Cd-ISe AND MEMBRANE TECHNIQUE DEVICE FOR IN SITU MONITORING

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The response of cadmium (II) ion-selective electrodes based on chalcogenide glassy matrix CdS-AgI-Ag$_2$S-As$_2$S$_3$ is described. The electrode exhibits a Nernstian slope of 29 mV per decade in a large range of Cd^{2+} ion and a detection limit of 10^{-7}M. Physical and electrochemical characteristics of ion-selective electrode are presented. The chalcogenide membrane/solution interface has been investigated using X-ray photoelectron spectroscopy (XPS) in order to understand the sensing properties. The second part is devoted to a system allowing detection of toxic species at low concentration. The pre-conditioning module is based upon electro-dialysis and the first tests conducted on model solution are presented.

1. Introduction

The development and application of ion-selective electrodes continue to focus attention and expanding areas of analytical research [1, 2]. This tendency is noticeable in environmental monitoring which requires continuous measurements [3]. The detection of heavy metal ions in aqueous solutions represents one important measurement task in the fields of environmental and industrial water analysis. For practical applications, devices for on-site measurements can be recommended, but the major problem is still the lack of suitable sensor. Chalcogenide glasses doped with metal impurities are promising membrane materials for the preparation of ion-selective electrodes [4-7]. Since more than twenty years, chalcogenide glass bulk materials for detection of various heavy metal ions in aqueous solutions are well investigated [8-12]. Chalcogenide glass exhibit better chemical durability in acidic and redox media, and in many cases, possess better selectivity and reproducibility of the analytical characteristics, and longer time of life [13, 14]. Concerning the detection of Cd^{2+} ion, authors have shown that various kinds of bulk glasses from "CdS-Chalcogenide" system were interesting sensitive membranes [15-19]. However the membranes might not be able to work properly because of an insufficient limit of detection. These data clearly show the need for pre-conditioning the waters before sensor measurements. It is known that the combination of electro-dialysis and ion-exchange methods can be applied to the removal of cations from low concentration solutions. Such a process is used to deal with desalination of salted waters, waste water minimization and separation processes [20-23]. Our goal was to develop autonomous system for in situ and continuous detection of metallic species in solution. The first part of this work presents investigation of CdS-AgI-Ag$_2$S-As$_2$S$_3$ sensitive membrane tested in water site conditions for the cadmium detection. X-ray photoelectron spectroscopy (XPS) [9, 24], was used to get some knowledge on the phenomena giving rise to the electrode sensing properties. Sensing electrode ability to in situ monitoring has been checked. The aim of the second part is to allow the detection of Cd^{2+} species in low polluted solution. Solutions

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containing pollutants were then treated in order to extract cations from diluted solutions and to produce a concentrate for studied sensor experiments. The very first developments of a pre-conditioning module are presented.

2. Experimental methods

CdS-AgI-Ag$_2$S-As$_2$S$_3$ sensing materials were synthesized by melting the mixture of reagents at 950 °C for about 24 h in silica tubes evacuated to 10^{-5} Pa and further quenching in water at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo Electron® spectrometer (model ESCALAB 250) using a focused monochromatised Al Kα radiation (hν = 1486.6eV). The residual pressure inside the analysis chamber was ca. 5.10^{-8} Pa. The spectrometer was calibrated by using the photoemission lines of Au (Au 4f(7/2) = 83.9 eV, with reference to the Fermi level) the Au 4f(7/2) line, the full width at half maximum (FWHM) was 0.86 eV under the recording conditions. The peaks were recorded with constant pass energy of 50 eV. The binding energy scale was calibrated using the C 1s line (284.6 eV) from the carbon contamination. Neutralization of the surface charge was performed using low energy flood gun. Repeat runs were made on all the samples to assure the quality of the data. All the measurements were carried out on massive samples. The XPS signals were analyzed by using a peak synthesis program in which a nonlinear background is assumed and the fitting peaks of the experimental curve are defined by a combination of Gaussian and Lorentzian distributions.

