



Voltammetric behaviour of Cu alloys toward hydrogen peroxide and organic species

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ABSTRACT

The communication reports on the electrocatalytic properties exhibited by five Cu alloys (Cu-Zn, Cu-Sn, Cu-Ni, Cu-Zn-Ni, Cu-Al) and of pure Cu, Ni and Al in the reduction or oxidation of a number of representative species. A prototypical strong oxidising agent, namely hydrogen peroxide, and some of the most important oxidisable species, namely methanol, ethanol, and formaldehyde, are tested. Both cathodic and anodic processes are facilitated by using specific alloys in the case of strong oxidants and different organic molecules, respectively.

1. Introduction

Literature articles dealing with bulk Cu-based alloys electrode that do not contain noble metals are rare. Most of the studies deal with laboratory-made Ni-Cu alloys, employed for the anodic oxidation of few alcohols and carbohydrates [1–4]. Other Cu alloys are only occasionally investigated as to the electrochemical properties [5] and most reports only consider corrosion phenomena: voltammetric studies are mainly limited to polarisation curves in conventional aqueous systems such as sea water and physiological solutions [6–8].

In this communication the electrochemical behaviour of five different commercially available bulk Cu-based alloys (see Table 1) and of three pure metals (Cu, Ni, Al) toward reduction of H₂O₂ and hypochlorite ions and toward oxidation of methanol, ethanol, glycerol, glucose, and formaldehyde is investigated. H₂O₂ and hypochlorite ions have been selected as prototypical examples of strong oxidising species; they have been chosen on the basis of the importance in different applications, such as chemical synthesis, treatment of drinking and waste waters, bleaching of cellulose pulp, etc. [9]. The organic species dealt with are among the most important oxidisable compounds that are deeply studied at a variety of electrodes in the frame of fuel cells, amperometric sensing, and electrochemical synthesis [10–16].

In many of the investigated cases, synergic effects between the components of a multi-metallic electrode system lead to the activation of electrocatalytic processes. This characteristic can be exploited in amperometric sensing, electrochemical synthesis, and fuel cells. The

selected alloys are representative of the most important classes of commercially available Cu-based bulk electrode materials, namely brasses, bronzes, and Cu alloys containing Ni. Their chemical composition and crystal structure are standardised by recognised organisations such as Copper Alliance [17] and ASTM [18]; as a consequence, the electrochemical results can be easily replicated, at variance with many alloys fabricated at the laboratory scale. Furthermore, the choice of the alloys was made also considering higher resistance to corrosion in aqueous media, with respect to Cu.

Finally, in the frame of an investigation on the different pure metals constituting the alloys, we demonstrated for the first time the possibility to cathodically reduce H₂O₂ using an Al electrode, despite the lower sensitivity with respect to Cu. It is worth noticing that the interaction between H₂O₂ and Al has been rarely investigated. Examples are only found in quite different frames, i.e. in chemical-mechanical polishing in electronic industry [19] and corrosion [20].

2. Experimental section

All chemicals were from Sigma Aldrich, pure grade. All solutions were prepared using ultrapure water, 18 MΩ·cm resistivity. The solvent medium for the electrochemical investigations on H₂O₂ reduction was 1 M citrate buffer, pH 4 [21]. In the case of the anodic oxidation of organic species, 0.1 M KOH solution has been employed, since it is one of the most common media for the development of novel electrocatalysts for sensors and fuel cells [22]. This solvent was also used for

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Table 1

Electrochemical behaviour of different Cu alloys and of bulk Cu and Ni in presence of 50 mM electroactive species under investigation.

