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Cu-based amorphous alloy electrodes for fuel cells

K. BRUNELLI*, M. DABALÀ and M. MAGRINI
DIMEG – University of Padua, via Marzolo, 9, 35131 Padova, Italy
*(*author for correspondence, fax: +39 049 827 5500, e-mail: katya.brunelli@unipd.it)*

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Abstract

The present work describes the characteristics of Cu–Zr and Cu–Ti amorphous alloys as catalysts for oxidation of methanol and formaldehyde in alkaline solutions. Two Cu-based amorphous alloys, $Cu_{60}Zr_{40}$ and $Cu_{60}Ti_{40}$ both prepared by melt spinning were investigated. Two types of electrode were used: as-quenched amorphous alloys and surface-activated amorphous alloys. The surface-activation treatment consisted in the immersion of the ribbons in 1 M HF solution for 30 s. The determination of the oxidation activity of methanol and formaldehyde was carried out by galvanostatic and by steady-state polarization measurements and cyclic voltammetry experiments in 1 M NaOH solutions containing CH_3OH or CH_2O, deoxygenated by nitrogen bubbling for 30 min at 30 °C. The HF-treated amorphous alloys exhibit catalytic activity only for formaldehyde oxidation; Zr-based alloys show higher current densities than pure crystalline copper and Ti-based alloys.

1. Introduction

For methanol fuel cells to be economically comparable with other power sources it is necessary to develop materials, other than precious metals, which have high electrocatalytic activity for the oxidation of organic fuels. Amorphous alloys are suitable for this purpose, because, besides possessing high strength and good corrosion resistance, they can also be obtained in a wide range of compositions, giving the best compromise between the material properties and the specific reaction. In recent studies, amorphous alloys have been employed as electrodes for the electrolysis of hot concentrated sodium chloride [1] and in the electroxidation of sulfite [2]. In particular, Pd-based and Ni-based alloys have been used for oxidation of methanol and its derivates in alkaline and acid solutions, respectively. Their activities, after surface treatment, are higher than the traditional Pt-platinized electrode [3, 4].

In this work the activity of Cu-based alloys for oxidation of methanol and formaldehyde is investigated. Among methanol derivates, formaldehyde has been chosen because it can readily be electroxidized by IB group metals (Au, Ag and Cu) in alkaline solutions, and this suggests the possible use of Cu-based amorphous alloys as anodes for HCHO oxidation [5]. In previous work we have reported that Cu-based alloys containing Zr or Ti needed pretreatment with HF solutions to enhance their electrocatalytic activity for the hydrogen evolution reaction [6]. Therefore, in this work the samples were submitted to chemical etching to remove the thin oxide layers formed during rapid quenching.

2. Experimental details

The amorphous alloys were prepared by melt spinning *in vacuo* at a cooling wheel rate of 3000 cm s^{-1}. The formation of the amorphous structure was confirmed by XRD. The surface of the alloys was investigated by SEM, equipped with EDS.

The specimens, which had compositions $Cu_{60}Zr_{40}$ and $Cu_{60}Ti_{40}$, were ribbon shaped 1.0–1.2 mm in width and 30 μm in thickness, with apparent surface area of 0.15–0.20 cm^2. To prepare the electrodes for the electrochemical measurements, the end of the ribbons were welded to a copper wire which was then sealed into 5 mm diameter Pyrex glass tubing with epoxy resin. The electrodes underwent two different surface activation treatments with immersion in 1 M HF solution for 30 s or in 0.1 M HF solution for a few minutes and then were rinsed with H_2O.

A pure crystalline Cu electrode, with apparent surface area of about 0.5 cm^2, was used as reference catalyst and its surface was cleaned before use by brief immersion in a solution containing 5% (v/v) H_2O_2 and 10% (v/v) H_2SO_4, and then rinsed with H_2O.

The electrochemical characterization of the sample was achieved by means of cyclic voltammetry, with a scanning rate of 10 and 100 mV s^{-1}, potentiostatic and galvanostatic measurements carried out in 1 M NaOH solutions which contained CH_3OH (1 M) or CH_2O (0.3–1 M) at 30 °C, under a stream of nitrogen gas. A Pt electrode and a SSE were used as counter and reference electrode, respectively. The electrocatalytic activity was evaluated on the basis of apparent unit area of the electrodes.