To prepare electrodes, small discs were cut from the ingot. The two faces were polished with a very fine diamond paste. Electrochemical characteristics were checked using high impedance millivoltmeter (Radiometer Tacussel). Measurements were performed between a reference electrode, i.e. a double junction Ag/AgCl electrode and the sensor.
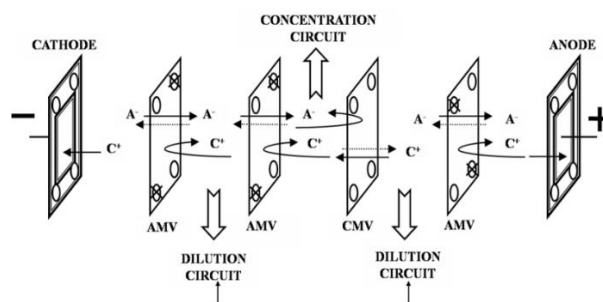

Fig. 1. Pre-conditioning prototype based on the electrodialysis principle.

Electrodialysis (ED) is a combination method. One of its components is dialysis. The other component is electrolysis. The principle of ED involves removal of ionic components from an aqueous solution through ion-exchange membranes using an electrical driving force. The waste water to be treated is pumped through a membrane stack which consists of alternately placed anionic and cationic selective membranes separated by gasket frames and spacers. The membranes are fixed between two end plates that contain the electrodes producing the electric field. In the compartments of the membrane stack, the ion content is diluted or concentrated according to the ion penetration through the membranes. Thus, waste water is separated into a dilute and a brine stream. Fig. 1 is a schematic representation of laboratory cell. It was composed of five compartments separated by ion-exchange membranes. Each separating membrane had an effective area of 5 x 8 cm^2. The central compartment or concentration compartment was delimited by cation and anion exchange membranes. On both sides of the central compartment were dilution compartments. The thickness was 0.3, 1.0 and 1.0 mm for the central, dilution and electrode compartments of the cell, respectively. Both electrodes are made of pure platinum. Two types of membranes were used in these experiments. AMV and CMV anion and cation exchange

membranes made by Asahi Glass (Tokyo, Japan) [22]. Their main characteristics are given in the Tab. 1. Circulation of the solution was insured by a debit-metric pump and the potential difference (pd) applied between the two electrodes was equal to 6V. In order to transfer the electric current and to remove gases produced by electrode reactions, the electrode chambers are rinsed with an electrolyte solution.

Table 1. Characteristics of the ion-exchange membranes.

Membrane type	Thickness (mm)	Electrical resistance ($\Omega.cm^{-2}$)	Bursting strength ($kg.cm^{-2}$)	Transport Number	IEC (meq/g dry)
CMV	0.13 – 0.15	2.0 – 3.5	3.0 – 5.0	T-Na^+ > 0.91	5.2
AMV	0.11 – 0.15	1.5 – 3.0	2.0 – 5.0	T-Cl^- > 0.93	4.4
CR67, MK111	-	-	-	-	2.4
R204SXR412	-	-	-	-	2.8

The current I flowing through the cation exchange membrane induces an ionic flux for the cationic species k directed to the concentrate and equal to:

$$J_k = \frac{T_k I}{z_k F}$$

(1)

where T_k is the cation k transport number, z_k the cation valence and F is the Faraday constant.

On the other hand, if Q is the volume flow rate of the concentrate solution, the convective ionic flux of the cation k due to the convection entering the electrodialyser is equal to QC_{in} and its counterpart existing in the system is QC_{out}. Thus, the mass balance equation for the inner concentrate solution can be written as:

$$\frac{\partial n_k}{\partial t} = \frac{I}{Q z_k F}\left(T_k^{CMV} - T_k^{AMV}\right) + Q\left(C_{in} - C_{out}\right)$$

(2)

where T_k^{CMV} and T_k^{AMV} are the transport numbers of the cation k through the cation exchange membrane and the anion exchange membrane, respectively. In steady state operation, the concentration factor between the incoming and the outgoing solution can be deduced:

$$\frac{C_{out}}{C_{in}} = 1 + \frac{I\left(T_k^{CMV} - T_k^{AMV}\right)}{Q^2 z_k F C_{in}}$$

(3)

It can be noticed that the concentration factor increases with the current value and the greater the convection flux QC_{in} the lower the concentration factor.

