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CORRESPONDENCE

Anodic Oxidation of Cuprous Sulfide and the Preparation of Nonstoichiometric Copper Sulfide

Sir: We have studied the anodic oxidation of cuprous sulfide in acidic medium, using a carbon paste electrode. This electrode, developed by Schultz and Kuwana (*1*) and French (*2*), is essentially used for the study of sparingly soluble electroactive compounds (*3–6*).

The paste consists of a mixture of powdered graphite, the electroactive compound, and a pasting liquid or "binder" which is either a nonconductive liquid, such as Nujol (*1–3*) or an electrolyte (*4–7*).

Electrodes are made by packing the paste into a tube, against a glassy carbon contact, and covering the paste with a glass frit (*6*).

The carbon paste electrode, a reference electrode, and a counter electrode are immersed in an electrolytic solution. Voltamperometric curves can be obtained, using the electrode in a stationary mode. The curves present a low residual current.

The characteristics of the voltammograms are influenced by the nature of the pasting liquid, the amount of electroactive compound introduced in the electrode, and the potential scan rate.

If the binder is an electrolyte, all of the compound can be oxidized or reduced.

For low potential scan rates (for instance 10^{-3} V/s) and small amounts of electroactive compound, the current–voltage curves are similar to those obtained in thin-layer electrochemistry; for reversible systems, they present symmetric anodic and cathodic peaks (*6, 7*).

The maximum of the current occurs at the standard potential of the corresponding redox system. The peak heights are given by the relation

$$i_{\mathrm{p}} = \frac{n^2F^2 v m_0}{4MRT}$$

in which m_0 denotes the weight of solid electroactive compound introduced in the electrode, M its molecular weight, and v the potential scan rate.

For high potential scan rates, or large amounts of electroactive compound, the curves are shifted toward more positive or negative potentials because of the ohmic drop, but the half sum of the anodic and cathodic peak potentials remains constant and equal to the standard potential of the corresponding redox system (*7*).

Table I. Anodic Oxidation of Cuprous Sulfide at Different Potential Scan Rates

m_0, mg	v, V·s^{-1}	Q,^{a} C	n = QM/ 96500 m_0
0.81	2.5×10^{-3}	0.95	1.95
0.84	10^{-3}	1.02	2.02
0.45	5×10^{-4}	0.55	2.03
0.61	10^{-4}	0.72	1.97

^{a} Q represents the total area between the current-voltage curve and the residual current; Q is determined by weighing the corresponding recording paper.

The electrochemical behavior of cuprous sulfide has been studied by means of a carbon paste electrode containing a 1 M sulfuric acid solution as the binder.

For scan rates higher than 5×10^{-4} V/s, the current–voltage curve is characterized by one anodic peak A (Figure 1). The area under the curve indicates a two-electron transfer. This peak is related to the oxidation of cuprous sulfide, to cupric sulfide and cupric ions (*6*) according the reaction:

$$\mathrm{Cu_2S} \rightarrow \mathrm{CuS} + \mathrm{Cu^{2+}} + 2\,e^-$$

With decreasing potential scan rates, the peak A splits gradually into five different peaks $A_1 \ldots A_5$ (Figure 2); the total area under the curve remains constant and always corresponds to a two-electron transfer (Table I). For $v \le 2.5 \times 10^{-4}$ V·s^{-1}, the peaks $A_1 \ldots A_5$ are well defined: the oxidation of cuprous sulfide to cupric sulfide then proceeds via the formation of a succession of stable phases $\mathrm{Cu_{2-\delta}S}$ according to the reactions:

$$\mathrm{Cu_2S} \rightarrow \mathrm{Cu_{2-\delta_1}S} + \delta_1\mathrm{Cu^{2+}} + 2\delta_1 e^-$$

$$\mathrm{Cu_{2-\delta_1}S} \rightarrow \mathrm{Cu_{2-\delta_2}S} + (\delta_2 - \delta_1)\mathrm{Cu^{2+}} + 2(\delta_2 - \delta_1)e^-$$

