J ournal of Non-Oxide Glasses Vol. 3, No 1, 2011, p. 8 -15

STUDY OF CHALCOGENIDE THIN LAYER Cu-ISE

MARC MARIE-MAURICE MELEDGE ESSI*
Université de Cocody, Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT, 22 BP 582 Abidjan 22, Côte d'Ivoire

The $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ membrane ageing was studied by characterizing the solid/liquid interface. The change in the sensor surface depending on time was observed by scanning electron microscopy (SEM) and measured by atomic force microscopy (AFM). The Cu-ISE out-put signal is described according to the soaking time in a 10^{-4} M copper(II) nitrate solution. The sensor/solution interface has been investigated using electrochemical impedance spectroscopy (EIS) in order to understand the ageing process. Experimental data were then analyzed using an equivalent circuit.

(Received February 8, 2011; accepted February 23, 2011)

Keywords: Chalcogenide membrane; Ageing; Ion-Selective Electrode (ISE), Electrochemical impedance spectroscopy (EIS)

1. Introduction

Heavy metals are the most dangerous environmental contaminants, which present a serious threat to human health, even in trace quantities [1]. Several analytical techniques, such as atomic absorption spectrometry (AAS), inductive coupled plasma-atomic emission spectrometry (ICP-AES), etc., are available for the quantification of heavy metals. However, all of these traditional methods are generally expensive and can hardly be used for in situ analysis. Therefore, the analysis is often limited to laboratory level only. It is clearly evident that, a low-cost and reliable system needs still to be developed for in situ measurements, such requirements are greatly met with ISE [2]. Ion-selective electrodes are useful analytical instruments in order to determine the concentration of a specific or several components in a liquid test sample [3, 4]. Therefore, different types of ISEs have been developed in the past [5, 6], where chalcogenide glass materials represent one class of functional membrane with a high performance. One of the most promising application of these materials is as membranes in potentiometric chemical sensors, micro-sensors and multi-sensors system, which are recently widely used [7, 8]. Chalcogenide glass sensors for determination of heavy-metal ions are well known [9] and successfully applied in industrial and environmental pollution control [10]. Chalocegenide glasses are promising materials because of their several advantages: higher sensitivity of the electrode function, better selectivity in the presence of some interfering ions and excellent stability against the chemical attack in acidic and oxidation media [11, 12]. Miniaturized devices have potentially significant future applications in the area of medicine and chemical processing [13]. From this point of view, the technological aspect of fabrication and miniaturization of thin-film sensors based on chalcogenide materials have been reviewed [14, 15].

Chalcogenide glass-based ISEs have been introduced by Baker and Trachtenberg in the 1970's [16, 17]. Authors were the first to use $Ge_{28}Sb_{12}Se_{60}$ glassy matrix doped with metal impurities for the determination of copper (II) and iron (III) ions in aqueous solution. Driven by these activities, Taillades et al. prepared potentiometric micro-sensors as well as ISFET devices with a copper-selective thin film by means of RF co-sputter process [18, 19]. Later, Pejcic et al. [20] started new investigations concerning structural and interfacial study of the iron chalcogenide

---

*Corresponding author: marc.essi@yahoo.fr glass [i.e., $Fe_x(Ge_{28}Sb_{12}Se_{60})_{100-x}$] ISE. In addition, De Marco et al. [21] have employed the Fe(III) ISE [$Fe_{2.5}(Ge_{28}Sb_{12}Se_{60})_{97.5}$] in buffer saline media in order to assess the suitability of this electrode for seawater analyses. The sensor properties of the sputtered Cu[Ge-Sb-Se] thin film were studied in both potentiometric measurements and composition analysis [22]. Lately, Mear et al. report some investigations of the chalcogenide membrane lifetime tested in water site conditions [9].

In this report attention will be focussed mainly on to ageing study of chalcogenide thin film with composition $Cu_{40}[Ge_{28}Sb_{12}Se_{60}]_{60}$. Electrochemical Impedance Spectroscopy technique which was already proved to be successful for such studies was used for investigations. Surface modification of the membrane in function of the ageing time was observed by Scanning Electron Microscopy. The evolution of the out-put signal with time is presented. Potentiometric analyses were used to investigate the modification of the membrane electrochemical behaviour after soaking in copper nitrate solution.