3. Results and discussion

A XPS analysis of the surface was undertaken in order to get information on the environment of the different elements of the sensing membrane. Moreover, this powerful

technique was used to investigate the modification of the membrane surface after soaking in a cadmium nitrate solution, $Cd(NO_3)_2$ (10^{-4} M), for different periods of time.
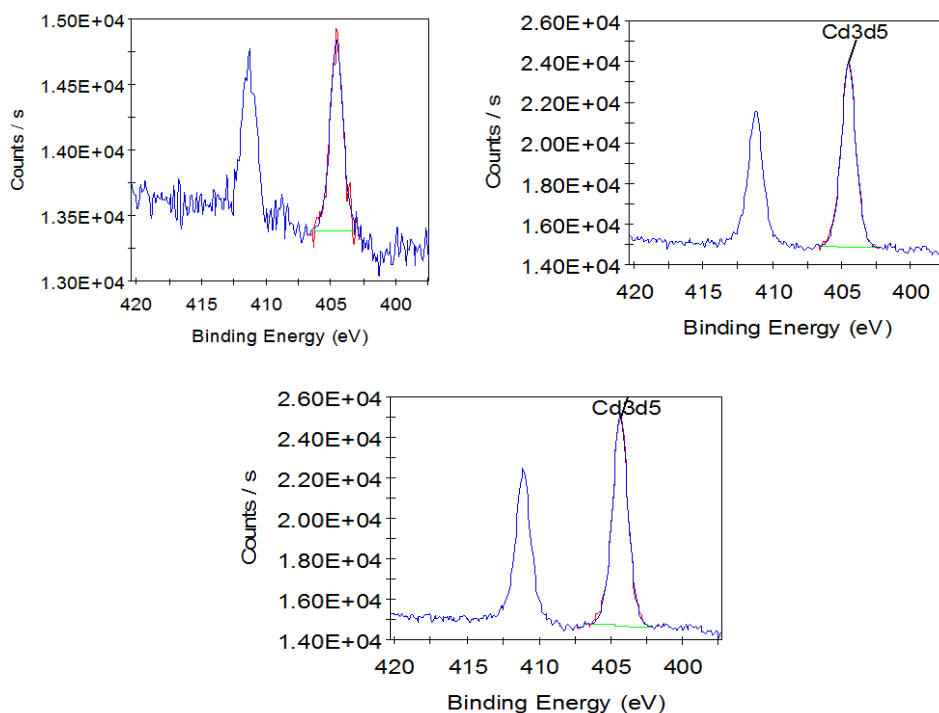

Fig. 2. XPS analysis on a CdS-AgI-Ag$_2$S-As$_2$S$_3$ bulk material. XPS spectra of Cd 3d : (a-up) fresh membrane, after a soaking period time in a 10^{-4} M cadmium nitrate solution, (b-middle) 15 min and (c-down) one hour.

Fig. 2(a) shows the signal of a fresh sensing membrane. A single peak located at 404.55 eV and corresponding to Cd 3d(5/2) is observed. No satellite structure was observed in the Cd 3d region. The binding energy of the Cd 3d(5/2) photopeak corresponds to that of Cd(II) ions in a sulphur environment, type CdS [25]. In addition to the surface analysis, a fresh surface of the sample was analyzed just after being fractured in an ultra high vacuum (5.10^{-8} Pa) in order to obtain bulk information. The composition for chalcogenide membrane is similar for both surface and core. An interaction of the freshly prepared materials with the electrolyte solution, $Cd(NO_3)_2$ did not caused metal oxidation of the cadmium at the surface. The single oxygen peak at a binding energy of 533.0 eV is similar to that observed on an untreated membrane and shows that no metal oxide is present in the samples [26]. Moreover, no change in the chemical state of Cd (II) is observed as shown in Fig. 2(b) and (c). The relative fractions of cadmium have been calculated from the area of the corresponding Cd 3d(5/2) peaks and are listed in Table 2. The relative fractions (before and after exposure) indicate an increase of cadmium atoms percentage at the surface after soaking in $Cd(NO_3)_2$ solution.

Table 2. Peak positions (eV) relative to C 1s (248.6 eV), their corresponding full width at half maximum (FWHM) peak area for the core-levels Cd 3d and Ag 3d.

