CHALCOGENIDE MATRIX DOPED WITH METAL IMPURITIES FOR ENVIRONMENTAL MONITORING

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$Ge_{28}Sb_{12}Se_{60}$ glassy matrix doped with metal impurities has been used for the determination of copper (II) in aqueous solution. The structural analysis of the sensing materials was performed using X-ray diffraction. In addition to chemical analysis, microstructural and morphological characterisations of the samples have been carried out by microscopy. Micro-ISE gave a Nernstian response versus Cu^{2+} ion. To characterize the chemical sensor further electrochemical investigations have been carried out. The evolution of the thin membrane with soaking time in copper nitrate solution has been investigated by electrochemical spectroscopy.

(Received May 15, 2011; Accepted June 1, 2011)

Keywords: Chalcogenide glass; Copper (II) sensor; Thin film; Ion-Selective Electrode (ISE); Electrochemical impedance spectroscopy (EIS)

1. Introduction

Heavy metal ions (i.e. mercury, copper, lead, cadmium, etc…) are ones of the most toxic species of industrial waters. The majority of existing techniques used for trace analysis of heavy metals can detect species at low concentrations. However, all of these traditional methods can hardly be used for in situ analysis [1]. Of the many analytical methods available for the determination of copper, only direct potentiometry with a Cu-ion-selective electrode enables the in situ measurement of the free copper(II) concentration (to which copper toxicity is generally attributed) without perturbing the natural speciation [2, 3]. Therefore, Intensive investigations in the field of sensitive materials development and construction of various types of chemical sensors have been enforced during the last two decades [4–6]. The miniaturization revolution of measurement devices has witnessed a sustained increase of interest in the analytical chemistry field [7]. For instance, the combination of the sensors and circuits on a single substrate (i.e. integrated micro sensors) represent an attractive approach in being able to realize compact measurement devices [8]. Enhanced chemical durability, suitable and actually unlimited ability to be doped or modified thus changing their structure and properties suggest an application of non-crystalline chalcogenides as promising membrane materials for conventional chemical sensors selective to heavy metal ions in various liquid media [9-13]. Baker and Trachtenberg were the first to use $Ge_{28}Sb_{12}Se_{60}$ glassy system doped with metal impurities for the determination of metal ions in aqueous solution [14, 15]. Further investigations have been carried out on copper (II) selective electrode [6, 8, 16, 17, and 18]. The lead off experiment for depositing a Cu (II)-selective chalcogenide glass device by means of radio frequency co-sputtering process onto micro-devices has been done by Tarantov and co-workers [19]. This process for the fabrication of Cu-SE thin sensors was also employed by Bychkov et al. [20]. Driven by these activities, integrated system had been prepared by means of RF co-sputter process too [8]. In this paper, we present results concerning characterization of a copper (II) micro-electrode. Thin amorphous films of Cu-containing devices have been prepared by cathodic co-Sputtering. Physical and electrochemical

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characteristics of ion-selective electrode are presented. The very first measurements in solution withdrawn from polluted sites have been carried out using a conventional potentiometric measuring set-up. Attention has been focused on to ageing study of the sensing membrane. Evolution of the sensor in function of soaking in $Cu(NO_3)_2$ solution have been investigated.

2. Experimental methods

Thin films of Copper(II) ion sensitive materials were prepared by RF co-sputtering of IG5 VITRON commercial target (i.e. $Ge_{28}Sb_{12}Se_{60}$) and copper metal assembled as a composite target as shown in figure 1. Alcatel Dion 300 apparatus equipped a 300 W generator, 13.56 MHz was used. Argon pressure was fixed to 10^{-2} mbar. A low power of 25 W was fixed because of the dielectric character of the chalcogenide matrix. The sensing film was deposited over a microscope slide substrate covered with a chromium layer. This metallic connection helped indeed in improving the continuity of the electrochemical chain. It also helped in increasing the adhesion of the film to the substrate. Chromium and sensing membrane thicknesses are respectively 300 nm and 500 nm. A wire was attached with a silver micro adhesive. Then the inner side was coated with an epoxy resin.