2. Experimental methods

Thin films of Copper(II) ion sensitive glasses were prepared by RF co-sputtering of chalcogenide glass $Ge_{28}Sb_{12}Se_{60}$ and copper metal assembled as a composite target. The chalcogenide 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. A wire was attached with a silver micro adhesive. Then the inner side was coated with an epoxy resin.

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 (0.1 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 $Cu(NO_3)_2$, $5H_2O$ 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. The pH of the solution was maintained at the same value (pH=3) for all measurements to avoid $Cu(OH)_2$ formation. The electrochemical measuring cell can be schematically present as following:

Ag,AgCl||KCl,AgCl (sat.) ||0.1 M KNO_3||Analysed solution||ISE||Inner reference electrode

Electrochemical Impedance Spectroscopy (EIS) studies were undertaken using Potentiostat/Galvanostat (PGSTAT100, Autolab) (100V, 10nA – 0.3A) coupled with a response analyser in frequency (FRA). A three electrode configuration was used with the chalcogenide sensor as the working electrode, a Ag/AgCl electrode used with double junction, as the reference one and a platinum wire as the auxiliary electrode. The working electrode is a revolving one 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 Pt/membrane interface. Impedance spectra were recorded in the frequency range 0.1 Hz – 1×10^5 Hz with an applied ac signal of 10 mV. The measurements were performed at open circuit potential in solutions of 0.5 M $KNO_3 + Cu(NO_3)_2$ at room temperature. All EIS spectra were fitted to equivalent circuits using the ZView2 software.

3. Results and discussion

The data obtained by SEM, EDS and SIMS indicated that the layers were homogeneous and were poorly contaminated. The sensitive membrane has a surface of good quality. $Cu_{40}[Ge_{28}Sb_{12}Se_{60}]_{60}$ membrane composition was found to be constant throughout the depth of the layer. It is shown that Cu_2Se, $GeSe_2$ and Sb_2Se_3 coexist at the thin film surface. Moreover, a columnar film structure is observed. Such morphology is often observed for films deposited by RF Sputtering [23]. These results are comparable to those already reported for similar Cu-ISEs [7, 9, 18].

In order to get a physical insight in the observed phenomena, additional experiments were carried out. In particular, the change in the surface of the thin film in function of the ageing time in 10^{-4} M copper nitrate solution was observed by Scanning Electron Microscopy (SEM) using a HITACHI S-4500 I. A 5 kV voltage was applied in all observations and a magnification of ×50000 was used. The resulting micrographs are shown in figure1. The microstructure shows the presence of grains that are probably due to the presence of a columnar structure. It is different from the structure reported for the bulk chalcogenide membrane Cu-As-S where a multiphase system exists due to the presence of crystallites of cinnerite [24]. During the ageing process a deterioration of the film surface with appearance of some cracks was observed. This change went along a decrease in the roughness of the film as measured by Atomic Force Microscopy : 5.5 before ageing and 4.0 after 168 hours in the copper solution. To complete the study two ageing solutions, i.e. the solutions obtained after 1 hour and 168 hours of ageing, were analyzed by Inductive Coupled Plasma (ICP-MS). The analysis showed the presence of selenium, germanium and antimony in both solutions while it did not show any significant change in their copper content. Obviously a chemical attack of the membrane occurred in solutions containing 10^{-4}M $Cu(NO_3)_2$. The oxidation of the surface might be at the origin of the attack.