3. Results and discussion

Figure 1 shows cyclic voltammograms on Cu electrodes in 1 M NaOH containing various amounts of formaldehyde. The curve in 1 M NaOH shows an anodic peak at about −0.6 V. The peak is broad because the formation of more than one species is probably involved. At the peak potential, in fact, the Cu electrode became darkened, suggesting that both the conversion of Cu to Cu_2O and the conversion of Cu_2O to a mixture of CuO and $Cu(OH)_2$ probably occurred [7].

The voltammograms obtained from HCHO solutions exhibit a further anodic peak at about −0.9 V (SSE), which can be attributed to oxidation of HCHO [8]. The highest maximum oxidation current density is about 3 mA cm^{-2} for a 1 M HCHO solution and about 1.5 mA cm^{-2} for a 0.5 M HCHO. Moreover, the peak height at about −0.6 V decreases as the HCHO concentration increases. The presence of formaldehyde thus appears to inhibit the oxidation of the Cu electrode in this region.

We have reported previously [6] that Cu-rich porous layers formed through HF treatment on the surface of amorphous Cu–Ti and Cu–Zr show a high electrocatalytic activity for the hydrogen evolution reaction in comparison with the pure crystalline Cu electrode. Similarly, very high HCHO electro-oxidation currents were observed on HF-treated amorphous Cu–Ti and Cu–Zr electrodes, while the activity was negligible for the as-quenched alloys because of an inert oxide layer, TiO_2 and ZrO_2, which covers the electrode surfaces.

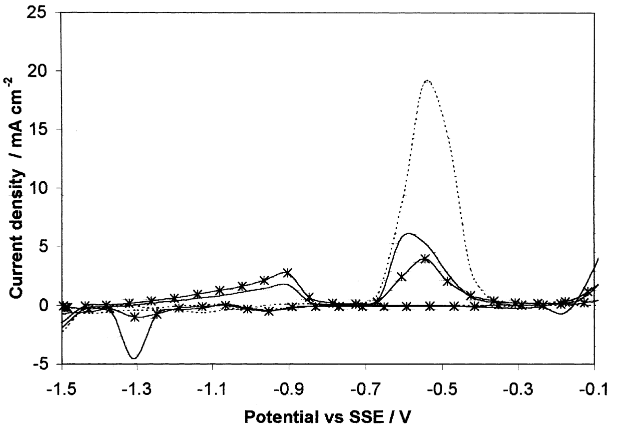

Fig. 1. Cyclic voltammograms of pure crystalline Cu electrodes measured in 1 M NaOH containing various amounts of HCHO at a sweep rate of 10 mV s^{-1}. Key: (···) Cu 1 M NaOH; (——) Cu 0.5 M HCHO; (*) Cu 1 M HCHO.

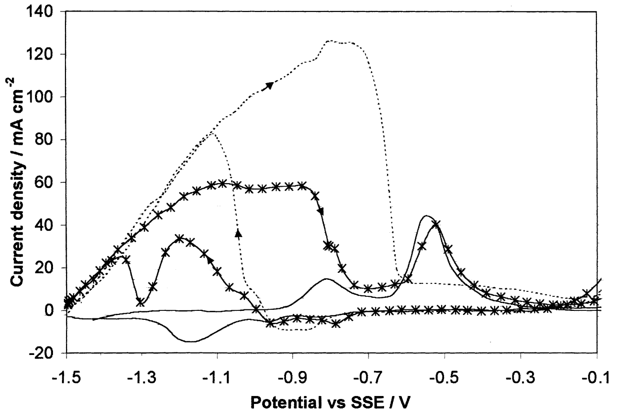

Fig. 2. Cyclic voltammograms of 1 M HF treated amorphous $Cu_{60}Zr_{40}$ electrodes measured in 1 M NaOH containing various amounts of HCHO at a sweep rate of 10 mV s^{-1}. Key: (···) CuZr 1 M HCHO; (*) CuZr 0.5 M HCHO; (——) CuZr 1 M NaOH.