Figure 1

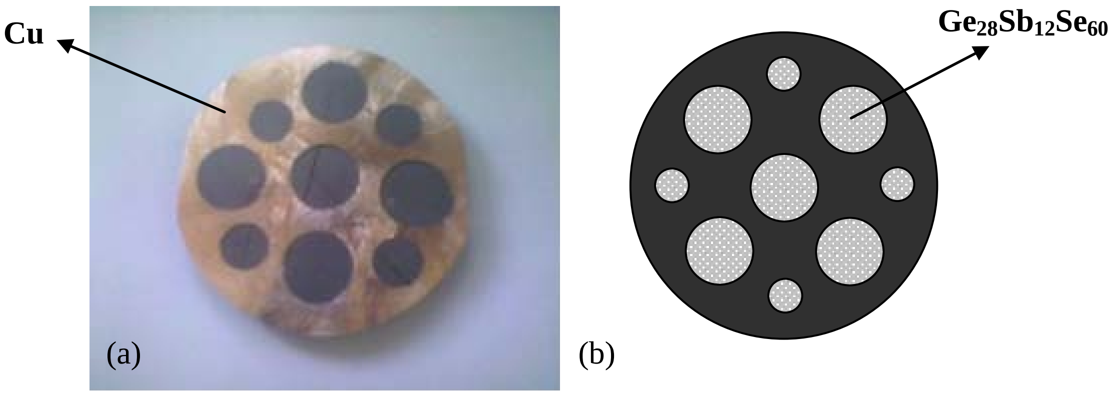


Fig. 1. Experimental composite target (a) and its Schematic representation (b)

The structural analysis of the bulk materials was performed using a SEIFERT diffractometer with Cu-Kα radiation ($\lambda = 1.5406$Å). An operating voltage of 40 kV and a beam current of 25 mA were selected. The amorphous nature of the thin films was investigated using glancing incidence X-ray diffraction. Experiments were performed using copper X-ray tube working at 45 kV and 35 mA. Data were then recorded a measuring time of 120 s per step. The glancing angle between X-rays and the thin film surface was 0.1°. A CAMECA SX100 electron probe micro-analyser employing five wavelength-dispersive spectrometers was used for chemical analysis. The experiments were made with a beam intensity of 10 nA and an accelerating voltage of 20 keV. In addition to chemical analysis, microstructural and morphological characterisations of the samples have been carried out. The SEM analysis has been recorded with a HITACHI S-4500I scanning electron microscope operating at 15 kV.

The electrode potential was measured with a high impedance millivoltmeter. The silver/silver chloride reference electrode was used with a double junction. KNO_3 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 $Cu(NO_3)_2$, $5H_2O$ solution by the supporting electrolyte. Calibrations were performed in a large range of copper (II) concentration by addition of a known volume of copper (II) nitrate test solutions to supporting electrolyte. Chemical micro-device was tested in polluted waters taken on contaminated site. Table 1 presents ion concentrations measured by Inductive Coupled Plasma. Waste waters were filtered and kept at +4°C.

Table 1. Cation concentrations of waste solutions measured by Inductive Coupled Plasma.

Element	**Al**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Sr**	**Cd**	**Sb**	**Ba**	**Tl**	**Pb**
Concentration (μg.L^{-1})	10298	2	3357	117	142	108	5699	5209	255	38	2	24	29	623

Electrochemical Impedance Spectroscopy studies were undertaken using Potentiostat/Galvanostat (PGSTAT100, Autolab) (100V, 10nA – 0.3A) coupled with a response analyser in frequency (FRA). A conventional three electrode cell was used with the sensing layer as the working electrode, a silver/silver chloride electrode used with double junction, as the reference one and a platinum wire as the counter electrode. The working electrode is a rotating disc electrode with a speed equal to 3000 rpm. Such a configuration could be chosen because of the predominant electronic conductivity of the membrane and the low resistance of the Cr/layer interface. In addition, this RDE configuration was carried out in order to minimize Warburg behaviour in low frequency region. EIS spectra were collected at the open circuit potential using an applied ac signal of 10 mV and a frequency range of 0.1 Hz – 10^5Hz. The measurements were performed in solutions of 0.5 M KNO_3 + $Cu(NO_3)_2$ at room temperature.