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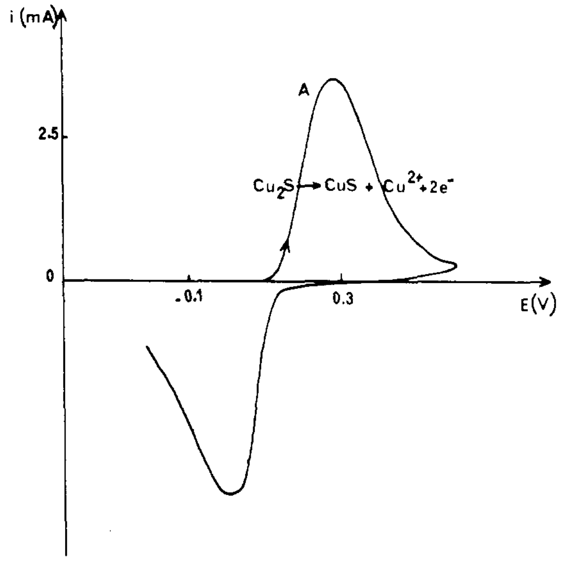

Figure 1. Current-voltage curve of chalcocite (Cu_2S) included in a carbon paste electrode: Cu_2S (0.3 mg); H_2SO_4 1 M (40 mg); carbon (50 mg); scan rate: 10^{-3} V·s^{-1}

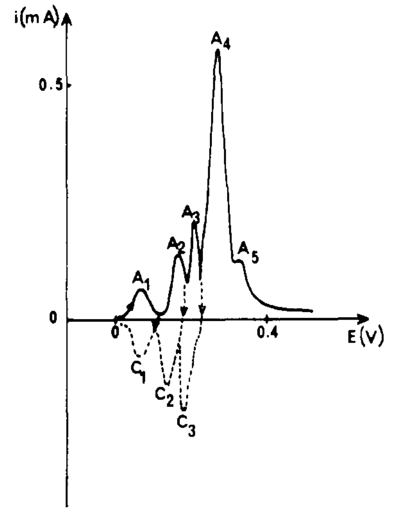

Figure 2. Current-voltage curve of chalcocite (Cu_2S) included in a carbon paste electrode: Cu_2S (0.6 mg); H_2SO_4 1 M (40 mg); carbon (50 mg); scan rate: 10^{-4} V·s^{-1}

The compounds $Cu_{2-\delta}S$ are nonstoichiometric copper sulfides which are formed with increasing removal of copper.

It is probable that the rate of formation of the nonstoichiometric compounds is controlled by the diffusion of copper in the solid; solid state diffusion is a slow phenomenon which is allowed to reach equilibrium only for low potential scan rates ($v \leq 2.5 \times 10^{-4}$ V·s^{-1}) and which must be neglected at higher potential scan rates.

Cyclic voltammetric experiments have shown that the first, second and third transformations are reversible (Figure 2), while the fourth transformation is not reversible (Figure 3). The oxidation of cuprous sulfide to cupric sulfide can then be explained by the following scheme:

$$\begin{tikzcd} Cu_2S \arrow[r, phantom, "\rightleftarrows"] & Cu_{2-\delta_1}S \arrow[r, phantom, "\rightleftarrows"] & Cu_{2-\delta_2}S \arrow[r] & Cu_{2-\delta_4}S \arrow[r, phantom, "\rightleftarrows"] & CuS \arrow[llll, bend left] \end{tikzcd}$$

The composition of the nonstoichiometric compounds have been determined from analysis of the anodic curves obtained at low potential scan rates ($v \leq 2.5 \times 10^{-4}$ V·s^{-1}). The values of $\delta_1 \ldots \delta_4$ were calculated either from the peak heights or from the number of electrons involved in the electrochemical reaction, after integration of the area under each peak (5). We have obtained: $\delta_1 = 0.080 \pm 0.005$; $\delta_2 = 0.23 \pm 0.01$; $\delta_3 = 0.40 \pm 0.02$; and $\delta_4 = 0.69 \pm 0.03$. These values correspond to the formation of:

$$Cu_{1.92}S,\ Cu_{1.77}S,\ Cu_{1.60}S,\ \text{and}\ Cu_{1.31}S$$

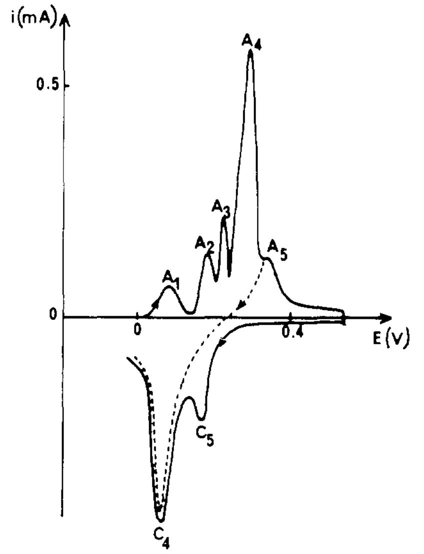

Figure 3. Current-voltage curve of chalcocite (Cu_2S) included in a carbon paste electrode: Cu_2S (0.6 mg); H_2SO_4 1 M (40 mg); carbon (50 mg); scan rate: 10^{-4} V·s^{-1}

Table II. Preparation of $Cu_{2-\delta}S$ by Electrolysis of Suspensions of Cu_2S (1 g) in 1 M H_2SO_4 (60 mL). Determination of δ

potential, mV/ECS	elemental analysis of the product	coulometric determination of δ	evaluation of the Cu^{2+} concentration in solution
105	0.085	0.08	0.08
200	0.22	0.23	0.23
285	0.67	0.68	0.70
400	1.03	1.02	1.00

We have isolated some of these compounds from controlled-potential electrolyses of suspensions of cuprous sulfide in 1 M sulfuric acid solutions.

The preparative electrolyses were carried out on a platinum electrode; the suspensions were vigorously stirred, and the current–time curves recorded during the electrolyses.

At the end of the electrolyses, the products were isolated, and their composition has been determined by elemental analysis (Table II).

The value of δ was confirmed by two other methods: (a) determination of the number of electrons involved in the electrochemical reaction:

$$Cu_2S \rightarrow Cu_{2-\delta}S + \delta Cu^{2+} + 2\delta e^-$$

by integration of the current–time curves; and (b) evaluation of the cupric ion concentration in solution, at the end of the electrolysis; this concentration was determined by measuring the height of the polarographic reduction wave of Cu^{2+} in acidic medium (1 M H_2SO_4).

In a series of experiments, measurements showed a good reproducibility. The results, summarized in Table II, indicate that the isolated compounds correspond to $Cu_{1.92}S$, $Cu_{1.77}S$, and $Cu_{1.32}S$. Their voltammograms at the carbon paste electrode are shown in Figure 4.

In conclusion, we have shown by different methods: electrolyses of suspensions of cuprous sulfide, and studies by means of a carbon paste electrode, that the oxidation of cuprous sulfide, to cupric sulfide, in acidic medium and at low

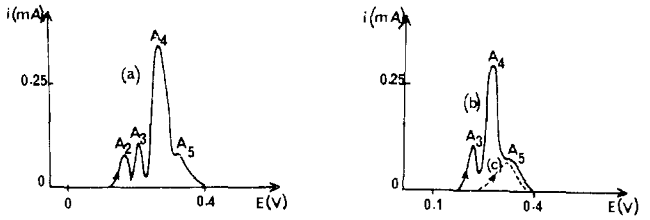

Figure 4. Current–voltage curve of: (a) $Cu_{1.92}S$ (0.25 mg), (b) $Cu_{1.77}S$ (0.25 mg), and (c) $Cu_{1.31}S$ (0.25 mg) included in a carbon paste electrode; H_2SO_4 1 M (40 mg); carbon (50 mg); scan rate: 10^{-4} V·s^{-1}

current densities occurs via the formation of different intermediate compounds. The oxidation may be explained by the following scheme:

$$Cu_2S \rightleftarrows Cu_{1.92}S \rightleftarrows Cu_{1.77}S \rightleftarrows Cu_{1.60}S \rightarrow Cu_{1.31}S \rightleftarrows CuS$$

Some of these sulfides are known as minerals: $Cu_{1.92}S$ (djurleite), $Cu_{1.77}S$ (digenite), $Cu_{1.60}S$ (anilite); Koch and McIntyre have recently prepared a new phase ($Cu_{1.40}S$–$Cu_{1.35}S$) by anodic oxidation of thin films of cuprous sulfide evaporated onto glass (*8*).

