MICRO-ELECTRODE FOR COPPER ION DETECTION IN SOLUTION

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Chemical micro-sensor for the detection of Cu^{2+} ions in solution was prepared. Cu-Ag-S sensing material is build by electrolysis of copper – silver RF sputtered thin film. Analytical behaviour of developed sensor was fully characterised in terms of sensitivity, selectivity and stability. The potentiometric measurements showed a quasi-Nernstian behaviour with a detection limit close to 10^{-6} M. In the presence of interfering ions the sensing system is very selective, since low selectivity coefficients are obtained versus various ionic species. The very first measurements carried out in waste waters are presented.

1. Introduction

Measurements of the activity of toxic heavy metal ions in aqueous systems is of importance from an environmental point of view, because their toxicity. To date quality control of water results from reliable analytical measurements carried out in laboratory. However such a control is not easy to achieve. Typical analysis techniques are very expensive and require a withdrawal from the site [1]. For practical applications, reliable, sensitive and low-cost on-line monitoring systems need still to be developed. Recently, considerable interest is attracted by the chemical micro-sensors which is closely connected with trends of device miniaturization, ecology of the production and natural raw materials economy [2, 3]. Thin films based chemical micro-sensors produced with silicon technology compatible methods [4-6] are aimed at the fabrication of primary systems for analytical devices for the needs of in-situ measurements. There are net benefits to using glassy materials for micro-sensor fabrication. Beyond the advantages of all solid state devices, vitreous materials are well suited for producing homogeneous thin layers. From an electrical point of view the low impedance of a thin film compared to that of the corresponding bulk material allows the use of poor conducting glass. Since more than twenty years, chalcogenide glass materials for detection of various heavy metal ions in aqueous solutions are well investigated [7-11]. Chalcogenide glass exhibit better chemical durability in acidic and redox media [12], and in many cases, possess better selectivity and reproducibility of the analytical characteristics [13].

In this work we present new results concerning the fabrication of Cu^{2+} selective electrode. On the basis of Huller et al. investigation [14] and CuS/Ag₂S well-established electrode [15], we had chosen to work with the Cu-Ag-S sensing thin film. A broad variety of deposition techniques permits the deposition of metal-sulphur films [16]. Sintering process and chemical bath deposition are well-known deposition techniques [17-19]. In our study we used electrochemical deposition technique and RF sputtering. Preparation and characterisation of chemical device presented in this paper may be regarded as the first stage of development of a suitable Cu^{2+} ion sensing micro-

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system. Since the device is intended to provide in situ analysis, the very first measurements have been carried out in polluted solutions.

2. Experimental methods

Sensitive membrane was carried out by electrolysis using metallic thin film as working electrode. The deposition of copper-silver sub-micronic film was performed in a RF sputtering set-up Alcatel Dion 300 [20]. Metallic layer was sputtered on glass substrate covered on one side by a chromium film such as sensor internal reference. The chromium thin film also helped in increasing the adhesion of the copper-silver membrane to the substrate. Cu-Ag Thin layers were prepared by RF co-sputtering of silver pieces and copper metal fold assembled as a composite target. Both kinds of materials were Alfa Aesar® products of high purity. A base pressure of 10^{-6} mbar was first achieved in the deposition chamber using turbo molecular pumping unit. The chamber was filled two times with argon to eliminate residual element under vacuum. To strike the argon plasma, the pressure was then brought back to 10^{-1} mbar. The RF sputtering power was fixed to 60 w and the distance target – substrate was equal to 5 cm in order to obtain the optimum thickness of the thin layer. After striking the work pressure was fixed to 5×10^{-2} mbar. The sputtered thin film was then convert to sensitive membrane by electrolysis in a two electrode system, using metallic alloy film as working electrode (anode) and Pt wire as auxiliary electrode (cathode). The deposition cell was a standard 250 cm^3 glass laboratory beaker that contains aqueous Na$_2$S solution of 4.10^{-2} M concentration and both electrodes. Using a Velleman PS 907 generator, a direct current of 5 mA is applied during 1 min to the electrolysis cell. Anodic oxidation is observed since metal released electrons. Therefore, brownish coloration indicates metal – sulphide deposition by reaction of anions with metallic ions at working electrode surface. In the same time, reduction of water was observed at the cathode. At last sensitive layer is rinsed in deionised water. Figure 1 shows the electrolysis cell.
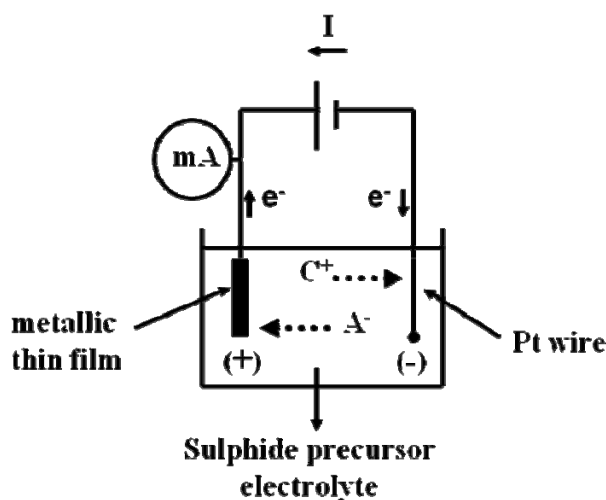

