A CYCLIC VOLTAMMETRIC STUDY OF THE INFLUENCE OF SUPPORTING ELECTROLYTES ON THE REDOX BEHAVIOR OF Cu(II) IN AQUEOUS MEDIUM

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Abstract

The electrochemical redox behavior of Cu(II) has been investigated at glassy carbon electrode (GCE) in Britton-Robinson (BR) buffer as well as in a mixture of BR buffer and potassium chloride media. It is apparent that BR buffer can act as a supporting electrolyte and modify the electrochemical behavior of Cu(II) ion in aqueous medium. In BR buffer medium, Cu(II) undergoes one two-electrons redox process, while in a mixture of BR buffer and KCl media it follows two one-electron electrochemical reaction routes. Because of the formation of hydrogen bridge bond between the supporting electrolyte and GCE surface, the Cu(II) ion follows Cu(II)/Cu(0) electrochemical reaction path, while in presence of KCl such a hydrogen bridge bond is not formed and it undergoes successive Cu(II)/Cu(I) and Cu(I)/Cu(0) electrode reaction processes. Moreover, the linear variation of peak current with the square root of scan rate indicates that the electrochemical redox processes are diffusion controlled.

Keywords: Supporting electrolytes, Britton-Robinson buffer, Cu-reduction, Peak current

Introduction

Electrochemistry of copper has been studied at different levels because of its application in electrocatalysis, sensors, batteries, microelectronics, electroplating and biochemical catalytic systems[1-4]. The electrochemical characteristics of Cu(II) reduction in aqueous and non-aqueous media have been well demonstrated[5-8].

$$Cu(II) + e^- \rightarrow Cu(I) \tag{1}$$

$$Cu(I) + e^- \rightarrow Cu(0) \tag{2}$$

$$Cu(II) + 2e^- \rightarrow Cu(0) \tag{3}$$

In absence of complexing agents aquated Cu(I) is unstable and undergoes disproportionation.

$$2Cu(I) \rightarrow Cu(II) + Cu(0) \tag{4}$$

While, in presence of complexing ligands or non-aqueous solvents, Cu(I) becomes stabilized and the Cu(II)/Cu(I) redox couple appears in voltammetry as a quasi-reversible

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wave[2]. In the presence of chloride, the intermediate Cu(I)[9] may form a porous film[10] of CuCl that dissolves in an excess of chloride with the formation of several chloride species such as $CuCl_2^-$, $CuCl_3^{2-}$ and $CuCl_4^{3-}$ [11-13].

The redox behavior of copper system can be even more dramatically modified by changing of solvents[14-16]. Different aspects of copper electrochemistry in non-aqueous solvents are detailed in the literatures[17-23]. However, reports on the electrochemical behavior of Cu(II) in aqueous medium in presence of different electrolytes are quite a few and deserves further exploration. In this paper, we are presenting the results of the influence of supporting electrolytes on the redox behavior of Cu(II) in aqueous medium.

Experimental

Materials

Analar grade $Cu(NO_3)_2.3H_2O$ was purchased from E. Merck, Germany. For the preparation of BR buffer, extra pure acetic acid (BDH, England), phosphoric acid (BDH, England), and boric acid (Merck, Germany) were procured.

Methods

$Cu(NO_3)_2.3H_2O$ was dissolved in BR buffer to prepare 0.5-2.0 mM Cu(II) solutions. The buffer solution was prepared as follows: 0.4 M acetic acid, 0.4 M phosphoric acid and 0.4 M boric acid solutions were prepared separately in 100 mL volumetric flasks and then the solutions of identical volume ratio of three acids were mixed together and thus a BR buffer solution of pH 1.63 was obtained. Milli-Q deionized water was used throughout the experiments.

GCE was polished with fine alumina powder of 0.3 and then 0.03 micron sized on a wet polishing cloth. For doing so a part of the cloth was made wet with deionized water and alumina powder was sprinkled over it. The GCE was then polished on this surface for about 10-30 minutes by pressing softly the electrode against the polishing surface. A shiny black mirror like electrode surface was then thoroughly washed with deionized water. Under computer controlled stirring, experimental solution was deaerated by purging for at least 10 minutes with 99.9977% pure nitrogen gas. Traces of dissolved oxygen were thus removed from the solution.