3. Results and discussions

X-ray diffraction patterns shown in figure 2 indicated no diffraction peaks for the sensing thin film confirming the amorphous character of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ membrane. It is different from the structure reported for the bulk chalcogenide sensor $Cu_{10}(As_2S_3)_{90}$ where partial crystallization with the presence of sinnerite is observed. The produced layers have a smooth surface. The membrane surface does not present any defects and secondary phase. A columnar structure can be observed from AFM study. Images obtained by Scanning Electron Microscopy confirmed the column-like structure within the layers. The microstructure shows the presence of grains that are probably due to the presence of the columnar structure. The chemical composition of the membrane has been checked. EPMA analysis was aimed as completing EDX experiments. It is demonstrated that the composition was constant throughout the depth of the sensing device. Experimental data showed that deposited films contained 40 at. % of copper. XPS measurement indicated that copper was present in the film as Cu^I. All these data are comparable to those already reported for chalcogenide sensors [6, 8, 16, 18, and 21].

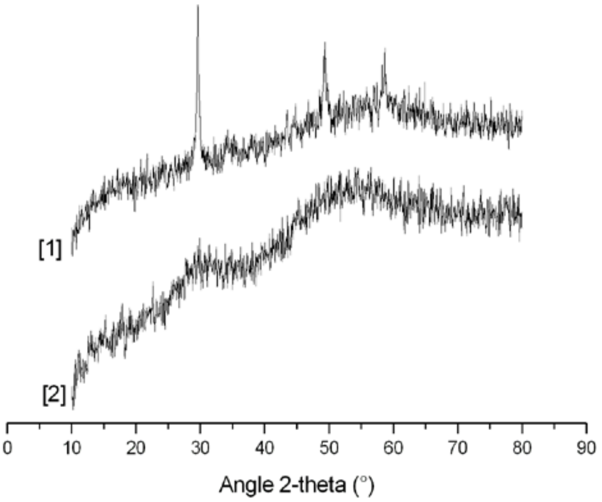


Fig. 2. X-ray diffraction patterns of $Cu_{10}(As_2S_3)_{90}$ bulk membrane [1] and $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ thin layer [2].

The electrochemical behaviour of the micro-sensor $Cu_x(Ge_{28}Sb_{12}Se_{60})_{100-x}$ (x = 40 and 70 at.%) was checked. Figure 3 shows calibration curves of both membranes. The electrode with higher copper atomic percent is not sensitive to variation in concentration of copper (II) ions. However, It can be seen from the curves that micro electrode with x = 40 at.% of copper metal give a Nernstian response versus Cu^{2+} ion. The potentiometric response obeyed the Nernst law (1) with a slop of 30 mV per decade. The limit of detection is close to 10^{-6} M.

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

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 and $[Cu^{2+}]$ is the concentration of the reducing agent (species, Cu^{2+}).

Further experiments have been carried out to describe the electrochemical characteristics. The sensing device showed good long term stability. The reported stability of the electrode was 40 days. High selectivity in the presence of alkali and alkaline-earth metal ions was observed. We used Midgley equation and the fixed interference method to determine the membrane selectivity in presence of interfering ions. According to experimental data studied sensor is not reliable in presence of Fe^{3+} and Fe^{2+} species. The reversibility of the thin layer had been studied. It is demonstrated that the electrode potential shifted in the direction of more positive values with a Nernstian response when primary ion concentration increases. The response time of the ISE was about 20s (10^{-4}M-10^{-3}M). Moreover, the sensor response returned reversibly to the original lower potential with $Cu(OH)_2$ formation.

