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In memoriam prof. dr. Liviu Oniciu

STRUCTURE, MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES OF HIGH SURFACE AREA COPPER ELECTRODES OBTAINED BY THERMAL SPRAYING TECHNIQUES

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ABSTRACT. Three types of high surface area copper electrodes were prepared by thermal spraying techniques. CuAl electrodes were obtained by thermal arc spraying of two different wires (Cu and Al) followed by the alkaline dissolution of aluminum. Cu wire and Cu powder electrodes were obtained by combustion spraying of copper wires and powders, respectively. Several methods have been used to characterize the electrodes, including scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction. The electrocatalytic activity of the electrodes was evaluated based on the steady-state polarization curves and electrochemical impedance data. It has been found that the structure of the prepared electrodes depends to a great extent on the deposition method, i.e. combustion spraying gives deposits with higher surface roughness and porosity. Decreasing the particles size leads to the increase of the porosity and surface roughness and also to the increase of the copper oxide content.

Keywords: *high surface area electrodes, thermal spraying, electrocatalysis, electrochemical impedance spectroscopy*

INTRODUCTION

Electrochemistry has been often seen as a potential route for the development of environmentally friendly and sustainable methods for energy generation and organic synthesis [1]. However, an important issue is the increase of the rate of electrochemical reactions, which is equivalent to the reduction of the overpotential. There are two important methods which may be applied independently or combined to attain this purpose: the increase of the electrode real surface area and the increase of the electrode intrinsic activity. The real surface area may be enlarged by appropriate preparation

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methods such as composite coating [2-4], powder pressing [5-7] or thermal spray [8-11], whereas the electrocatalytic activity is increased by doping [12] or surface modification.

High surface area electrodes have found numerous applications in electrocatalysis, especially for the gas evolution / consumption reactions such as: hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), in some organic reduction reactions, in batteries and fuel cells [13].

Considerable research has been done in the past years on performant hydrogen cathodes with low hydrogen overpotential. The major application for such cathodes is the alkaline water electrolysis and alkaline chloride electrolysis. The activity for the hydrogen evolution reaction can be substantially improved by increasing the surface area of the electrode [14].

The aim of this work is to study the influence of the structure and morphology on the electrochemical activity of high surface area copper electrodes. The method used in this study to prepare the electrodes is the thermal spray deposition of an electroactive coating based on copper on a conducting carbon-stel support.

RESULTS AND DISCUSSION

SEM and EDX studies

The SEM micrographs taken for the surface of the electrodes and the OM micrographs taken for the cross-section of the electrodes are shown in Figures 1-3.

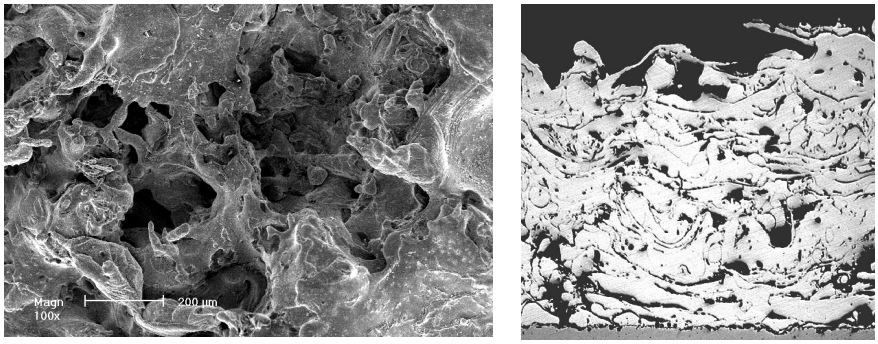

Figure 1. CuAl electrode after leaching;
(a) surface, magnitude 100×; (b) cross-section, magnitude 50 ×

The CuAl electrode shows a high irregular and rough structure, characterized by the formation of wide pores in the structure after the dissolution of aluminum. The cross section image reveals a complex layered structure with interlamelar porosity and inclusion of voids and oxide particles. The dimension of pores varies in a large range between 70 – 200 µm.