Electroactive species	Cu alloys ^a					Cu ^a
	Cu-Zn (C464) Cu: 60, Zn: 40 Naval brass	Cu-Sn (C510) Cu: 95, Sn: 5 Phosphorous bronze	Cu-Al (C954) Cu: 89, Al: 11 Aluminium bronze	Cu-Zn-Ni (C792) Cu: 63, Zn: 25, Ni: 12 Cu-Zn-Ni Nickel silver	Cu-Ni Cu: 69, Ni: 31 Cu-Ni Monel 400	Cu: 100 Pure copper
Hydrogen peroxide	$E_{p,c} = -0.50$ V $I_{p,c} = 848$ μ A $E_{p,c,2} = -0.82$ V $I_{p,c,2} = 250$ μ A OCP = +0.02 V	$E_{p,c} = -0.55$ V $I_{p,c} = 850$ μ A OCP = +0.02 V	$E_{p,c,1} = -0.20$ V $I_{p,c,1} = 380$ μ A $E_{p,c,2} = -0.82$ V $I_{p,c,2} = 580$ μ A OCP = +0.25 V	$E_{p,c} = -0.55$ V $I_{p,c} = 824$ μ A OCP = +0.02 V	$E_{p,c} = -0.55$ V $I_{p,c} = 794$ μ A OCP = +0.05 V	$E_{p,c,1} = -0.50$ V $I_{p,c,1} = 854$ μ A $E_{p,c,2} = -0.82$ V $I_{p,c,2} = 510$ μ A OCP = +0.03 V $E_{p,a} = +0.60$ V $I_{p,a} = 666$ μ A OCP = -0.27 V
Formaldehyde	–	–	–	$E_{p,a} = +0.55$ V $I_{p,a} = 780$ μ A OCP = -0.33 V	–	$E_{p,a} = +0.60$ V $I_{p,a} = 666$ μ A OCP = -0.27 V
Ethanol	–	–	–	–	$E_{p,a} = +0.55$ V $I_{p,a} = 104$ μ A OCP = -0.15 V	$E_{p,a} = +0.70$ V $I_{p,a} = 233$ μ A OCP = -0.26 V
Methanol	–	–	–	–	$E_{p,a} = +0.55$ V $I_{p,a} = 122$ μ A OCP = -0.14 V	$E_{p,a} = +0.70$ V $I_{p,a} = 367$ μ A OCP = -0.25 V

^a The header of the table reports i) the electrode material, ii) the alloy code defined by Copper Alliance [26] and meeting ASTM B21, B139, B151, B164, B505 specifications [27], in parentheses, iii) the composition (%w/w) and iv) the commercial name. $E_{p,c}$, $E_{p,a}$, $I_{p,c}$, $I_{p,a}$ indicate cathodic and anodic peak potential and current, respectively, after proper background subtraction.

hypochlorite ions.

The electrochemical measurements were performed with Autolab PGSTAT12 (Ecochemie) and DPS101 (DELPROSENS) potentiostats, in single-compartment three-electrode cell, at room temperature. 3 mm diameter disks were the working electrodes. The electrodes were polished using 1200 emery paper and 6, 3, 1 μ m diamond spray (Arfex monocrystalline diamond spray from Remet) until mirror-like surfaces were obtained. An aqueous Ag/AgCl, 3 M KCl, from Amel, was the reference electrode and a graphite rod was the auxiliary electrode. The solution was stirred for 20 s between two subsequent potential sweeps, the working electrode being at Open Circuit Potential (OCP). All voltammetric investigations were recorded at 50 mVs⁻¹ potential scan rate. A steady state voltammetric curve was achieved since the fourth potential scan onwards, supporting the repeatability of the responses.

In the case of H₂O₂, voltammetric curves were recorded from OCP to -1.00 V [21]. We could ascertain that a suitable pre-treatment of the electrode leads to more repeatable and reproducible results [23,24]. We verified that the most suitable pre-treatment consists of 25 potential sweeps from OCP to -1.00 V, 50 mVs⁻¹ potential scan rate, in 1 M citrate buffered solution, pH 4, in presence of the maximum tested H₂O₂ concentration, namely 200 mM [21]. As to hypochlorite ions, the electrode was pre-treated through 20 potential sweeps from +0.05 to -1.70 V starting from OCP, in 0.1 M KOH solutions, at the maximum concentration (100 mM) considered. Both for H₂O₂ and for hypochlorite ion the potential range in the voltammetric investigation was the same as in the pre-treatment. In the case of the organic species, no pre-treatment was necessary to obtain repeatable responses. The potential interval for the voltammetric tests, from -0.80 V to +0.90 V starting from OCP, was chosen on the basis of preliminary results gained with Cu electrodes. In all cases the potential limits prevent significant solvent discharge and electrode oxidation from occurring.

Tests have been performed at different concentrations; in order to overcome the consequences of eventual occurrence of memory effect, the different solutions have been randomly tested. Reproducibility of the material and effectiveness of the pre-treatment were ascertained repeating the experiments with three electrodes. All electrochemical tests have been carried out in solutions in equilibrium with the atmosphere. The removal of oxygen by bubbling nitrogen for 30 min through the solution does not lead to significant variation of the electrochemical responses.

3. Results and discussion

The results gained with the different alloys are summarised in Table 1. As a general assumption, repeatability and reproducibility of the responses represents a major issue to draw sound conclusions. For this reason the discussion is only limited to the alloys exhibiting a repeatable and reproducible behaviour. The voltammetric responses of glycerol, glucose and hypochlorite, in fact, do not result reproducible when adopting polishing procedures of the electrode leading to exposition of renewed surfaces to the solution.