Fig. 1. Principle of electrolysis cell used to convert metallic thin film to sensitive membrane.

The electrode potential was measured with a Minisis high impedance millivoltmeter (Radiometer Tacussel). The external reference electrode was a saturated Ag/AgCl electrode used with a double junction. KNO$_3$ (10^{-1} M) was used as the supporting electrolyte. Tests solutions in the concentration $10^{-1} – 10^{-4}$ M were prepared by successive 10-fold dilutions of a 1 M Cu(NO$_3$)$_2$, 5H$_2$O solution by the supporting electrolyte. Calibrations were performed in the concentration range $10^{-7} – 10^{-3}$ M by addition of a known volume of copper (II) nitrate test solutions to 100ml of supporting electrolyte. After calibration sensor was kept in deionised water to limit membrane ageing [1]. Studied sensor was tested in waste waters taken on contaminated site of Auby area in the north of France. Table 1 presents cation concentrations measured by ICP-AES of Pz1 and Pz2 polluted waters. Waste waters were filtered and kept at +4°C.

Table 1. Cation concentrations of PZ1 and PZ2 polluted solutions measured by ICP-AES.

	ppm			ppb	
	Pz 1	Pz 2		Pz 1	Pz 2
Al	0.432	< 0.250	As	30.6	56.3
Ba	< 0.080	< 0.080	**Cd**	**125775**	**23907**
Ca	**648**	**811**	**Co**	**355**	48.5
Fe	< 0.075	< 0.075	Cr	< 20	< 20
K	17.8	8.78	**Cu**	**45.1**	**39.9**
Mg	**47/7**	**54.7**	Mo	< 20	< 20
Mn	4.83	0.807	**Ni**	**302**	**216**
Na	4.20	5.44	**Pb**	**4731**	**701**
P	0.233	0.197	**Zn**	**779696**	**186463**
Ti	< 0.025	< 0.025			