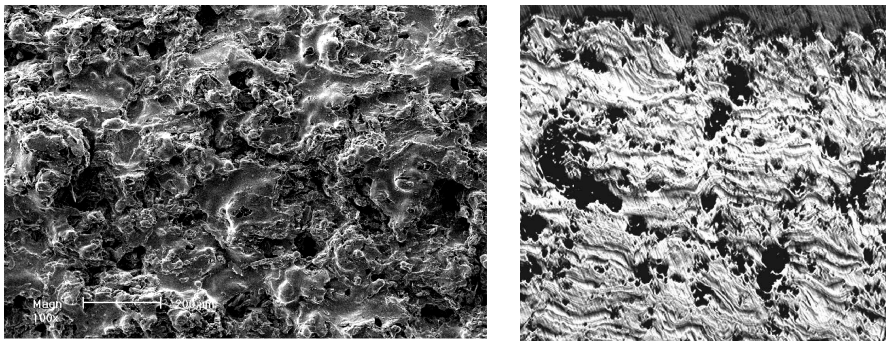

Figure 2. Copper wire electrode;
(a) surface, magnitude 100×; (b) cross-section, magnitude 50 ×

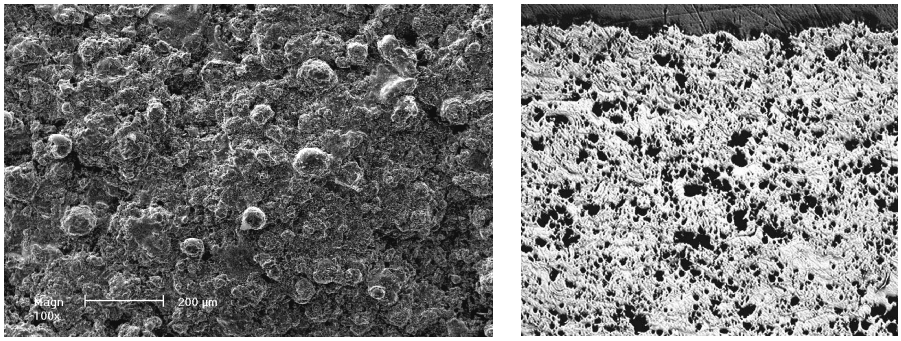

Figure 3. Copper powder electrode;
(a) surface, magnitude 100×; (b) cross-section, magnitude 50 ×

The Cu wire and Cu powder electrodes show a much more regular structure and a uniform distribution of the pore sizes. The surface of the Cu wire electrode is characterized by the presence of molten droplets flattened during the impact with the substrate. The diameter of pores varies between 50 – 70 µm. In the case of Cu powder electrodes spherical shaped particles are present on the surface and the pore diameter is 10 – 30 µm.

The Energy Dispersive X-Ray analysis allows a semi-quantitative determination of the element composition of the coatings. The composition of the copper electrodes is given in Table 1.

Table 1.

Results of the EDX analysis of the copper electrodes.

Electrode	CuAl			Cu wire		Cu powder	
Composition	Cu wt%	Al wt%	O wt%	Cu wt%	Al wt%	Cu wt%	Al wt%
As sprayed	67.5	19.2	13.3	82.9	17.1	88.8	11.2
Leached	88.7	1.6	9.7				

Before leaching, the CuAl electrode has a relatively high content of aluminum which decreases more than tenfold after leaching. In all cases oxygen was also detected, indicating a certain degree of oxidation of the copper electrodes. Comparing the oxygen content of the electrodes the oxidation degree can be determined. Based on this values it has been calculated that the oxidation degree of Cu powder electrodes is 1.53 times higher than that of Cu wire electrodes.

X-Ray Diffraction was used to determine the phases obtained during the deposition process. The diffraction patterns of the CuAl coating (here not shown) before leaching shows the presence of the aluminum. After the dissolution of the aluminum only the peaks corresponding to copper appear.

The diffraction patterns of the Cu wire and Cu powder electrodes reveal the presence of the copper oxide, formed during the thermal spray process. As a representative example the X-ray spectra for the Cu powder electrode are given in Figure 4.

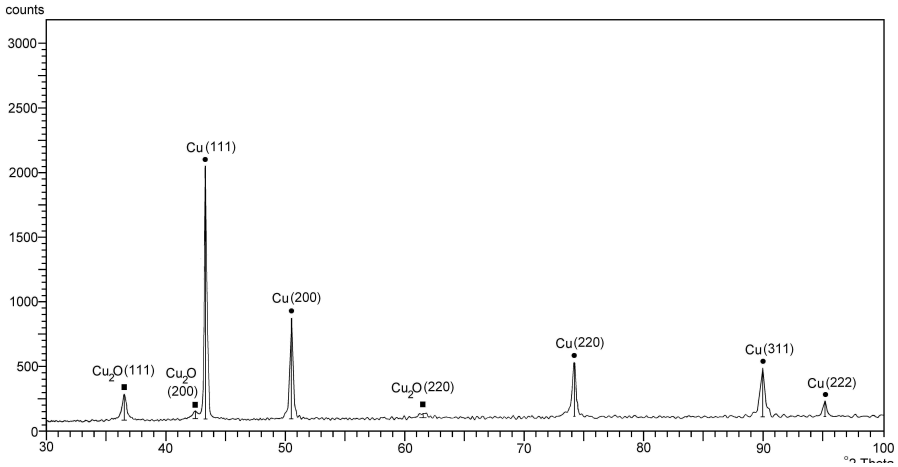

Figure 4. Diffraction patterns of the Cu powder electrode.