It is worth noticing that shifts of the peak potential toward more negative or positive values is observed at increasing H₂O₂ and formaldehyde concentrations, respectively. This behaviour is often observed in similar experimental conditions.

Noteworthy, the behaviour of pure Zn and Sn has not been studied, due to the dramatic difference in reactivity with respect to the corresponding Cu alloys.

3.1. Cathodic reduction of H₂O₂

In the case of H₂O₂ reduction, Cu and different Cu-based alloys exhibit a satisfactory reproducibility. The background voltammetric response of Cu-based electrodes in 1 M citrate buffer is shown in Fig. 1A and B. In the case of Cu and Cu-Zn, two cathodic peaks are recorded at ca. -0.50 V and -0.82 V. These current signals may be ascribed to the reduction of a thin layer of Cu oxides at the surface. The solvent and dissolved O₂ are responsible for the formation of these oxides by a non-faradic metal oxidation, occurring at OCP [6,25]. No peak is observed in the case of Cu-Sn, Cu-Al, Cu-Ni, and Cu-Zn-Ni alloys.

The addition of H₂O₂ to the solution leads to the appearance of a further cathodic peak (Fig. 1A) in the case of Cu, Cu-Sn, Cu-Zn, Cu-Ni and Cu-Zn-Ni alloys. On the contrary, in the case of Cu-Al, the voltammetric responses show two peaks located at ca. -0.20 V and -0.85 V, respectively (Fig. 1B), demonstrating that the cathodic reduction of H₂O₂ occurs at significantly lower potentials with respect to the other electrode materials tested.

In order to verify whether the voltammetric response of Cu-Al alloy should be only ascribed to the presence of Al, pure bulk Al electrodes have been tested. The background voltammograms do not show any signal. Furthermore, by addition of H₂O₂, no well-defined peak is observed up to -1.00 V. Despite the significant increase of the cathodic