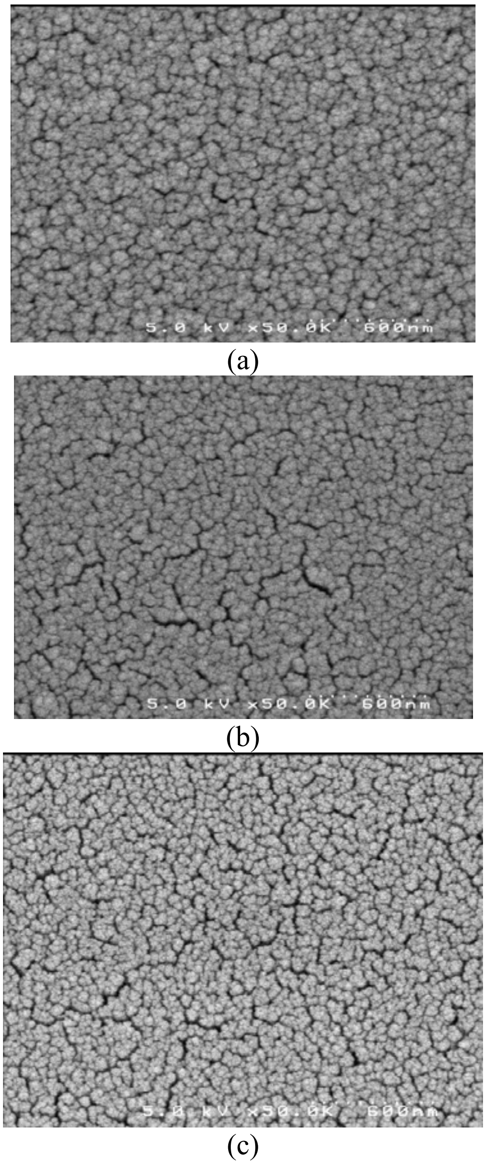
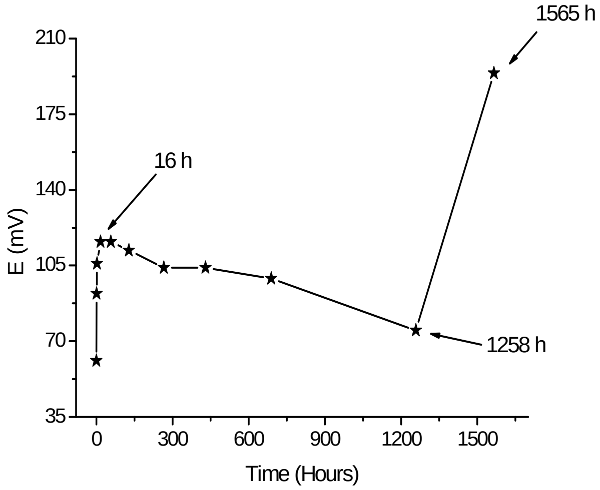


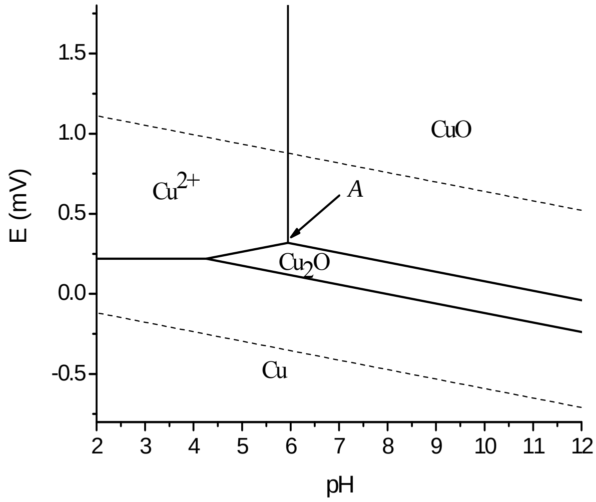
Fig. 1. SEM micrographs of the surface of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})$ thin film after different periods of ageing, (a) without ageing, (b) 1 hour, (c) 168 hours.

XPS clearly shows that the chemical composition of the membrane is modified as soon as the membrane is soaked in a copper (II) solution and its alteration corresponds to an oxidation of the membrane surface and dissolution of the chalcogenide glassy Ge_{28} $Sb_{12}Se_{60}$ in the copper nitrate solution [7]. It is to be noted that some previous works [5, 24, 25] on chalcogenide membrane indicate a modification in the copper content of the membrane surface soaked in copper (II) solution. In our work, modified surface formation is observed with no change in the copper content, as detected by ICP-MS analysis.

