant value appeared. The potentiodynamic polarization measurements were performed at the scan rate of 0.5mV/s. The EIS measurements at the OCP were made over a frequency range of 0.01Hz to 100kHz with 10mV signal amplitude. The test solutions were not deaerated before or during the electrochemical measurement.

## **Results and discussion**

#### *Open circuit potential measurements*

The dependence of the OCP on electrode immersion time is shown in Fig.1. Initially, the OCP decreased rapidly, but then gradually slowed down to reach a stable value. The stable value was the corrosion potential. The addition of HSA significantly moved the corrosion potential to negative values, while hemoglobin and gamma-globulin showed slighter influence on the corrosion potential. Jianjun Zhu et al. [10] also reported a similar trend. And the corrosion potential shift in SUS with  $\gamma$ -globulin was smaller than that in SUS with Hb. The decline of corrosion potential suggested a reduction in the corrosion resistance of copper and that the original film dissolved more rapidly after immersion.

The passive oxide film of copper has been extensively investigated [14-16]. After the immersion of the copper electrode into the electrolyte, a copper oxide film began to grow on the electrode surface. Owing to the protecting effect of the oxide film, the corrosion resistance of the electrode increased and eventually reached a relatively steady state. As the OCP is determined by both the anodic and cathodic reaction, according to the electro-neutrality theory, the increase of the anodic current will move the OCP gradually into the negative direction so that the cathodic current and the

increased anodic current can keep balance. When the copper oxide film reached a relatively steady state, the anodic current and therefore the OCP also reached a relatively stable value.

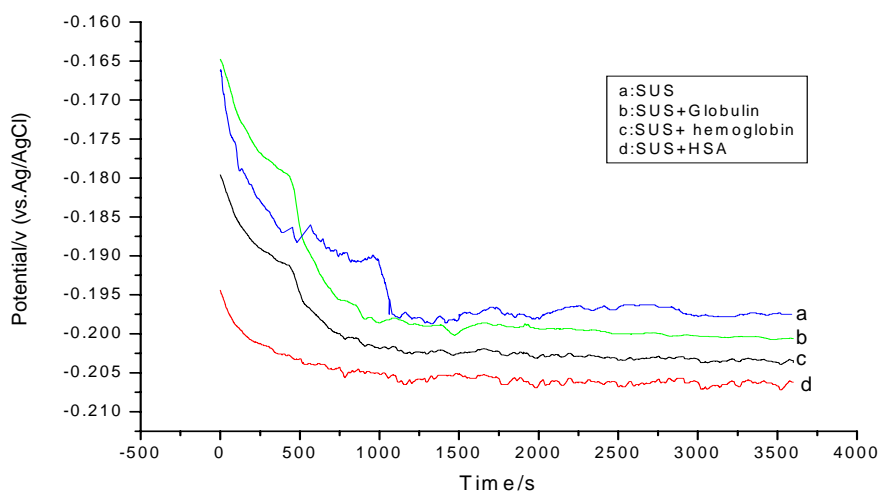
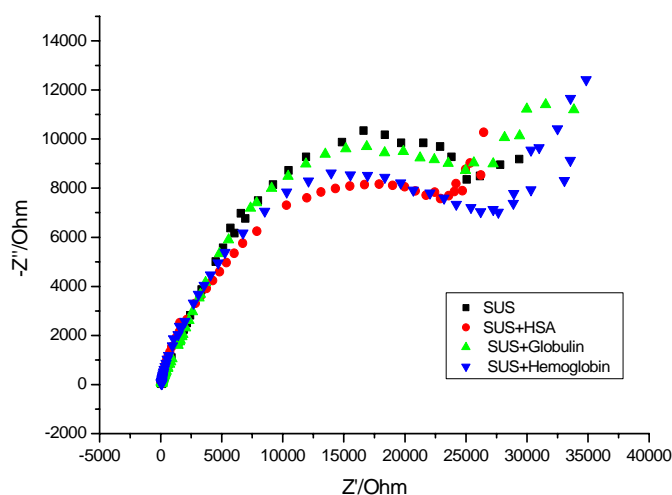


Fig.1. Dependence of the OCP of copper sample with time in: SUS; SUS+0.5g L<sup>-1</sup> HSA; SUS+0.5g L<sup>-1</sup> Hb; SUS+0.5g L<sup>-1</sup> globulin.