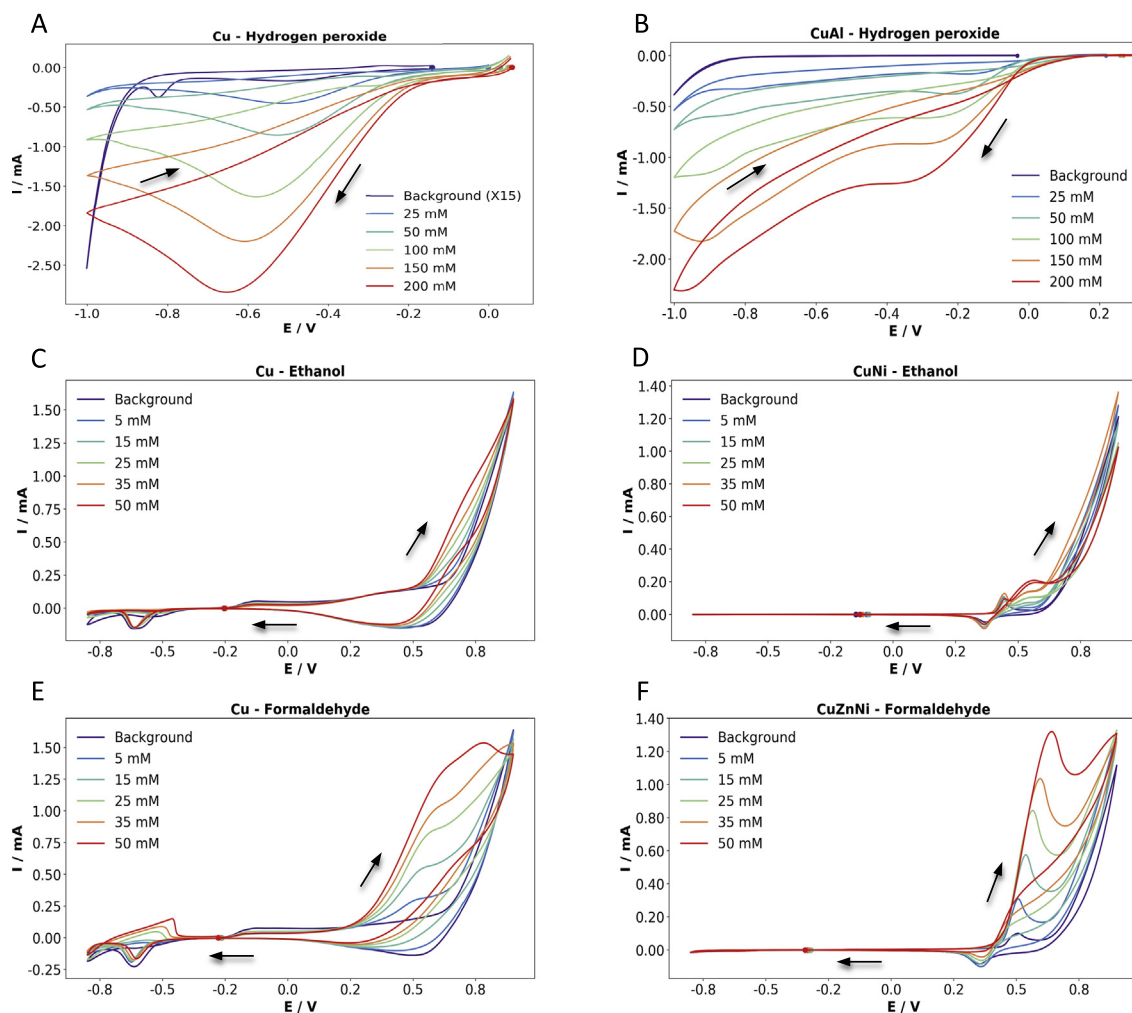


Fig. 1. Voltammetric curves recorded in the presence of different electroactive species in citrate buffer (A, B) and KOH (C, D, E, F) solutions. The fourth scans are shown. The bullet points indicate the starting OCP. Note that in A the currents for the background should be divided by 15.

current at increasing the concentration of the electroactive species, Al electrodes are less sensitive to H_2O_2 than Cu-Al and bulk Cu electrodes. The actual nature of Al in contact with aqueous solutions deserves some considerations. Al, in fact, is well known to be a very reactive metal toward H_2O ; the formation of a few nanometres thick, compact layer of Al(III) oxides prevents from significant corrosion of the bulk [26]. It is evident that the response of Cu-Al is not the mere sum of those of Cu and Al electrodes: synergic effects should be invoked to account for the voltammetric behaviour.

Although the reaction mechanism for H_2O_2 cathodic reduction has not been completely clarified, literature reports that a CE mechanism occurs on Cu-based electrodes: the process involves the chemisorption of H_2O_2 , its decomposition to two hydroxyl groups anchored to Cu atoms and the cathodic reduction to two H_2O molecules [27]. The rate determining step seems to be the decomposition reaction of H_2O_2 , which precludes the formation of water molecules by reduction. The presence of defects, ad-atoms included, on the surface on the electrode in alkaline conditions [28–33] favours the reduction process, also as to the H_2O_2 decomposition. The acidic character of Al(III) oxides in intimate contact with Cu in the CuAl alloy makes protons well available to reduction. The presence of two peaks may be accounted for by the well-known presence, within the alloy, of two phases possessing significantly different crystal structure and composition [34].

For all the electrode materials the OCP shifts toward more positive values at increasing H_2O_2 concentration, which is a typical effect caused by the presence in solution of strong oxidants. The highest

corrosion resistance is ascribed to Cu-Al, as testified by the highest OCP value in 200 mM H_2O_2 and by the lack of significant etching.

3.2. Anodic oxidation of alcohols

Only Cu and Cu-Ni led to reproducible results. The background cyclic voltammetric response of Cu electrodes in 0.1 M KOH (Fig. 1C) shows two broad peaks in the forward scan toward positive potentials, located at ca. -0.13 V and $+0.40$ V, respectively, ascribed to the oxidation of the electrode [35,36]. Reduction of the generated oxides occurs in the backward scan past ca. -0.40 V [35,36]. In the case of Cu-Ni, the background responses show two main peaks located at ca. $+0.45$ V and $+0.37$ V (Fig. 1D), due to the oxidation of Ni atoms and relevant reduction process. No evident peak ascribed to Cu oxidation is noted.

The anodic oxidation of ethanol was first considered. In the case of Cu electrode (Fig. 1C), the oxidation of the surface in the region close to ca. -0.13 V is progressively hampered when ethanol concentration increases. In addition, a significant current increase is observed above ca. $+0.50$ V, ascribed to the oxidation of ethanol. The backward scan shows a peak also consisting of positive currents. These findings are in agreement with the model developed by Burke for the anodic oxidation of alcohols on different metal surfaces, Cu included [28–33].