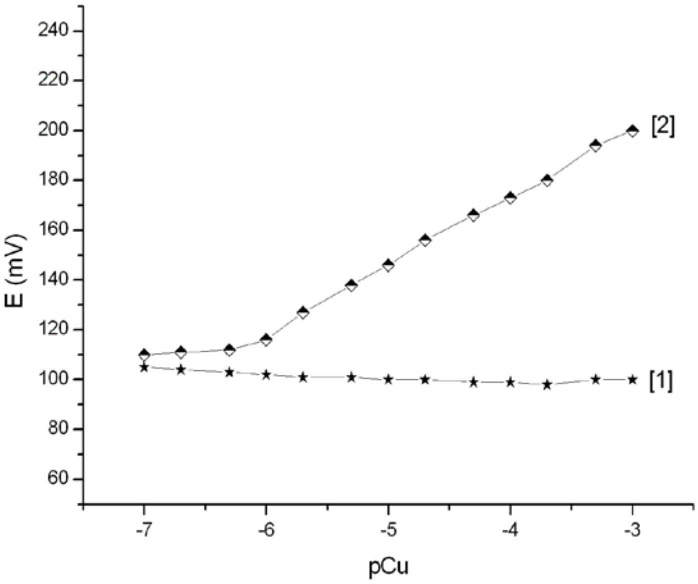


Fig. 3. Potentiometric responses of $Cu_x(Ge_{28}Sb_{12}Se_{60})_{100-x}$ devices; x = 70 [1] and x = 40 at.% [2].

The effect of the measured solution pH on the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ chemical sensor was checked in a large range of pH. Figure 4 indicated that the electrode response versus primary ions does not depend on the pH at pH values from 3,5 to 5,5 in a solution containing 10^{-2} M of $Cu(NO_3)_2$. Working in acidic media, the increase in the values of electrode potential is explain by a response to H^+ ion or a slow dissolution of the membrane [11, 22]. However, short times measurements can be carried out in acidic media. The decrease in the electrode response at higher pH is explained with the formation of copper hydroxide results in the decrease of Cu^{2+} ion concentration in the test solution.

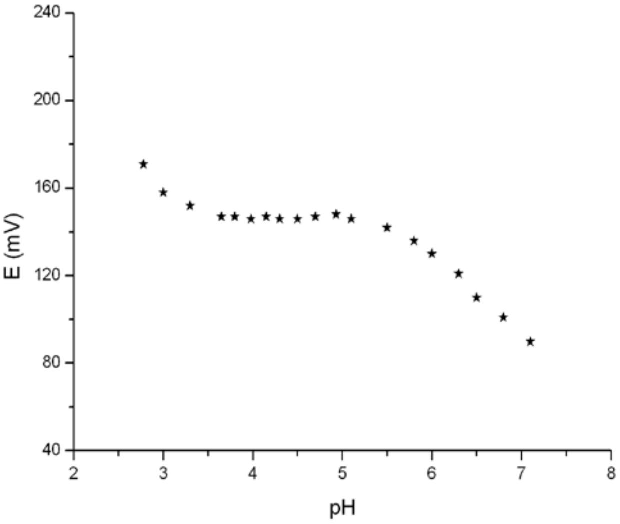


Fig. 4. pH influence on the response of $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ selective electrode.

In addition to previous work [18], the evolution of the chemical sensor with time has been checked. Our goal was to understand the ageing process. Potentiometric measurements have been carried out after soaking in $Cu(NO_3)_2$ solution. Figure 5 shows potentiometric responses to Cu^{2+} ion after different period of soaking in copper (II) solution. It is shown that after conditioning the film for 16 hours in a solution containing 10^{-4} M of copper nitrate the sensor characteristics became stable and Nernstian. Since the micro-device still run after 1258 hours of ageing one can consider that the life time of the membrane is very satisfying.