Some examples of cyclic voltammograms, recorded for the treated amorphous $Cu_{60}Zr_{40}$ in alkaline solutions containing varying concentrations of formaldehyde, are shown in Figure 2. Comparison with the curves resulting from pure crystalline Cu shows that, in 1 M NaOH solutions without HCHO, two different surface oxidation processes take place on amorphous alloys at potentials of about −0.8 V and about −0.5 V. These two anodic peaks become less pronounced after each cycle, and disappear altogether after about ten cycles, if the latter are recorded between −1 V and −0.1 V. To restore the initial voltammetric behaviour an electrochemical reduction of the oxides at −1.3 V is necessary.

In alkaline solutions containing HCHO the curves also show a broad peak in the potential range between −1.5 V and −0.7 V, which can be attributed to the oxidation of the aldehyde. A depletion of the anodic peak at −0.5 V is recorded in formaldehyde environments, while the anodic peak at 0.8 V is overlapped by the HCHO oxidation signal. These behaviours are more pronounced especially for the higher aldehyde concentrations. The strong decrease in the oxidation current recorded at very positive potentials can be attributed to the formation of an insulating oxide layer on the electrode surface and the detection of an oxidation peak in the reverse sweep may be due to the regeneration of a clean surface in the reduction processes occurring at the cathodic peak. This clean surface is able to oxidize the HCHO in the reverse sweep.

$Cu_{60}Ti_{40}$ shows a lower electrocatalytic activity than $Cu_{60}Zr_{40}$, as reported in Figure 3. The activity of the Zr alloy is four and forty times higher than Ti alloy and pure crystalline Cu, respectively. This suggests a difference in the surface characteristics of the treated amorphous alloys. SEM micrographs indeed confirm that the surface of the treated Zr alloy has a much more porous structure (Figure 4), than the Ti-based alloys.

The effect of HF concentration in chemical pretreatment on both the surface morphology and the catalytic activity was also investigated. In Figure 5 the

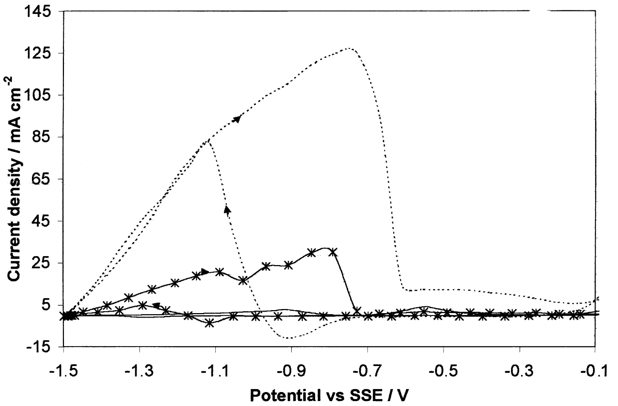

Fig. 3. Cyclic voltammograms of 1 M HF treated amorphous $Cu_{60}Zr_{40}$, $Cu_{60}Ti_{40}$ and crystalline Cu electrodes measured in 1 M NaOH containing 1 M HCHO at a sweep rate of 10 mV s^{-1}. Key: (···) CuZr 1 M HCHO; (——) Cu 1 M HCHO; (*) CuTi 1 M HCHO.

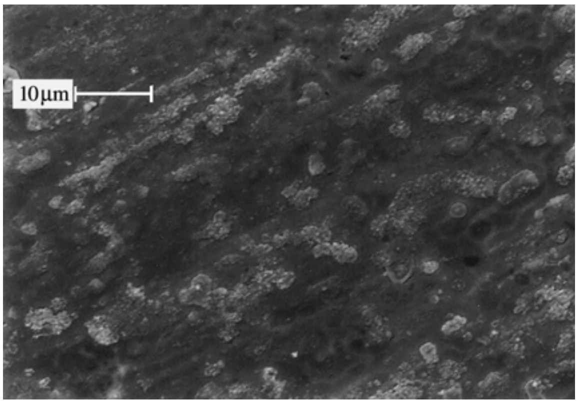

Fig. 4. SEM image of 1 M HF treated $Cu_{60}Zr_{40}$ surface.