In the case of Cu-Ni the voltammograms in presence of ethanol show an increase of the current in correspondence to the oxidation/reduction processes of Ni (Fig. 1D); in addition, a further anodic peak appears at

ca. +0.55 V, ascribed to ethanol oxidation [37]. Although the overall current for these materials is lower than on pure Cu, the peak and the onset potential of the anodic response are significantly lower. Once the background currents are subtracted, the onset occurs at ca. +0.40 and +0.50 V in the case of Cu-Ni and pure Cu, respectively. It is worth noticing that the voltammetric responses are not reproducible in the case of pure Ni electrode. Hence, it is possible to conclude that effective electrocatalysis occurs and synergic effects are operative. Despite some differences in terms of the adopted experimental conditions, the current density registered is significantly higher with respect to other Cu alloys reported in the literature, e.g., ref. [38–41]. Taking into account the much higher corrosion resistance of Cu-Ni with respect to other Cu-based alloys, this alloy is a promising material for electrocatalytic applications. Similar results were gained using methanol, while neither glycerol nor glucose led to reproducible results.

Widely accepted electrode mechanisms for species under investigation, even on extensively studied noble metal electrodes, are not present in the literature. In our experimental conditions the oxidation process occurs at potential values close to the Ni(II)/Ni(III) redox process [42]. On the other hand copper at the surface has been reported to be under the form of Cu(I) oxides [6]. The anodic oxidation of ethanol is supposed to lead to acetate ions; the addition of hydroxyl groups are required both to generate acetaldehyde primary intermediate and to achieve the final product [42]. Similarly to the case of PtRu bimetallic electrocatalysts [43], Cu(I) oxides may be hypothesised to act as supplier of hydroxides for both oxidation steps: similar oxides are present on Cu surfaces at the potentials at which oxidation of ethanol takes place [28–33].

3.3. Anodic oxidation of formaldehyde

A similar set of experiments has been carried out in formaldehyde solutions. Only pure Cu and Cu-Zn-Ni led to reproducible results. Similar, although less reproducible responses, are obtained in the case of Ni-Cu. Voltammetric responses are not reproducible on pure Ni electrode. As to Cu (Fig. 1E), the oxidation of its surface in the region close to ca. −0.13 V is progressively hampered at increasing the formaldehyde concentration; a single peak located at ca. +0.60 V, ascribed to the oxidation of formaldehyde, appears. The peak splits into two peaks at the highest concentration values, namely ≥ 35 mM. Moreover, an additional peak located at ca. −0.50 V, ascribed to copper oxidation, is well evident [35,36]. In the case of Cu-Zn-Ni (Fig. 1F), the background responses show an anodic-cathodic peak system located at ca. +0.50 and +0.35 V, respectively, due to a quasi-reversible redox system involving Ni. By addition of formaldehyde, a well-defined oxidation peak, sharper than that exhibited by Cu electrode, is observed in the forward scan at ca. +0.55 V. By comparison with the voltammograms collected on Cu, the current is 20% higher in the case of Cu-Zn-Ni, once a proper subtraction of the background is carried out. No evident corrosion of the alloy electrode surface is observed. Similarly to the case of ethanol, the current density is much higher than in other Cu alloys reported in the literature (see, e.g., ref. [2,44–46]). The oxidation process occurs at potential values close to the Ni(II)/Ni(III) redox process, indicating the active role of this metal in formaldehyde oxidation process. Similarly to the case of acetaldehyde, which represents the intermediate in ethanol oxidation, Cu(I) oxides are supposed to act as the donors of the required hydroxyl groups.

As a final observation, it is worth noticing that OCP is not affected by the addition of ethanol, methanol and formaldehyde.

4. Conclusions

Reproducible voltammetric responses in presence of the studied electroactive species have been obtained by a careful choice of the Cu alloy: the best results in the case of ethanol and methanol have been obtained using Cu-Ni. Cu-Zn-Ni, and Cu-Al are the best choices in the

case of formaldehyde and H_2O_2 . The selected alloys significantly facilitate all the electrode processes examined, testifying the occurrence of electrocatalytic processes. Corrosion phenomena, commonly observed at Cu-based materials, are absent. The cited electrocatalytic properties of these materials and easy conditions under which repeatable and reproducible responses are obtained suggest the possible use of these electrode materials for sensing systems, e.g. electrochemical detectors for HPLC, and for electrochemical reactors. These features make these alloys particularly promising for electrocatalytic applications. Finally, the results gained suggest that the general issue of the influence of alloying non-noble metals on the electrocatalytic behaviour deserves more attention than paid so far; comparable attention should be devoted to unusual electrode materials, such as pure Al.

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