Potentiometric measurements of the sensitive layer have been carried out after soaking in copper nitrate solution, for different periods of times (from 0 to 1565 hours). The result of the first calibration of the sensor differed from the subsequent ones. After conditioning the film for 16 hours in a solution containing 10^{-4} M of $Cu(NO_3)_2$ the sensing membrane give a stabilized and Nerntian response. The film that has interacted with a copper nitrate solution during 1565 hours gives a flat response to Cu^{2+} ions. It is clearly evident that the life time of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ membrane is great since the sensor still run after 1258 hours of ageing.



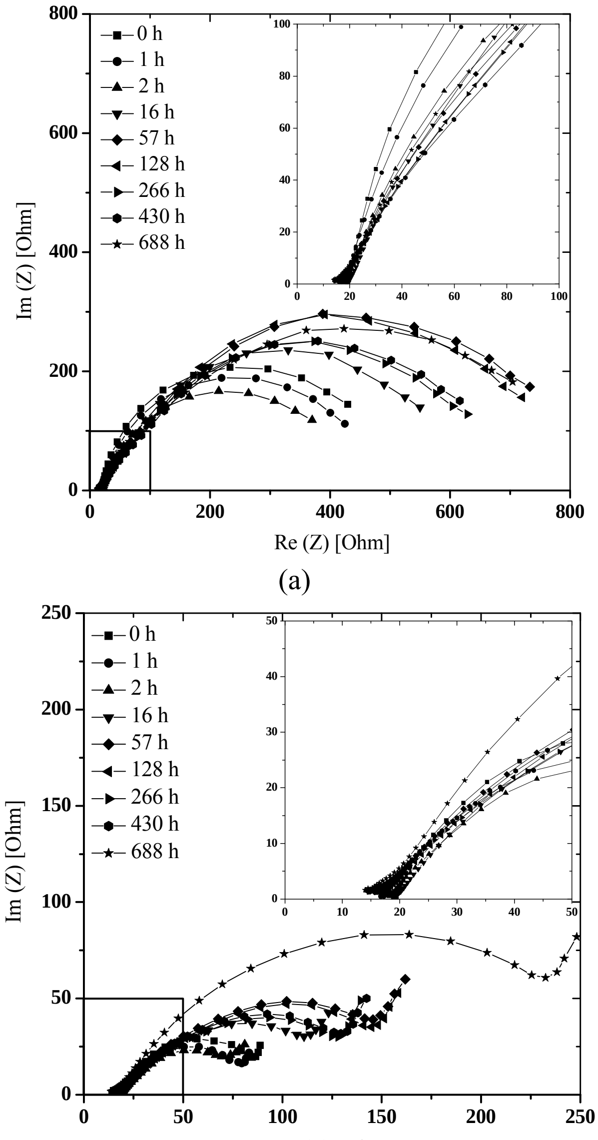
(a)



(b)

Fig. 2. Evolution of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})_{60}$ electrode potential with time of soaking in a 10^{-4} M copper nitrate solution (a) and Pourbaix diagram of copper at 25°C, the copper concentration equal to 10^{-6} M (b).

Fig. 2(a) presents the evolution of the electrode potential with time of soaking. An example of data obtained in the 10^{-4} M solution is presented. According to XPS data [7], the increase of the sensor potential from 0 to 16 hours of soaking time is explained with the presence of Cu^{2+} ion in solution and both kinds of copper, i.e. Cu(I) and Cu(II), at membrane surface. Thus, Copper Pourbaix diagram (Figure 2(b)) indicates that, the out-put signal has to increase to reach a steady-state value (point A). From 16 to 1258 hours of ageing the evolution of the electrode potential is due to the slight drift of about 1mV per day in potential with time. For a ageing time of 1565 hours in a solution containing 10^{-4} M of $Cu(NO_3)_2$, one can consider that only Cu(II) is present at the modified layer surface because of the strong oxidation. Therefore, the electrode potential has to increase to reach a steady-state value in agreement with copper Pourbaix diagram.



(a)

(b)

Fig. 3. Complex impedance plane plots of the $Cu_{40}(Ge_{28}Sb_{12}Se_{60})$ sensor in solutions with different times of ageing (a) Im(Z) = f(Re(Z)) for a 10^{-4} copper concentration, (b) Im(Z) = f(Re(Z)) for a 10^{-3} copper concentration.

