Voltammetric behaviour of Cu alloys toward hydrogen peroxide and organic species

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A R T I C L E   I N F O
Keywords:
Copper alloys electrodes
Aluminium electrode
Electrocatalysis
Hydrogen peroxide
Oxidizable species

A B S T R A C T
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...
gained with Cu electrodes. In all cases the potential limits prevent the experimental procedure. As far as Cu is concerned, the highest potential scan onwards, supporting the repeatability of the responses.

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 wereascertained 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.

Table 1

<table>
<thead>
<tr>
<th>Electroactive species</th>
<th>Cu alloys</th>
<th>Cu'</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>Ethanol</td>
<td>Cu: 100</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Ethanol</td>
<td>Pure copper</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Ethanol</td>
<td>Pure copper</td>
</tr>
<tr>
<td>Methanol</td>
<td>Ethanol</td>
<td>Pure copper</td>
</tr>
</tbody>
</table>

* 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. Ep,c,Ep,a,Ip,c,Ip,a indicate cathodic and anodic peak potential and current, respectively, after proper background subtraction.

3. Results and discussion

The results gained with the different alloys are summarised in Table 1. 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
current at increasing the concentration of the electroactive species, Al electrodes are less sensitive to H₂O₂ 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 H₂O; 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 H₂O₂ cathodic reduction has not been completely clarified, literature reports that a CE mechanism occurs on Cu-based electrodes: the process involves the chemisorption of H₂O₂, its decomposition to two hydroxyl groups anchored to Cu atoms and the cathodic reduction to two H₂O molecules [27]. The rate determining step seems to be the decomposition reaction of H₂O₂, which preludes 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ 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 electrocatalytical 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 act as the donors of the required hydroxyl groups. Which represents the intermediate in ethanol oxidation, Cu(I) oxides are much higher corrosion resistance of Cu-Ni with respect to other Cu-based alloys, this alloy is a promising material for electrocatalytical applications. The peak splits into two peaks at the highest concentration values, namely 25 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-Ni-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 achieved. 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 H2O2. 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 electrocatalytical 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.

References

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