Equipments

Three electrodes system consists of a GCE as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode was used. Cyclic voltammetric measurement was performed using Computerized Electrochemical System, Model HQ-2040 developed by Advanced Analytics, USA.

Results and Discussion

The electrochemical redox behavior of 0.5 to 2.0 mM Cu(II) solutions in BR buffer, and in a mixtures of BR buffer and 0.1 M KCl (Table 1) was investigated at GCE within the potential window of 500 to -500 mV. Beyond this potential window only solvent decomposition current was observed. Cyclic voltammogram recorded for 1.0 mM Cu(II) in BR buffer solution with scan rate of 25 mVs^{-1} is shown in Fig. 1. In the forward scan one cathodic peak, i_{pc} at about -92.0 mV and in the reverse scan a single intense anodic peak, i_{pa} at about 43.0 mV were observed. In the cathodic scan, a fused hump was also found at about -15.0 mV. This might be due to the formation of very little amount of Cu(I) electroactive species as an intermediate. In the consecutive redox couple of Cu(II)/Cu(0), the cathodic peak (i_{pc}) results from the reduction of Cu(II) to Cu(0) and the anodic peak (i_{pa}) is for the oxidation of Cu(0) to Cu(II). This observation is analogous to the previous study involving electrochemical reduction of Cu(II) in acidic aqueous nitrate and perchlorate media[6]. On the other hand the cyclic voltammogram of 1.0 mM Cu(II) in 0.1 M KCl (shown in Fig. 4(b)) show a pair of cathodic peaks together with their anodic counterparts.


(a)　　　　　　　　　　**(b)**
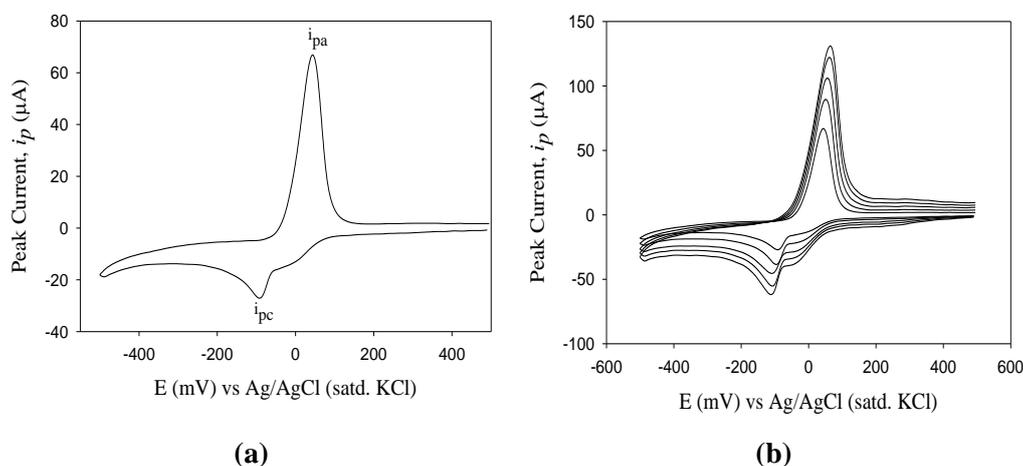
Fig. 1. Cyclic voltammetric response of (a) 1.0 mM Cu(II) in Britton-Robinson buffer with scan rate of 25 mVs^{-1} and (b) 1.0 mM Cu(II) in BR buffer with scan rate of 25, 50, 75, 100 and 125 mVs^{-1} at GCE.

A series of voltammograms of 1 mM Cu(II) in BR buffer at various scan rate were recorded and shown in Fig. 1(b). The peak current for both cathodic and anodic peak linearly increases with the increase of scan rate suggesting that the electrode process is diffusion controlled in this medium. The peak position of the cathodic peak slightly shifts towards the negative potential while the anodic peak moves a little towards positive

direction with the increase of scan rate. This behavior implies that the process is shifted towards irreversible path instead of quasi-reversible process.