The evolution of the complex impedance of the cell with soaking time in 10^{-4} M $Cu(NO_3)_2$ solution has been investigated during several cycles of calibrations in Cu^{2+} solutions. Figure 3(a) and figure 3(b) show data obtained respectively in 10^{-4} M and 10^{-3} M solutions. The impedance spectra are composed of a semicircle shifted from the origin for all the concentrations in solution. When the membrane is in contact with concentrated solution copper (II) ions (10^{-3} M), an additional straight line is observed at low frequency, corresponding to diffusion phenomena. The part of the Zview software dedicated to equivalent circuits, was used to simulate the impedance spectra with an electrical circuit. The EIS spectra were fitted to the equivalent circuit show in figure 4. Such a circuit was built on the basis of following assumption. First, R_s stand for impedance and was introduced to take into account the electrical behaviour of the solution. It corresponds to the shift of the semicircle on the real axis. The charge transfer resistance R_{ct1} in parallel with a double layer capacitance modelled by a constant phase element CPE_1 take into account the low frequency semicircle related to the interfacial charge transfer reaction. It is clearly evident that the semicircle does not intersect the x-axis and this is indicative of the electron transfer being sluggish in the medium. In addition, a capacity C is added and modelled the diffusion phenomena observed at higher concentration. The values of the parameters are summarized on the figure 5 excepted for R_s where in all the case, the values are small and similar (around 20 Ω) for the different aging time. It is attributed to the sum of the resistance of the solution and of the membrane

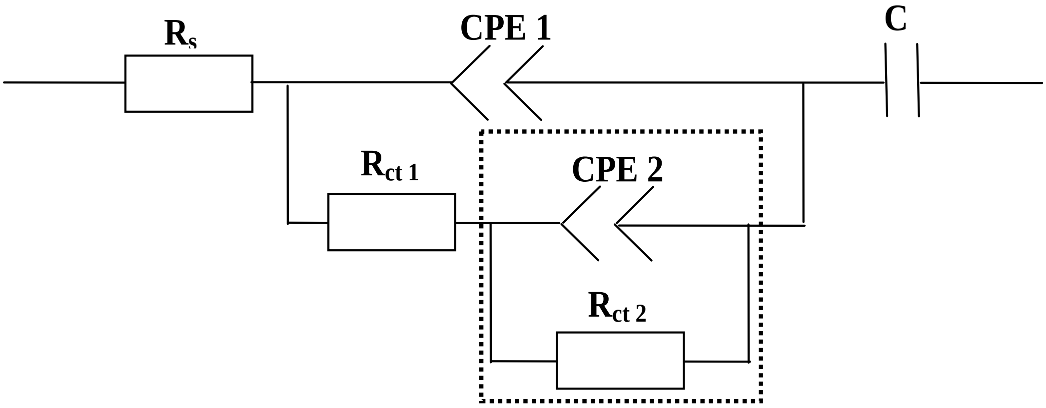


Fig. 4. Equivalent circuit used to model the impedance spectra presented on Fig. 3.

The measured value of R_s was in agreement with the high conductivity of the material and the presence of a concentrated supporting electrolyte. It has been found that R_{ct1} is strongly dependent on the copper (II) concentration of the solution and that the interfacial process is limited by the diffusion in concentrated solutions. R_{ct1} is also dependent on the aging time and increase when aging time increases as shown in figure 5. In the other hand, the parameters of the CPE_1, Q_1 and n_1 decrease when aging time increase until 16 hours of ageing as shown in figure 5. This result leads us to suggest that the limitation of diffusion phenomena was taking place with time. On the whole the data obtained indicated that the total impedance increased slowly with time. It has been shown that the experimental data are in good agreement with the theoretical data, that's confirming a good equivalent circuit presented in figure 4.