Considering the difference in experimental technique and method of preparation of the sulfides, the agreement between our results ($Cu_{1.31}S$) and the work of Koch and McIntyre (*8*) is reasonable.

We have also shown that, under certain conditions, carbon paste electrodes can be very useful for the study of sparingly soluble electroactive compounds such as minerals (sulfides or oxides). The preparation of such electrodes does not require specialized equipment, no pretreatment is needed. They give reproducible results with a precision of 5% and can be employed for quantitative and qualitative analyses of insoluble species.

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Complications in the Interpretation of Pulse Polarographic Data on Complexation of Heavy Metals with Natural Polyelectrolytes

Sir: At present, the interest for characterization of the interactions between heavy metal ions and natural polyelectrolytes by electrochemical techniques is growing strongly. Recent work by a. o. Stevenson (*1, 2*) and Buffle et al. (*3, 4*) indicates that both the static method of potentiometry using suitable ion-selective electrodes and dynamic methods involving different types of pulse polarography can provide useful information on the natural systems. In a study of copper(II)/fulvic acids solutions, Bresnahan et al. (*5*) compared results obtained from experiments with a solid state copper ion-selective electrode with differential pulse polarographic results. However, the two methods did not seem to yield consistent data. The authors (*5*) concluded that differential pulse polarography (DPP) is an "unreliable" method with respect to the system studied, and they put all their confidence in the results originating from potentiometric measurements.

The question now arises whether it is justified to use DPP as it was often used, that is: based on the supposition that DPP peak current is directly proportional to free metal ion concentration, the complexes with natural polyelectrolytes being assumed to be fully inert. Working with natural systems, at least three types of possibly complicating phenomena deserve our attention: (i) formation of fully labile complexes, (ii) kinetic effects due to limited rates of association/dissociation of the metal/polyelectrolyte complex, and (iii) adsorption of the polyelectrolyte on the mercury electrode, thereby inducing adsorption of the metal as well. A test for the presence of these effects is preferentially carried out using *normal* pulse polarography (NPP) with varying pulse duration. It has been described how kinetic effects influence the shapes of pulse polarograms and the corresponding relationships between limiting current and pulse duration (*6, 7*).

Experimentally obtained NP polarograms (see Figure 1) indicate that the Cd^{2+}/fulvic acids system is not affected by kinetic effects when experiments are carried out on the usual time scale for pulse polarography (typically 1–100 ms). However, the shape of the NP polarogram and more specifically its dependence on the effective pulse duration unambiguously shows the characteristics of reactant adsorption. As far as the shape of the polarogram is concerned, the characteristics of induced metal ion adsorption have been indicated by Barker and Bolzan (*8*) and Flanagan et al. (*9*). Experimental demonstrations were limited to systems with inorganic ligands like bromide and iodide, although Wolff and Nürnberg (*10*) observed analogous phenomena in NP polarograms of aromatic nitro compounds.

In fact, it is not very surprising that strong effects of induced reactant adsorption are exhibited in pulse polarograms of systems with natural polyelectrolytes. It is well known that these polyelectrolytes are adsorbed on the Hg electrode in quite a wide potential range (*11*). Normal pulse polarograms can therefore be expected to show the corresponding characteristics which are (i) a maximum at the beginning of the wave, the height of the maximum being strongly dependent on the pulse duration; (ii) decreased limiting currents, resulting from the depletion effect connected with the adsorption of the reactant; and (iii) a marked dependence of the shape of the wave on the initial potential chosen, in accordance with the potential dependence of the adsorption. The data given in Figures 1 and 2 are meant to illustrate that these qualitative characteristics are easily recognized in the normal pulse polarogram.

A rigorous analysis, taking into quantitative account the effects of induced adsorption, seems to be feasible (*9, 12*). In the case of normal pulse polarography, the vital part of this

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