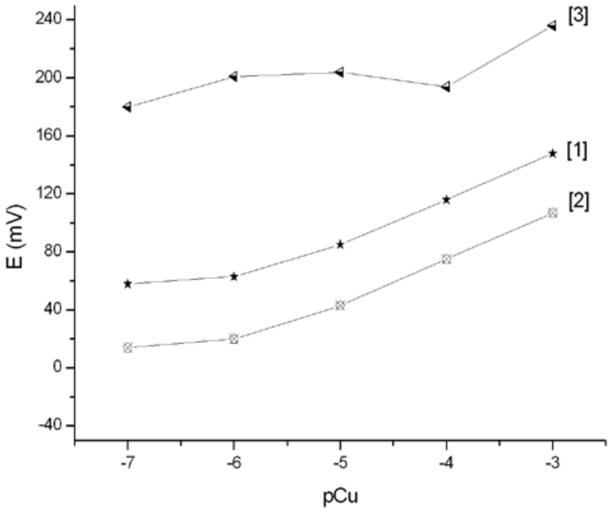


Fig. 5. Calibration curves versus copper (II) ion after different period of soaking in a 10^{-4} M $Cu(NO_3)_2$ solution, [1] 16 hours, [2] 1258 hours, [3] 1565 hours.

XPS was used to investigate the modification of the membrane surface after exposure to copper solution. Even though this technique cannot give absolute values for the element content the relative changes have been discussed. Table 2 presents surface composition for membrane treated during various times. The percentage of copper atoms stays approximately constant. At the same time a decrease in the percentage of selenium, germanium and antimony atoms is noticed. To complete the study, the solutions in which the membrane was treated were analysed by Inductive Coupled Plasma (ICP-MS). The investigation showed the presence of selenium, germanium and antimony in solutions while any significant change in their copper content is not observed. This result is consistent with SEM observation. The change in the surface of the thin film in function of the ageing time in copper nitrate solution was observed by Scanning Electron Microscopy. A deterioration of the film surface with appearance of some cracks was observed during the ageing process. This change went along a decrease in the roughness of the layer as measured by Atomic Force Microscopy. Obviously the ageing results in a partial surface dissolution. It is also demonstrated that the ageing process is related to a strong surface oxidation and an increase of the impedance [18].

Table 2. Evolution of the surface composition (at.%) for thin film treated in copper nitrate solution during various times.

		Soaking time			
		1h	24 h	48 h	168 h
at. % of elements	Cu	60.9	66.6	63.4	68.2
	Se	21.0	22.1	24.7	24.0
	Ge	5.1	2.2	4.2	3.0
	Sb	13.0	9.1	7.7	4.8

A powerful non-destructive technique has been used to monitor in situ the variations in complex impedance as a function of soaking time in copper nitrate solution. Figure 6 shows electrochemical impedance spectroscopy data for sensing thin film expose to 10^{-4} M copper (II) electrolyte. Bode phase plot shows the presence of high frequency relaxation process which is symbolic of a modified surface layer process, whereas the low frequency time constant is characteristic of an oxidation reaction. The relaxation frequency shifted in the direction of high frequency when soaking time increase. In addition the shape of the diagram changed and became larger. It might be interpreted by the appearance of complex phenomenon occurring at the interface.