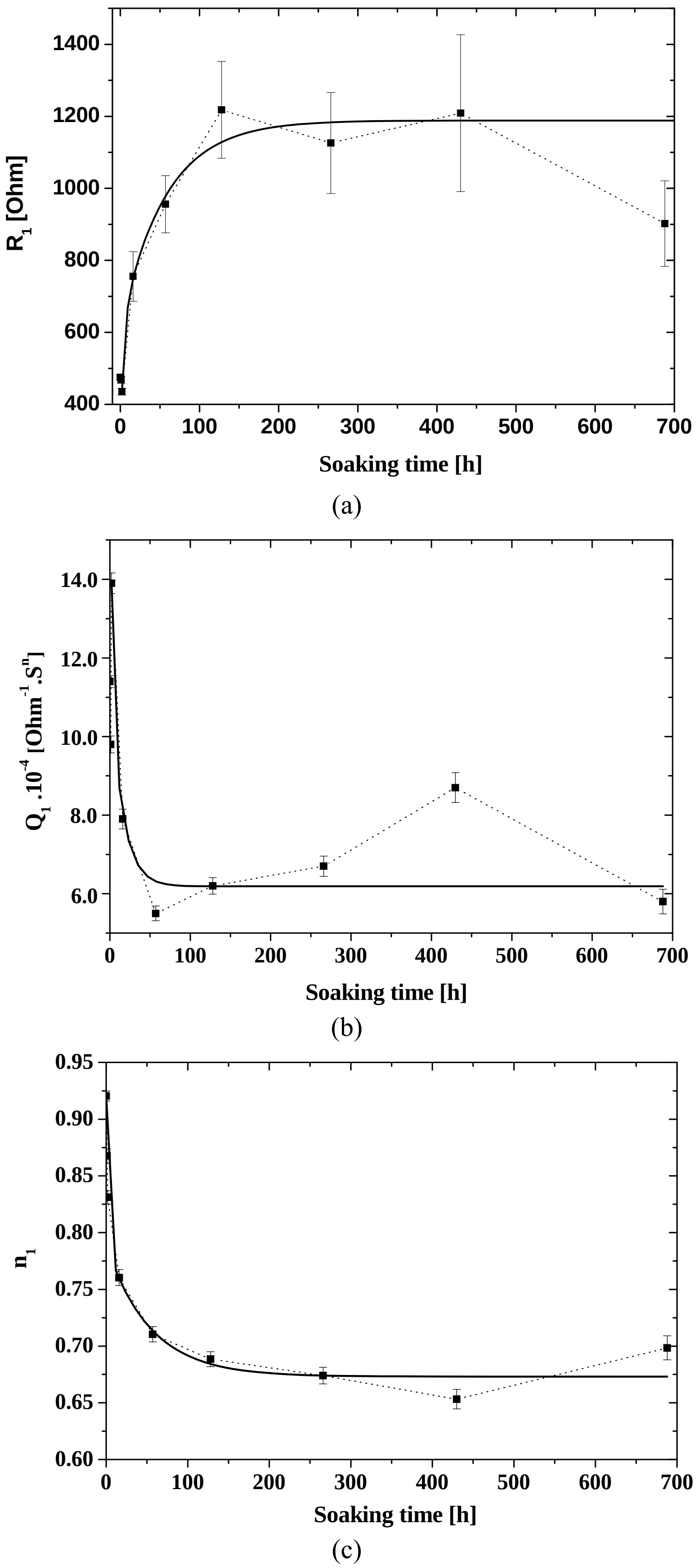


Fig. 5. (a) Charge Transfer Resistance [R_1]; (b) Constant phase element parameters [Q_1]; (c) and [n_1] plotted as a function of time obtained after fitting the experimental data with a part of the circuit shown Fig. 4.

After 16 hours of soaking, additional parameters, R_{ct2} and CPE_2 are needed to simulate the phenomena in the range frequency 0.1-1 Hz. The second charge transfer R_{ct2} in parallel with a second constant phase element CPE_2 is introduced in series with R_{ct1} for modelling the appearance of a new process observed with change in the shape of Bode diagrams [7]. The values of the additional parameters are difficult to explain but seem to understand interfacial complex phenomenon including strong oxidation observed elsewhere. All these changes indicated that an ageing process was taking place at the interface.