3. Results and discussion

A poor crystallization of the copper-silver film is observed while diffraction patterns of copper and silver indicated the presence of both elements in the layer. Electro deposition process leads to a homogeneous composition of the sensitive layer with a great amount of sulphur. The smooth membrane surface does not present any observable defects. The microstructures of chromium and metallic alloy layers were observed by Scanning Electron Microscopy (SEM) using a HITACHI S-4500 I. A 8 kV voltage was applied and a magnification of ×35000 was used. As shown in figure 2, a columnar structure is observed for both layers. Such morphology is often observed for films deposited by RF sputtering [21]. Chromium and copper – silver membranes thicknesses are respectively 500 nm and 400 nm. It should be noted that effect of ethylene glycol, such as sulphide precursor solvent has been studied. EDS analysis reveals that this electrochemical treatment leads to an inhomogeneous membrane composition. Moreover, the corresponding film surface presents defects and cracks.
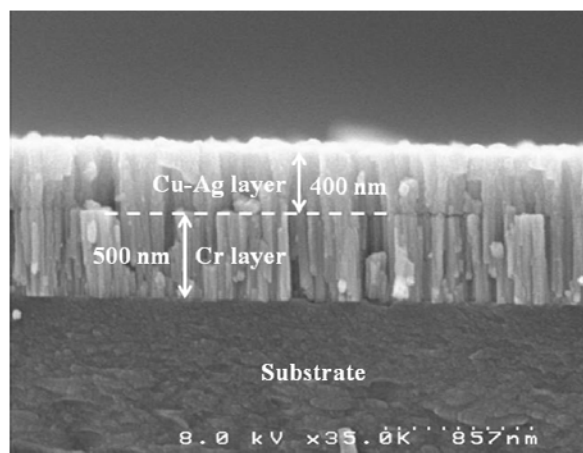

Fig. 2. Columnar structure of thin films observed by SEM.

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As shown in Fig. 3 the results of the first calibration of the sensor with unconditioned membrane can differ in a number of cases from subsequent measurements by a lower sensitivity in the diluted copper (II) ion solutions. However, after three calibrations the sensor parameters are stabilised. Near-Nernstian response of 27 mV/pCu is observed and the limit of detection is close to 10^{-6} M. This behaviour is comparable to those already reported for similar sensitive membranes based on chalcogenide glasses [12]. The slope of the third calibration curve is close to the theoretical $S_0 = RT/2F$ from the Nernst equation (1).

$$E = E_0 + \frac{RT}{nF} \log\left[Cu^{2+}\right]$$ (1)

where,

E_0 is the formal electrode potential;

R is the universal gas constant;

T is the temperature in Kelvin;

n is the number of electrons transferred in the half-reaction;

F is the Faraday constant (charge per a mole of electrons);

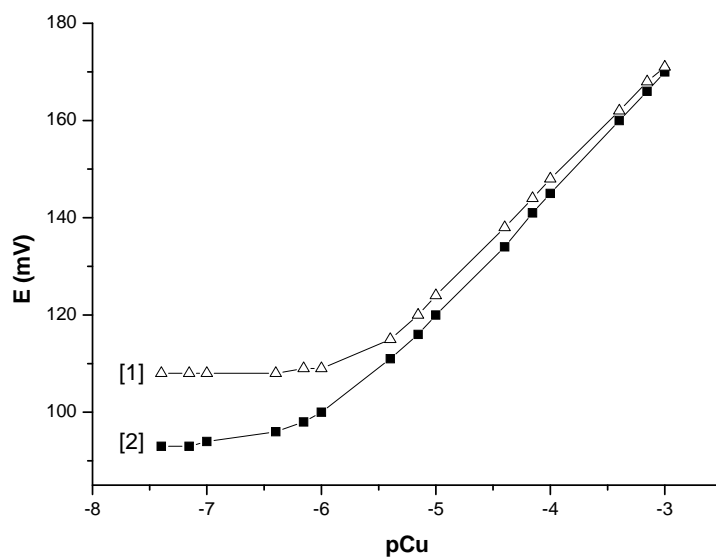$[Cu^{2+}]$ is the concentration of the reducing agent.

Fig. 3. Potentiometric responses of sensitive thin layer before conditioning [1] and after three subsequent measurements [2].