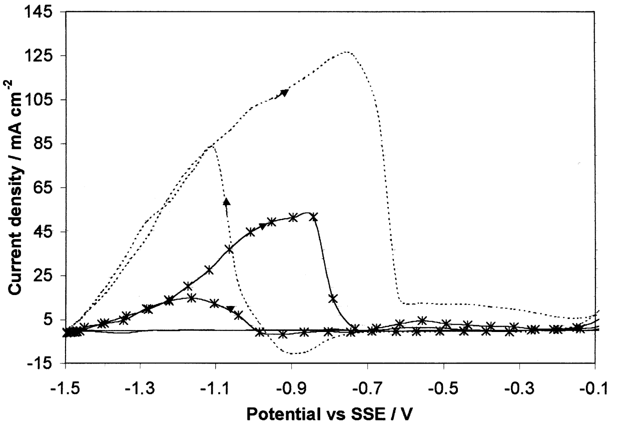

Fig. 5. Cyclic voltammograms of different treated amorphous $Cu_{60}Zr_{40}$ electrodes measured in 1 M NaOH containing 1 M HCHO at a sweep rate of 10 mV s^{-1}. Key: (*) CuZr 0.1 M HF; (···) CuZr 1 M HF; (——) CuZr.

voltammograms obtained in 1 M HCHO alkaline solutions for differently treated electrodes are exhibited. The catalytic activity of the untreated sample is very small, while the oxidation rate grows with increase in the HF concentration in the chemical etching process. The 1 M HF treatment causes a devitrification of the amorphous surface with formation of a large amount of copper crystals, while the 0.1 M HF treatment induces a weak structural changes on the electrode surface because this treatment is able to dissolve only a small portion of the surface oxides. From SEM investigation the surface of the 0.1 M HF etched alloy appears less porous than that treated in 1 M HF and is covered by small copper crystals, surrounded by undissolved Zr oxides (Figure 6). A higher concentration of HF produces a higher amount of crystalline copper and porosity, which are the main causes of the increased electrocatalytic activity.

The potentiostatic experiments confirm the results obtained by potentiodynamic methods. Furthermore, the electrocatalytic activity of the amorphous alloys is stable and large current density values are obtained, even after a prolonged period of steady-state polarization, especially with HF treated Zr based alloy (Figure 7).

During the anodic sweep, the formation of small gas bubbles on the electrode surface is observed in the HCHO oxidation potential range. This can be attributed to hydrogen evolution, in agreement with literature results [9, 10]. The mechanism proposed for the reaction

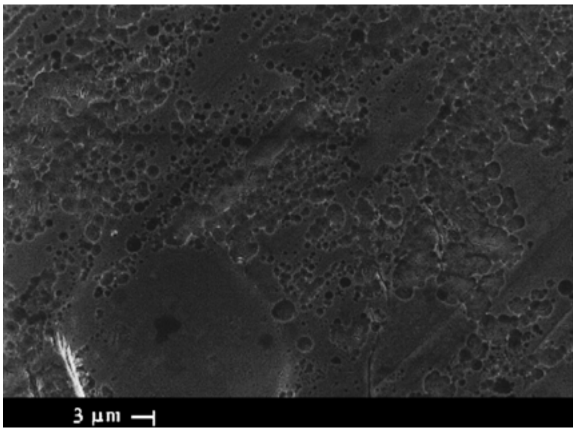

Fig. 6. SEM image of 0.1 M HF treated $Cu_{60}Zr_{40}$ surface.

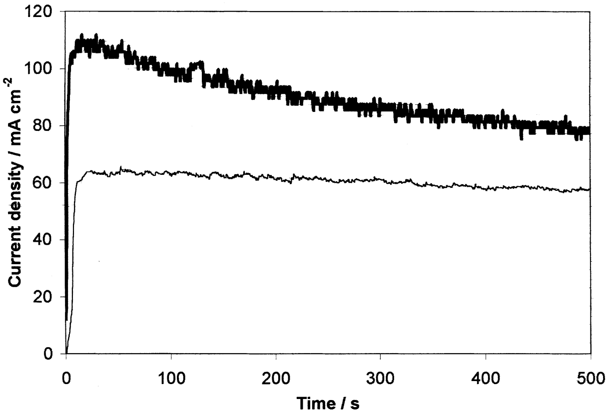

Fig. 7. Steady-state polarization curves at –0.9 V vs SSE for different treated amorphous $Cu_{60}Zr_{40}$ electrodes measured in 1 M NaOH containing 1 M HCHO. Key: (▬) CuZr 1 M HCHO; (—) CuZr 0.5 M HCHO.