4. Conclusions

Analyses were carried out in order to get some knowledge on the phenomena occurring at the membrane/solution interface with time. Studies by EIS and modelisation of the response by electrochemical equivalent circuit confirmed the presence of complex phenomena at the interface and an increase of the impedance with time. Ageing process also results in a partial dissolution and is related to a surface oxidation. Potentiometric measurements reveal that the evolution of the out-put signal is correlated with the interface composition. In fact, the surface modification does not alter the sensor detection performance and the sensing device exhibits a great time of life.

References

[1] Q. Liu, H. Cai, Y. Xu, L. Xia, M. Yang, P. Wang, Biosen. Bioelectronics **22**, 3224 (2007).
[2] A. K. Jain, V. K. Gupta, L. P. Singh, J. R Raisoni, Electrochim. Acta **51**, 2547 (2006).
[3] M.J. Schöning, J.P. Kloock, Electroanalysis **19**, 2029 (2007).
[4] F.O. Méar, M. Essi, P. Sistat, P. Huguet, A. Pradel, M. Ribes, Proc. in the 21st Inter. Conf. On Solid Waste Technol. and Manage^{nt} (ICSWM), Philadelphia, PA (USA), 2006.
[5] Yu. G. Vlasov, E. A. Bychkov, A. M. Medvedev, Analyt. Chim. Acta **185**, 137 (1986).
[6] Yu. G. Vlasov, E. A. Bychkov, A. V. Legin, Talanta **41**, 1059 (1994).
[7] F.O. Méar, M. Essi, P. Sistat, M.-F. Guimon, D. Gonbeau, A. Pradel, Appl. Surf. Sci. **255** 6607 (2009).
[8] V. Vassilev, K. Tomova, S. Boycheva, J. Non-Cryst. Solids **353**, 2779 (2007).
[9] F.O. Méar, M. Essi, M.-F. Guimon, A. Pradel, Chalcogen. Lett. **5**, 117 (2008).
[10] M. Essi, Chalcogen. Lett. **8**, 25 (2011).
[11] V. S. Vassilev, S.H. Hadjinikolova, S.V. Boycheva, Sens. Actuators B **106**, 401 (2005).
[12] V.S. Vassilev, S.V. Boycheva, Talanta **67**, 20 (2005).
[13] Frumar M., Frumarova B., Nemec P., Wagner T., Jedelsky J., Hrdlicka M. J. Non-Cryst. Solids **352**, 544 (2006).
[14] Yu. Mourzina, M.J. Schöning, J. Schubert, W. Zander, A.V. Legin, Yu.G. Vlasov, P. Kordos, H. Lüth, Sens. Actuators B **71**, 13 (2000).
[15] M. Essi, A. Pradel, Chalcogen. Lett. **8**, 15 (2011).
[16] C. T. Baker, I. Trachtenberg, J. Electrochem. Soc. **118**, 571 (1971).
[17] R. Jasinski, I. Trachtenberg, G. Rice, J. Electrochem. Soc. **121**, 363 (1974).
[18] G. Taillades, O. Valls, A. Bratov, C. Dominguez, A. Pradel, M. Ribes, Sens. Actuators B **59** 123 (1999).
[19] A. Pradel, O. Valls, C. Cali, G. Taillades, A. Bratov, C. Dominguez, M. Ribes, J. Optoelectr. Adv. Mater. **3**, 641 (2001).
[20] B. Pejcic, R. De Marco, C. E. Buckley, C. F. Maitland, R. Knott, Talanta **63**, 149 (2004).
[21] R. De Marco, J. Martizano, Talanta **75**, 1234 (2008).
[22] T. Yoshinobu, M. J. Schöning, R. Otto, K. Furuichi, Yu. Mourzina, Yu. Ermolenko, H. Iwasaki, Sens. Actuators B **95**, 352 (2003).
[23] V. Balan, C. Vigreux, A. Pradel, A. Llobera, C. Dominguez, M.I. Alonso, M. Garriga, J. Non-Cryst. Solids **326-327**, 455–459 (2003)
[24] C. Cali, D. Foix, G. Taillades, E. Siebert, D. Gonbeau, A. Pradel, M. Ribes, Mat. Sci. Engineering C **21**, 3 (2002).
[25] R. De Marco, R. W. Cattrall, J. Liesegang, G. L. Nyberg, Anal. Chem. **64**, 594 (1992).