In both cases the RX spectra shows the characteristic peaks of Cu_2O at diffraction angles equal to $2\theta = 36.52; 42.49; 61.45$ for Cu wire and $2\theta = 36.51; 42.46; 61.47$ for Cu powder respectively. The height of the first peak may offer quantitative information about the oxidation degree of the electrodes. Thus, it has been obtained a 1.66 higher oxidation degree of the Cu powder electrode as compared with the Cu wire electrode. This value is in good agreement with that calculated from EDX data.

Electrochemical measurements

The electrochemical activity of the prepared electrodes was compared with that of a smooth copper electrode. The steady state polarization curves recorded in NaOH solution are given in Figure 5. At low current density a

depolarization of approximately 200 mV was found for the Cu powder electrode compared with the smooth copper electrode. However, at higher current densities the depolarization reduces to 100 mV, probably due to the occlusion of pores by hydrogen bubbles due to the intensification of the HER at more negative overpotential.

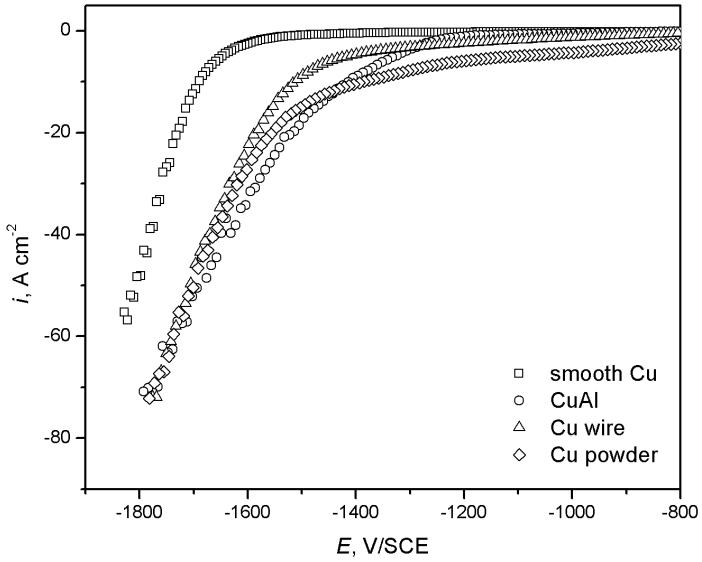

Figure 5. Current-potential curves in 1M NaOH solution at 21°C. Scan rate 1 mV/s.

EIS measurements were performed on the high surface area copper electrodes at electrode potentials located in the hydrogen evolution region. Complex plane plots for the smooth Cu, CuAl, Cu wire and Cu powder electrodes at −1.2 V are given in Figure 6.

In all four cases the shape of the impedance spectra corresponds to a depressed semicircle in the studied frequency range. The experimental impedance data were fitted to an electrical equivalent circuit consisting of the solution resistance R_S in series with a parallel connection between a constant phase element CPE and the charge transfer resistance R_{ct} [15,16]. The total impedance of this model is equal to:

$$Z = R_S + \left(R_{ct}^{-1} + T(j\omega)^{\Phi}\right)^{-1} \quad (1)$$

where T is a parameter related to the double layer capacitance and ϕ is the constant phase angle parameter. The double layer capacitance is given by [17]:

$$T = C_{dl}^{\phi}\left(R_S^{-1} + R_{ct}^{-1}\right)^{1-\phi} \quad (2)$$

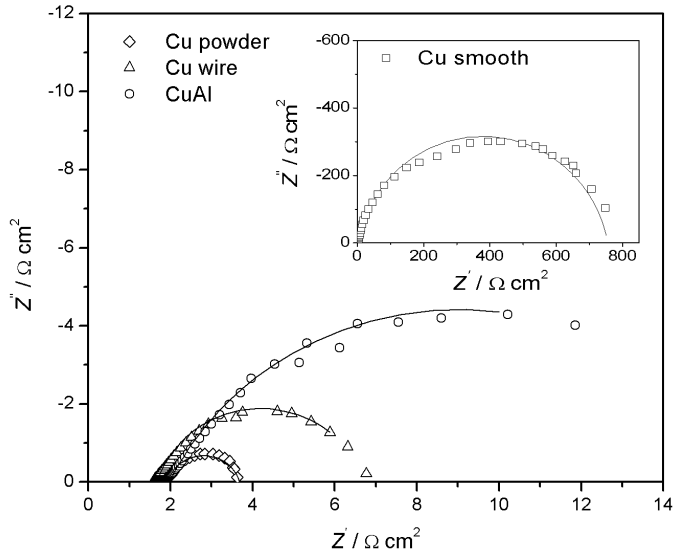

Figure 6. Nyquist plots obtained in 1M NaOH solution at 21°C. Symbols are experimental data and continuous lines are fitted data by the Levenberg-Marquardt procedure.