These results point out for the presence of a "modified surface layer" needed for the membrane to gets its sensing property. It is in agreement with some previous investigations on chalcogenide membranes [1, 7]. Since sensor displayed a reliable and reproducible behaviour, sensitive membrane has been characterized from an electrochemical point of view. The electrochemical characterisation of the Cu-ISE was done by means of ion-selective potentiometry. To study the effect of pH on the electrode response, the electrode potential was measured over a pH range of 2 – 10 for 10^{-4} M Cu^{2+} solution. The pH was adjusted by additions of nitric acid or potassium hydroxide. The data obtained are presented in figure 4. The potential was found to be independent of change in pH in the range of 3 – 5. A typical increase in the values of the electrode potential, which is characteristic for the membrane response in acidic media (pH<3), can be explained by the slow dissolution of the micro-sensor membrane, though insufficient selectivity to

H^{+} ions cannot be excluded. However, sensitive material can be used in acidic media with pH values less than 3. Thus, the measurements should be preferably carried out within short times because of the possible dissolution of the sensor membrane. The potential decrease in the alkaline pH range is explained with the precipitation of a suited metal hydroxide. The formation of copper hydroxide results in the decrease of Cu^{2+} ion concentration in the measured solution, followed by the drop of the sensor potential.
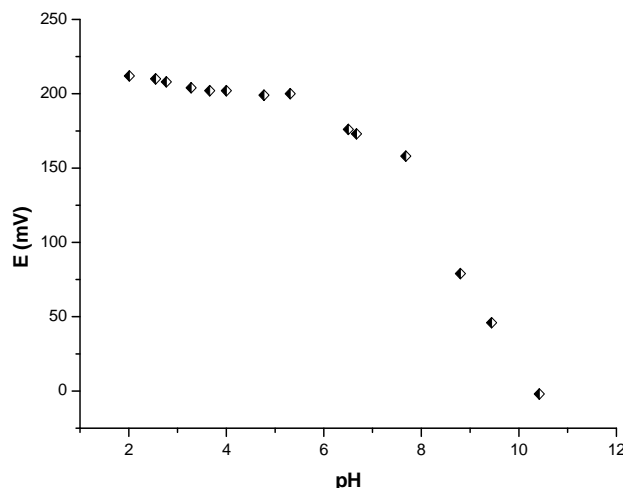

Fig. 4. Effect of pH value on electrode potential at constant copper concentrations of 10^-4 M; the ionic strength is fixed at 0.1 M KNO₃ background electrolyte solution.

Heavy-metal ions such as Pb^{2+} and Cd^{2+} are often associated with Cu^{2+} ions in polluted water. So it is important to know the additional contributions to the total measured activity that result from the presence of interfering species in the sample solution. The total measured potential is given by Nernst equation which takes into account the selectivity coefficients (2).

$$E = E_0 + \frac{RT}{nF}\log\left[\left[Cu^{2+}\right] + \sum_{j \neq Cu^{2+}} K_{Cu^{2+},j} \times a_j^{\frac{z_{Cu^{2+}}}{z_j}} \right] \tag{2}$$

where,
a_j is the concentration of the interfering ion j;
$z_{Cu^{2+}(j)}$ is the charge of the primary ion Cu^{2+}, (the interfering ion j);
$K_{Cu^{2+},j}$ is the selectivity coefficient of the thin film sensor in the presence of foreign ion j;

In order to determine the selectivity coefficients $K_{Cu^{2+},M^{n+}}$ (for an interfering ion M^{n+}), we used the fixed interference method [8, 12]. Thus, the out-put signal was measured with solutions of constant level of interference (10^{-2} M) and a varying activity of the primary ion (10^{-7} to 10^{-3} M). The sensitivity of the Cu(II)-ISE was investigated in the presence of two-valence (Ca^{2+}, Cd^{2+}, and Pb^{2+}) and three-valence ions (Cr^{3+}). After investigations, measurements without foreign species were performed in order to check the near-Nernstian membrane behaviour. Figure 5 shows typical copper calibration curves in the presence of considered ions. When measuring the selectivity in a constant concentration of interfering cations, one can consider that the selectivity limit occurs when a flat potentiometric response versus Cu^{2+} concentration is obtained.
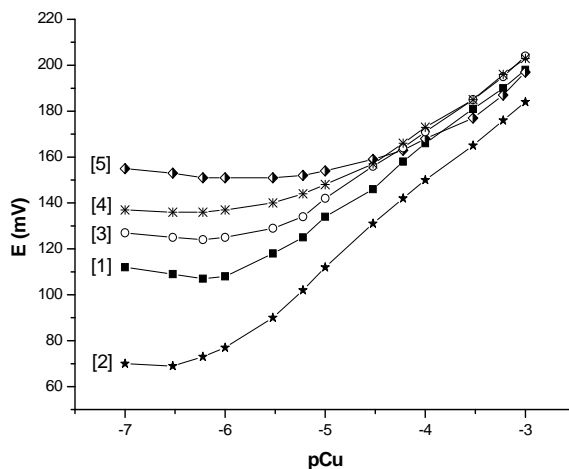
Fig. 5. Selectivity of the Cu electrode in [1] no interfering ion; [2] 10^{-2} M Ca(NO₃)₂; [3] 10^{-2} M Cd(NO₃)₂; [4] 10^{-2} M Pb(NO₃)₂; [5] 10^{-2} M Cr(NO₃)₃.