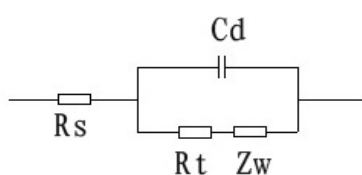
#### Electrochemical impedance spectroscopy measurements

The EIS results at the OCP were presented in Fig. 2a. Similar to references about copper electrodes [17], the Randles electrical-equivalent circuit (EEC) (Fig. 2b) was used to model the experimental spectra, and good agreement between experimental data and fitted data was obtained. The circuit elements in the figure have the following meanings:  $R_s$  is the resistance of the electrolyte,  $R_t$  is the resistance of the charge transfer,  $C_d$  is electrode surface double layer capacitance and  $Z_w$  is the impedance associated with diffusion process. According to the thesis [18], if the value of an experimental parameter  $n$  ( $0 \leq n \leq 1$ ) is 0.5,  $Z_w$  is Warburg impedance.

In a simple Randles circuit, the high frequency semicircle is associated with charge transfer reactions, while the low frequency tail is attributed to the diffusion process [19]. In the research of EIS, the charge transfer resistance is associated with the faradic current, and the faradic current can reflect the speed of different materials' corrosion behaviors [20]. The value of  $R_t$  of the copper tube in different electrolytes could be gotten by analyzing the data in the EIS plot (Table 2). It was shown that the value of  $R_t$  is the largest in SUS while the smallest in SUS with 0.5g L<sup>-1</sup> HSA, which indicated that the corrosion rate in SUS was the smallest and that in SUS with HSA was the largest.



(a)



(b)

Fig.2. EIS plot of Cu electrode at the OCP in: SUS; SUS+0.5g L<sup>-1</sup> HSA; SUS+0.5g L<sup>-1</sup> Hb; SUS+0.5g L<sup>-1</sup> Globulin

Table 2 Rt value in different electrolytes (kΩ) (mean±SD, n=5)

In SUS	In SUS+ 0.5g L <sup>-1</sup> HSA	In SUS+ 0.5g L <sup>-1</sup> Hb	In SUS+ 0.5g L <sup>-1</sup> γ-globulin
12.96±1.38	1.856±1.56	6.64±1.27	8.37±1.01

The impedance results indicated that the value of Rt of copper samples in SUS with no proteins is higher than those with proteins  $p < 0.05$ . This showed that the stability of the surface film formed in no-protein SUS was higher.

#### Potentiodynamic polarization measurements

Fig.3 shows the potentiodynamic polarization curves for copper in SUS with and without proteins. The polarization results are also in conformation with the impedance results. All the proteins decreased the cathodic current, but increased the anodic current. And the effect was the most significant with the addition of HSA. It is known that corrosion products prevent corrosion by depositing on copper surface and blocking the mass transportation of the corrosion process [12]. It is also well known that proteins have a high affinity for adsorption onto solid surfaces [21,22]. Therefore, the decreasing of cathodic current is interpreted with corrosion products and adsorbed proteins

covering the reaction sites and/or blocking the transportation of dissolved oxygen to the electrode surface.

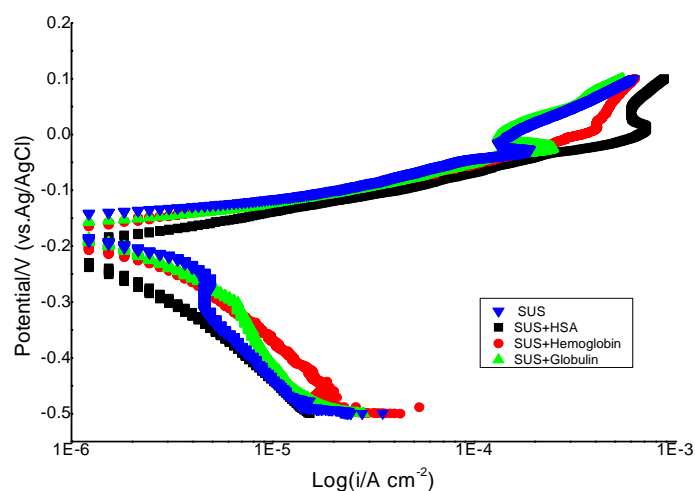


Fig.3. Polarization curves of Cu samples in : SUS; SUS+0.5g L<sup>-1</sup> HSA; SUS+0.5g L<sup>-1</sup> Hb; SUS+0.5g L<sup>-1</sup> globulin recorded at a scan rate of 0.5mV/s

### Conclusions

In vitro study, the copper corrosion of Cu-IUDs in simulated uterine solutions with different protein was investigated. The electrochemical results showed that the corrosion rate of the copper sample in simulated uterine solution with HSA was higher than those with Hb, and the corrosion rate of the copper sample in SUS with Hb was higher than that with  $\gamma$ -globulin. And the corrosion rate of the copper sample in simulated uterine solution with no protein was the lowest. The effect of protein in this process remains to be investigated.

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