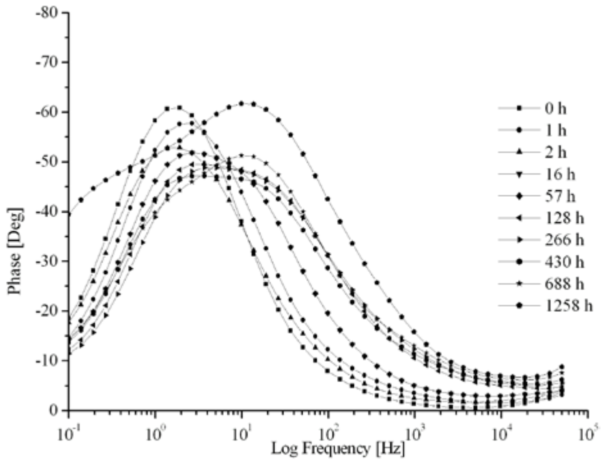
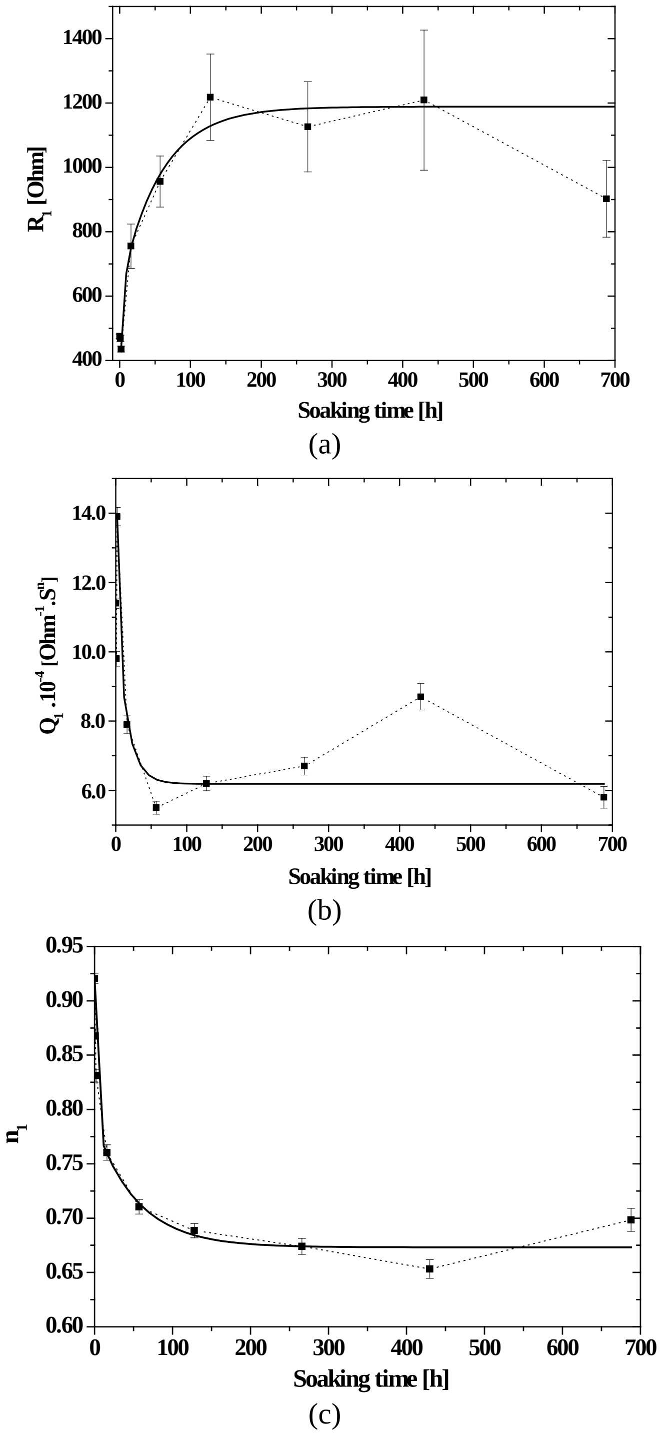


Fig. 6. Bode phase plots of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ thin layer in 10^{-4}M $Cu(NO_3)_2$ solutions with different times of aging.