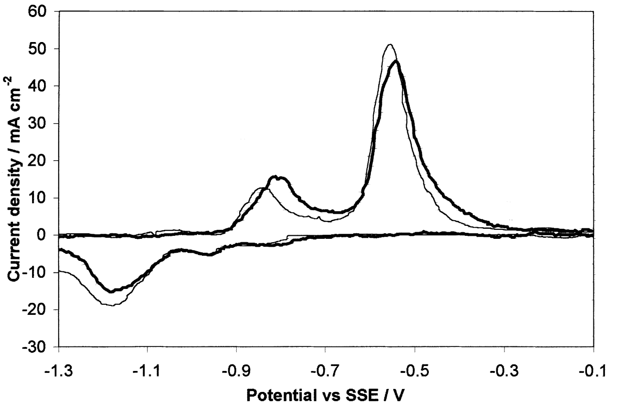

Fig. 8. Cyclic voltammograms of 1 M HF treated amorphous $Cu_{60}Zr_{40}$ electrodes measured in 1 M NaOH containing various amounts of CH_3OH at a sweep rate of 10 mV s^{-1}. Key: (—) CuZr 1 M methanol; (▬) CuZr 1 M NaOH.

of formaldehyde oxidation on IB group metals in alkaline environment involves the formation of a methyleneglycol ion HCH_2O^-:

$$HCHO + OH^- \longrightarrow H_2CO \cdot OH^-$$

$$H_2CO \cdot OH \xrightarrow{\text{rds}} H_2CO \cdot OH + e^-$$

$$H_2CO \cdot OH \longrightarrow HCOO^- + H + H^+$$

$$H \longrightarrow \tfrac{1}{2}H_2$$

with the overall reaction:

$$HCHO + OH^- \longrightarrow HCOO^- + \tfrac{1}{2}H_2 + H^+ + e^-$$

which produces 1 mol of H_2 per 2 mol of electrons. Therefore, the aldehyde is not completely oxidized to CO_2 and H_2O either on Cu or on Cu-based amorphous alloys at potentials required for practical fuel cell operation.

The oxidation reaction of methanol in alkaline environment was also investigated by potentiodynamic experiments. The Cu-based amorphous alloys showed no catalytic activity for this reaction. As shown in Figure 8, the voltammograms recorded in the absence and presence of methanol are similar. This suggests that the electrodes are unable to oxidize the alcohol to aldehyde. Moreover the positive values of the polarization potential (+0.75 V vs SSE for $Cu_{60}Zr_{40}$ and +0.8 V vs SSE for $Cu_{60}Ti_{40}$ alloys) obtained by galvanostatic polarization at a current density of 50 mA cm^{-2}, imply that oxygen evolution occurs instead of methanol oxidation [11].

4. Conclusions

The evaluation of the electrocatalytic efficiency in HCHO oxidation from potentiodynamic curves shows that interesting electrocatalytic performances of amorphous Cu-based alloys, higher than pure crystalline Cu, are obtained after chemical etching of the samples in HF solutions. Structural and morphological characterizations of the samples show that the increase in electrocatalytic activity of the amorphous alloys is mainly as a consequence of the surface structure modifications.

The Zr-based alloy shows higher catalytic activity than Ti-based alloys because the Zr and the Zr oxides on the electrode surface are dissolved more rapidly by 1 M HF treatments than Ti, so that a more porous surface is obtained on Zr-based alloy.

The reaction on electrodes treated through etching with lower concentration HF solution was studied. Although this etching induces weak structural changes on the electrode surface, dissolving only a small portion of the surface oxide, a significant increase in electrocatalytic activity is observed in comparison with the as-quenched case.

Moreover, the aldehyde is not completely oxidized to CO_2 and H_2O either on Cu or Cu-based amorphous alloys at potentials which are desirable for practical fuel cell operation, in agreement with the mechanism proposed for formaldehyde oxidation in alkaline media on IB group metals.

The Cu-based amorphous alloys exhibit no catalytic activity for methanol oxidation.

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