Element	Core-level	Properties	0 h	15 min	01 h
Cd (II)	Cd 3d(5/2)	BE (eV)	404.55	404.55	404.55
		FMWH	*1.10*	*1.17*	*1.20*
		Peak area (%)	14	87	100
Ag (I)	Ag 3 d(5/2)	BE (eV)	367.50	367.49	367.48
		FMWH	*1.21*	*1.17*	*1.15*
		Peak area (%)	100	92	65

The core-level 3d spectra for Ag are shown in Fig. 3 for the fresh materials (i.e. Fig. 3(a)) and for sensing devices that soaked in the cadmium electrolyte solution for 15 min (i.e. Fig 3(b)) and one hour (Fig. 3(c)). Fig. 3(a) exhibits Ag 3d(5/2) core peak at a binding energy of 367.5 eV. It is shown that silver is Ag (I) type [27]. The relative fractions of silver before and after exposure to Cd $^{2+}$ ions are listed in Table 2. As shown in Table 2 and Fig. 3, an evolution of the relative fraction occurred, after a soaking period of one hour. No shift in binding energy for the core-level 3d spectra is observed in the case of a soaking. Again, we confirmed the absence of any other by-product such as Ag_2O from the Ag 3d core level spectrum.
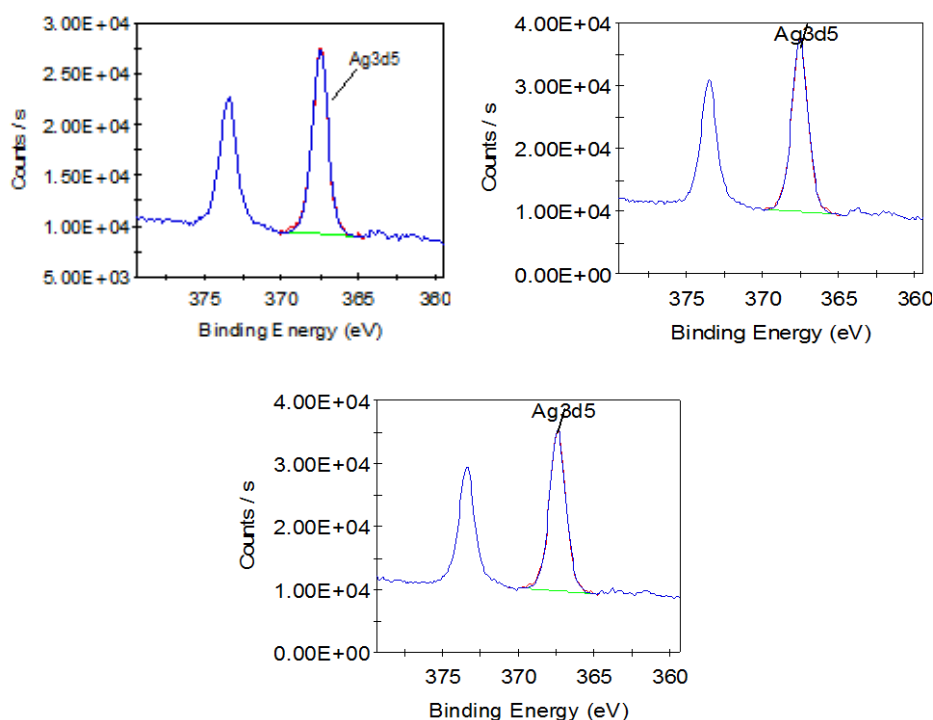

Fig. 3. XPS spectra of Ag 3d: (a-left) fresh membrane, after a soaking period time in a 10^{-4} M cadmium nitrate solution, (b-right) 15 min and (c-down) one hour.

The I 3d(5/2) peak was found to interfere significantly with the Cd 3p(3/2) peak. XPS data relating to iodine were then collected from the I 3d(3/2) photopeak.. The binding energies of the main peaks (I 3d, As 3d and S 2p) are reported in Fig. 4. The I 3d(3/2) peak reported at a binding energy of 630.16 eV characteristics of the AgI element [28]. The As XPS data have the same characteristics as in the reference compound As_2S_3 [29]. The core-level S 2p spectra of the fresh surface shown in Fig. 4(c) consists of a doublet corresponding to the 2p(3/2) and 2p(1/2) peaks of S. The doublet is located between 160 and 162 eV with a peak separation of 1.18 eV, corresponding to S(-II) [27, 28]. Even though XPS cannot give absolute values for the element content at low level, relative changes are observed. Experiments clearly show that the chemical composition of the surface membrane is modified as soon as the membrane is soaked in a cadmium (II) solution. The percentage of cadmium atoms increases with the length of treatment. At the same time, a decrease in the percentage of silver atoms is noticed while the other atoms content stays approximately constant. No further significant variation of the composition is observed. It is of interest to note that the alteration of the composition is not followed by any perceptible changes in the chemical state of the elements. No shift in binding energy for the Cd 3d, As 3d, I 3d, S 2p and Ag 3d peaks is also observed. To see if the evolution of the composition occurred in-depth, the bulk of the treated membranes was also analyzed. No composition change appeared compared to the untreated sample, which indicated that no diffusion process took place. XPS data are in agreement with previous study [29. 30]. Inductively coupled plasma-mass spectrometry analysis was carried out on the solution in which the membrane was treated. The