The general diminution in the phase angle is commensurate with a less prominent capacitive component of the impedance. EIS spectra are not well resolved then experimental data were fitted to equivalent circuit as discussed elsewhere [5]. All EIS spectra were fitted to equivalent circuits using the ZView2 software. To insure that the equivalent circuit modelling was realistic, it was restricted to a solution resistance in series with two R, CPE circuits. The first circuit contains a charge transfer resistance R_1 in parallel with the double layer capacitance CPE_1. Acceptable fits were obtained for R_1 and CPE_1 elements. As shown in figure 7, the decrease of CPE_1 parameters (i.e. Q_1 and n_1) is in agreement with the less capacitive component of the impedance. R_1 variation is consistent with an alteration in the charge transfer kinetics.



(a)

(b)

(c)

Fig. 7. (a) Charge Transfer Resistance [R_1]; (b) Constant phase element [Q_1]; (c) [n_1] plotted as a function of time obtained after fitting the experimental data.

The second circuit is introduced for modelling the change in the shape of Bode phase diagram observed at high ageing time. The circuit contains a resistance term R_2 in parallel with a constant phase element CPE_2. The evolution of the two elements with soaking time in 10^{-4} M $Cu(NO_3)_2$ solution is not well resolved. However the decrease of CPE_2 parameters (i.e. Q_2 and n_2) presents in figure 8 is in agreement with the general diminution in the phase angle observed with ageing.