Such a redox behavior of Cu(II) can be explained if it is assumed that the weak supporting electrolytes (BR buffer) are adsorbed on the electrode surface through hydrogen bridge bonds as shown in Fig. 2. This lowers the number of available active sites of the electrode surface. The decreasing of active sites on the electrode due to the presence of multi-electrolytes as it is reported in previous studies[24, 25]. These adsorbed species on the electrode surface also hinders the access of the Cu(II) ions to the active sites of the electrode. Both reduce drastically the diffusion of Cu(II) towards the electrode surface that increases the time of electrochemical process results into the reduction of Cu(II) to Cu(0).

$$R\text{-}O\text{-}H^{\delta+}\cdots \quad \begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \end{array} \quad \text{Electrode}$$

$$R\text{-}O\text{-}H = CH_3COOH, H_3PO_4 \text{ and } H_3BO_3$$
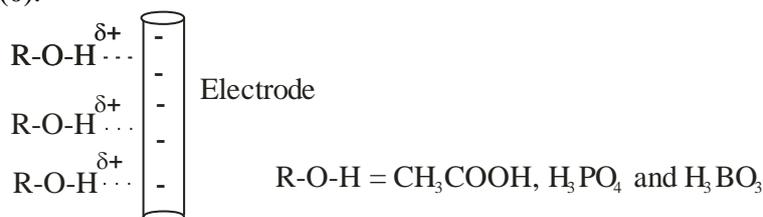
Fig. 2. Schematic description of multi-acids adsorption on the electrode surface.

The peak currents of both cathodic and anodic peak associated with electrochemical redox processes of Cu(II) in BR buffer have shown linear relationships with square root of scan rate (Fig. 3). This observation is again in favor of the fact that the electrode process is diffusion controlled.
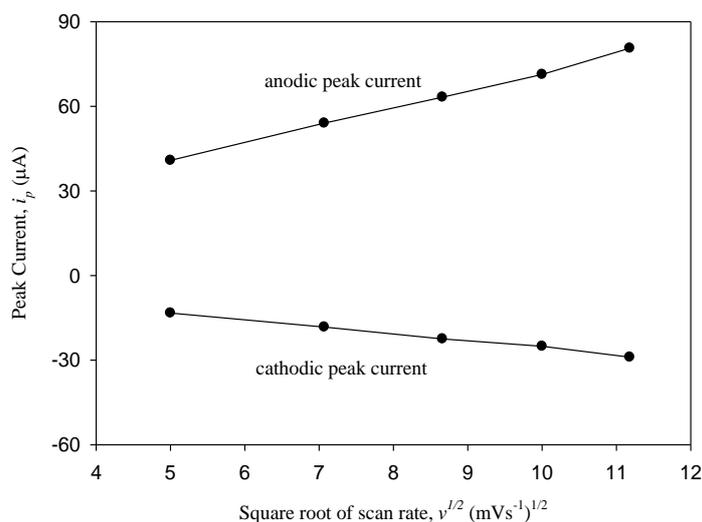

Fig. 3. Dependence of peak current with square root of scan rate for copper(II) in BR buffer.

The effect of electrolytes on the reduction of Cu(II) using mixtures of BR buffer and 0.1 M KCl solution as supporting electrolyte with different volume ratio has also been investigated. The volume percentage of BR buffer and KCl solution used was: 90% BR buffer and 10% KCl; 80% BR buffer and 20% KCl; 70% BR buffer and 30% KCl; 60% BR buffer and 40% KCl; 50% BR buffer and 50% KCl; 40% BR buffer and 60% KCl; 30% BR buffer and 70% KCl; 20% BR buffer and 80% KCl; and 10% BR buffer and 90% KCl. Cyclic voltammograms of 1.0 mM Cu(II), in only BR buffer, in 0.1 M KCl (without BR buffer), and in a mixture of 90% BR buffer and 10% KCl media are shown in Fig. 4 for comparison. In BR buffer (Fig. 4(a)), a cathodic peak and an intense anodic peak are observed. While in a mixture of BR buffer and KCl there are two cathodic and two anodic peaks (Fig. 4(c)) as in the case of pure KCl solution used as a supporting electrolyte (Fig. 4(b)). This is expected, because the KCl solution not only acts as a supporting electrolyte but also a source of complexing agent Cl⁻ which stabilizes the Cu(I) ion in the medium.