It can be seen from the curves that the out-put signal slightly gets damaged in the presence of Cr^{3+} ions. Table 2 presents the summarised data on the evaluation of the selectivity coefficients for the Cu thin film sensor developed. The values of $K_{Cu^{2+},Ca^{2+}}$; $K_{Cu^{2+},Cd^{2+}}$ and $K_{Cu^{2+},Pb^{2+}}$ are 10^{-6}; 10^{-4} and 10^{-4} respectively. These values seem interesting, since the lower the coefficient, the smaller is the influence of the interfering ion. The selectivity coefficient for chromium ion is somewhat larger (10^{-2}). Even so, it should be noted that an even more serious interference effect on the functioning of other selective electrodes based on chalcogenide glasses has been reported in the literature [12].

Table 2. Selectivity coefficients against several interfering ion species.

Interfering ion M^{n+}	$K_{Cu^{2+},M^{n+}}$
Ca^{2+}	10^{-6}
Cd^{2+}	10^{-4}
Pb^{2+}	10^{-4}
Cr^{3+}	10^{-2}

The response of micro sensor to Ag^+ ion was tested in silver (I) nitrate solution with constant ionic strength (KNO_3; 10^{-1} M). Tests solutions in the concentration $10^{-1} - 10^{-4}$ M were prepared by successive 10-fold dilutions of a 1 M silver nitrate solution by the supporting electrolyte. Calibrations were performed in the concentration range $10^{-7} - 10^{-3}$ M by addition of a known volume of silver (I) test solutions to 100ml of KNO_3. Ag/AgCl double junction electrode was used as external reference electrode. The electrode potential was measured with a high impedance millivoltmeter. At neutral pH or even acidic pH the membrane worked well over a wide concentration range of Ag^+. Calibrations displayed Nernstian slopes of 56-58 mV per decade of Ag^+ activity. The detection limit was closed to 10^{-6} M. It should be noted that the membrane showed a good stability and a fast response time (less than 10s). The micro sensor can be used several times against silver (I) ions with good reproducibility. Fluctuations in potential, i.e in toxic species concentrations, are observed in waste waters [22]. Therefore, the reversibility of the membrane response has to be checked. The potential was recorded (pH=3) depending on the time and the varying Cu-ion concentration. The copper-ion activity was changed by adding to the test solution known amounts of $Cu(NO_3)_2$ solutions. Figure 6 shows the potential change of the copper sensitive thin film. When the copper (II) concentration increases, the membrane potential shifted in