The values of the circuit elements obtained by modeling the experimental data are given in Table 2.

Tabel 2.

Impedance data obtained in 1 M NaOH solution for the studied copper electrodes.

Electrode	R_S [Ω cm^{-2}]	R_{ct} [Ω cm^{-2}]	C_{dl} [F cm^{-2}]	R_f
Cu smooth	1.88	753	$0.187 \cdot 10^{-3}$	7.5
CuAl	1.90	14.1	$13.8 \cdot 10^{-3}$	552
Cu wire	1.67	5.08	$14.7 \cdot 10^{-3}$	588
Cu powder	1.92	1.85	17.210^{-3}	692

The surface roughness factor R_f of the prepared electrodes was determined from the ratio of the double layer capacitance values and the double layer capacitance of a smooth copper electrode. Assuming a value of $25 \cdot 10^{-6}$ F cm^{-2} suggested in the literature for the double layer capacity of a smooth electrode, the highest surface area has been obtained for the Cu powder electrode, followed by the Cu wire electrode.

CONCLUSIONS

Thermal spraying is a suitable method to obtain porous structures with high surface area. The CuAl electrodes present a rough surface with large pores, with a diameter between 70 – 200 µm. The Cu wire and Cu powder electrodes reveal also a porous structure but the pores are much smaller, i.e. between 50 – 70 µm for the wire sprayed electrodes and 10 – 30 µm for the powder sprayed electrodes.

The shift of the current-potential curves to lower overpotentials, comparatively to a smooth copper electrode, is to be attributed to the surface area enhancement effect.

The values of the roughness factor determined from the impedance data are in good agreement with the increase of the porosity observed from the SEM and OM micrographs. The decrease of the charge transfer resistance values is consistent with the increase of the current densities obtained by polarisation measurements.

Based on the steady-state polarisation and impedance measurements, improved electrocatalytic activities for the hydrogen evolution reaction are attributed to the increase of the real surface of the electrodes.

EXPERIMENTAL SECTION

Electrode preparation

The high surface area copper electrodes were prepared by thermal arc and combustion spraying of three different types of materials: CuAl alloy wire, Cu wire and Cu powder.

The CuAl electrode was prepared by thermal arc spraying of a CuAl wire (92% Cu, 8% Al) with a diameter of 1.6 mm. The operating parameters were set to: arc current 200 A, arc voltage 30 V and gas pressure 3 bars. After depositon the coating was activated by alkaline leaching of the Al in 1M NaOH at 80^{o}C for 120 min.

The Cu wire and Cu powder electrodes were obtained by combustion spraying of copper wire (Cu 99.8%) with the diameter of 1.6 mm and copper powder with the particle size -90 +45 μm (-170 +325 mesh) respectively. The deposition was performed with an oxyacetylene torch and with air as atomizing gas (pressure 3 bars).

In all cases, as a support for the electroactive coating a carbon steel plate with the dimensions of 100×300×3 mm was used. Prior to the deposition the substrate was degreased and sanded with corundum in order to assure an adequate adherence.

Electrode characterization

The surface morphology of the electrodes was investigated by scanning electron microscopy (SEM) with a Philips XL 30 ESEM microscope operating at 20 kV and by optical microscopy (OM) using a LEICA D MR/M microscope. The elemental composition was determined by Energy dispersive X-Ray analysis (EDX) coupled with the scanning electron microscopy. For the phase composition X-Ray diffraction spectra were registered with a Philips X'pert diffractometer using the Cu-Kα radiation.

Electrochemical measurements

The electrocatalytic activity of the copper electrodes was investigated towards the hydrogen evolution reaction. Steady state current-potential curves were recorded with a VoltaLab 21 potentiostat in 1 mol L^{-1} NaOH solution with a scan rate of 1mV s^{-1}. A conventional three-electrode electrochemical cell was used with a platinum counterelectrode and a saturated calomel electrode as reference. The *iR* drop between the electrode surface and solution was minimized using a Haber-Luggin capillary, placed at about 1 mm of the surface. Electrochemical impedance spectroscopy (EIS) was applied to determine the surface roughness of the electrodes. Impedance spectra in the frequency range 1 kHz to 10 mHz were recorded using a Solartron Instruments 1287 Potentiostat and a 1255B Frequency Response Analyzer. The experimental data were fitted to the equivalent circuit by a complex non-linear least squares (CNLS) Levenberg-Marquard procedure using the ZView-Scribner Associates Inc. software.

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