Another interesting feature of Fig. 4 is that in BR buffer the peak currents are high and the cathodic peak potential positioned in between the counterparts found in KCl medium. Whereas in a mixture of BR buffer and KCl solution, the voltammogram (Fig. 4(c)) shows that cathodic and anodic peaks have low peak current in contrast. This can be explained by the fact that in KCl medium Cu(II) ions were diffused more comfortably towards the electrode surface, while in presence of BR buffer and KCl medium the diffusion tendency of the analyte to the electrode surface is somewhat decreased.
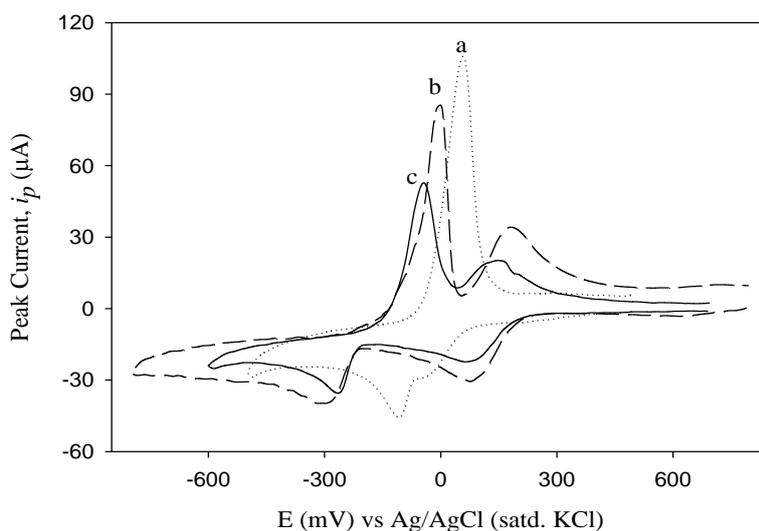

Fig. 4. Cyclic voltammograms of 1 mM Cu(II) in (a) BR buffer (dotted line), (b) 0.1 M KCl (dashed line) and (c) 90% BR buffer and 10% 0.1 M KCl (solid line) with scan rate of 75 mVs⁻¹ at GCE.

The electrochemical data obtained from the voltammograms recorded for the reduction of Cu(II) in different volume percentage mixture of BR buffer and KCl media are tabulated in Table 1. Both the cathodic and anodic peak currents increase with the increasing of percentage of KCl in BR buffer medium.

Table 1. Data for peak current and peak potential of 0.5 mM Cu(II) in different volume ratio of BR buffer and KCl at scan rate of 100 mVs^{-1}.

% BR buffer	% KCl solution	Cathodic peak current, i_{pc} (μA)		Anodic peak current, i_{pa} (μA)		Cathodic peak potential, E_{pc} (mV)		Anodic peak potential, E_{pa} (mV)	
		$i_{pc1}(-)$	$i_{pc2}(-)$	i_{pa1}	i_{pa2}	E_{pc1}	$E_{pc2}(-)$	E_{pa1}	$E_{pa2}(-)$
80	20	9.43	19.87	28.56	9.84	118.0	347.0	308.0	112.0
60	40	20.96	41.72	24.13	57.26	148.0	362.0	248.0	142.0
50	50	26.37	51.29	28.92	75.69	163.0	342.0	233.0	127.0
40	60	28.73	49.73	33.75	78.42	178.0	402.0	243.0	127.0
20	80	29.15	52.45	34.65	80.03	183.0	427.0	273.0	177.0

Conclusions

The electrochemical redox behavior of Cu(II) has been investigated using Britton-Robinson (BR) buffer, and in a several mixtures of BR buffer and KCl as supporting electrolytes. The presence of multi-acids modifies the electrochemical behavior of Cu(II) ions in aqueous medium. In BR buffer Cu(II) undergoes one two-electron redox process, while in a mixture of BR buffer and KCl medium it follows two one-electron electrochemical reaction routes. Due to the formation of hydrogen bridge bond between the supporting electrolytes and GCE surface, the Cu(II) ion follows Cu(II)/Cu(0) electrochemical reaction path, while in presence of KCl such hydrogen bridge bond is not formed and it undergoes successive Cu(II)/Cu(I) and Cu(I)/Cu(0) electrode reactions.

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