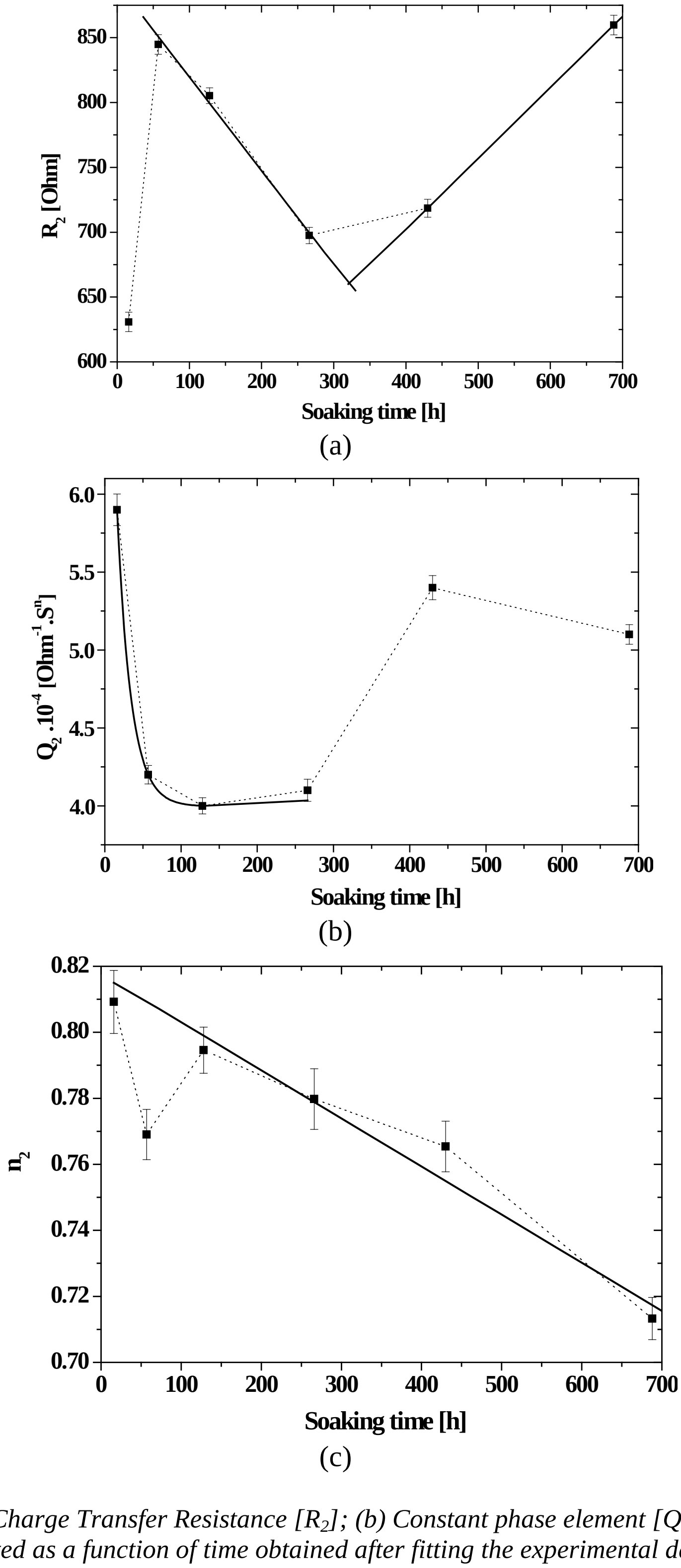


Fig. 8. (a) Charge Transfer Resistance [R_2]; (b) Constant phase element [Q_2]; (c) [n_2] plotted as a function of time obtained after fitting the experimental data.

Sensors based on chalcogenide materials are not widely used for in-situ monitoring. Selectivity of the majority of sensors is often poor in waste waters and low levels of concentration of heavy metals are commonly observed. Therefore, the ability of micro sensor to provide continuous monitoring has been checked in solutions withdrawn from polluted sites. To avoid metal hydroxide formation measurements have been performed in acidic media. Figure 9 presents corresponding calibration curve. $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ electrode exhibits Nernstian out-put signal in polluted sample in spite of high ion concentrations. The signal is in agreement with good selectivity of chalcogenide glass based sensor in presence of alkali and alkaline-earth ion. Further measurements indicated that exposure to polluted sample did not influence sensor performance.

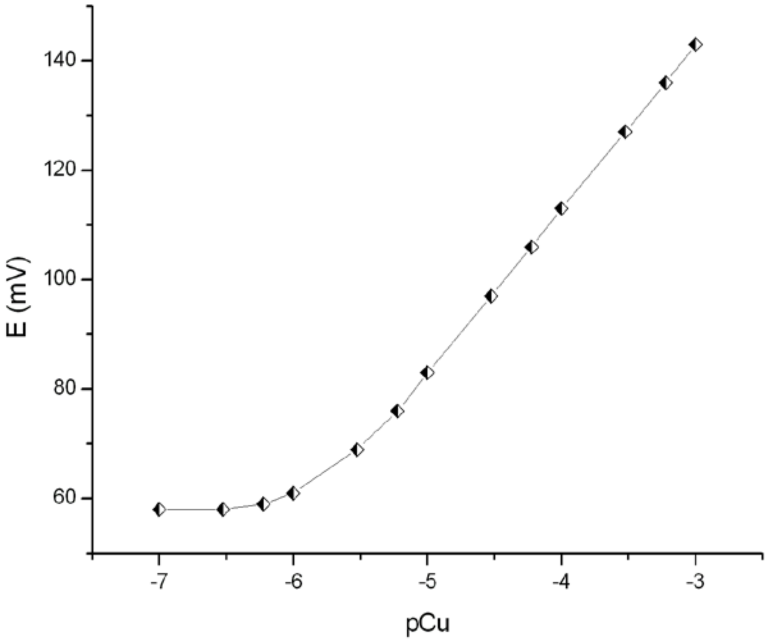


Fig. 9. Sensor potentiometric signal in polluted sample.

4. Conclusions

Amorphous thin membrane has been studied. Electrochemical analysis indicated that the micro-device was suitable for in-situ measurements. Moreover, the first experiments in waste waters have been carried out with success. Ageing process is related to a surface modification. The EIS calculation suggests that complex process was taking place at the membrane – electrolyte interface with time. Nevertheless the lifetime of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ sensitive membrane maintained in a copper (II) rich solution is very satisfying.

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