the direction of more positive values. A Nernstian behaviour is then observed. It is clearly evident that the response of the copper (II) ISE reaches a steady-state value within seconds of a step-wise change in the activity of Cu^{2+} ion in solution. The response time was determined to 18 s when copper concentration increase from 10^{-4}M to 10^{-3}M.
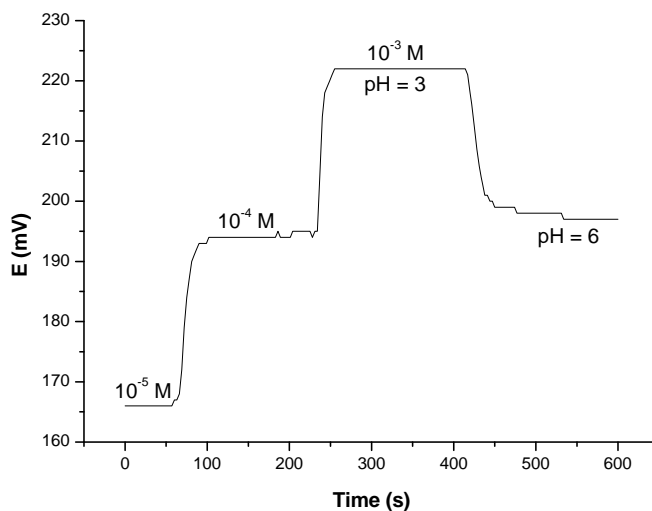

Fig. 6. Electrode potential depending on the time and the varying Cu-ion concentration.

By addition of KOH to the measured solution (the pH was then adjusted to 6), the electrode potential was found to return reversibly to the original lower potential. The formation of $Cu(OH)_2$ is due to the decrease of the primary ion concentration in the electrolyte, followed by the drop of the sensor potential. The long-term drift of the micro sensor was determined by registering the out-put signal in a 10^{-4} M $Cu(NO_3)_2$ solution during 11 h and the mean value was found to be 5mV/day.
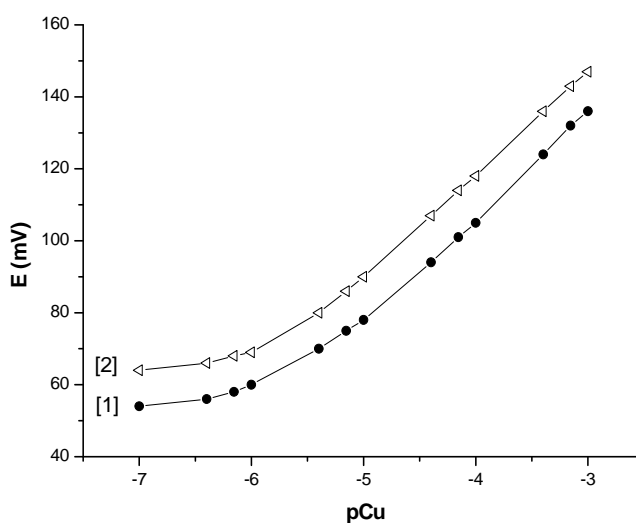

Fig. 7. Micro sensor response versus Cu^{2+} ion in Pz1 [1] and Pz2 [2] polluted solutions.

It is well known that different types of ion-selective chemical sensors are used for the control of the water quality but only few of them can be really applied widely for selective direct potentiometric measurements in natural media and waste effluents [23, 24]. A large part can be used only under laboratory conditions. Our goal was to check the ability of the studied sensor to work on polluted sites. The very first measurements have been carried out in waste waters withdrawn from polluted sites. Figure 7 presents calibrations curves of the sensitive membrane versus Cu^{2+} ion in Pz1 and Pz2 samples. The electrode exhibits Nernstian behaviour in contaminated solutions in spite of strong zinc concentration. Since good selectivity of chalcogenide glass based sensor is observed in presence of alkali and alkaline-earth cations, the high concentrations of Ca^{2+} and Mg^{2+} ions did not influence sensor response. In agreement with the calculated coefficients, a good selectivity is observed in presence of cadmium (II) and lead (II) ions. Further measurements indicated that the sensor still work well after exposure to the polluted samples.

4. Conclusions

A new Cu-ISE elaboration process based on electrolysis is presented. After a conditioning period the sensitive layer displays a near-Nernstian response over a large range of concentration with a detection limit close to 10^{-6} M. Electrochemical characterisation has shown typical chalcogenide glass membrane behaviour. The very first calibrations in contaminated solutions have shown the ability of micro-device for in situ measurements under suitable conditions.

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