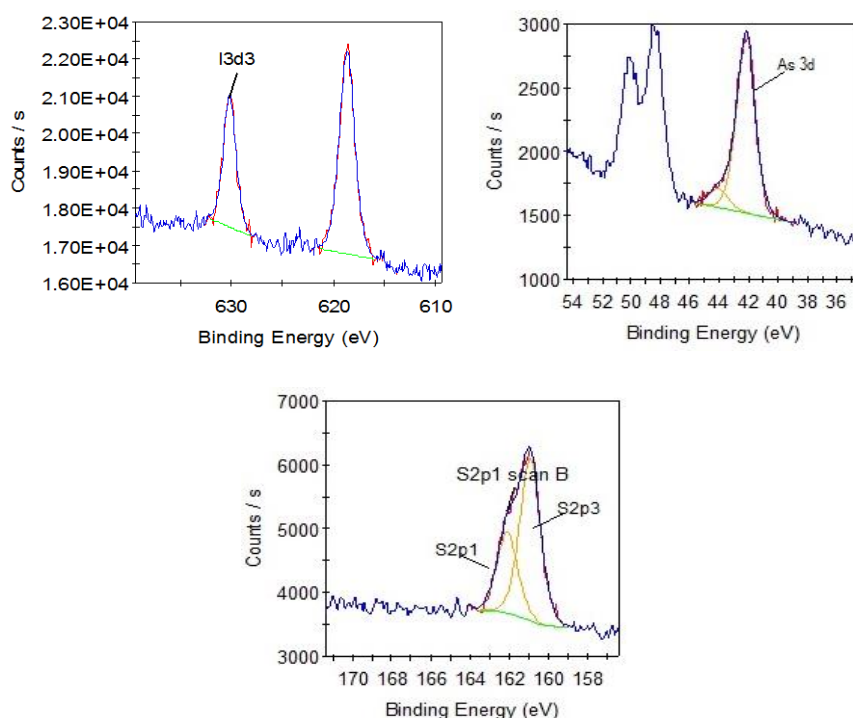experience revealed the appearance of silver in the solution while its cadmium content was decreasing.

Fig. 4. XPS spectra of fresh membrane: (a-left) X-ray photoelectron spectroscopy of I 3d, (b-right) As 3d and (c-down) S 2p.

In addition to XPS analysis, chemical and morphological characterisations of the samples have been carried out. The Scanning Electron Microscopy (SEM) images have been recorded with a HITACHI S-4500I scanning electron microscope operating at 15 kV. Fig. 5 present SEM micrograph of the membrane surface after one week of soaking in a 10^{-1} M cadmium nitrate solution. During the ageing process a deterioration of the membrane surface with appearance of some cracks and secondary phases was observed. Obviously a chemical attack of the membrane occurred in solutions containing Cd^{2+} ions. A CAMECA SX100 electron probe micro-analyser employing five wavelength-dispersive spectrometers was used for chemical analysis of the sample presented in Fig. 5. The experiments were made with a beam intensity of 10 nA and an accelerating voltage of 20 keV. The distribution of the phases can be easily distinguished. Some white spots randomly distribute in the matrix are observed. EPMA has shown that these white spots have a high cadmium concentration and average contents of Cd, S, Ag, I, and As taken from few spots are 13.69, 36.02, 27.91, 6.94 and 15.44 at.% respectively. The remaining area represents sensing alloy with average Cd, S, Ag, I, and As contents being 1.16, 38.66, 38.13, 7.94 and 14.11 at.%, very close to the stoichiometry of the starting materials. This suggests that there is an inhomogeneous distribution of Cd at the surface. It is clearly evident that few phases coexist at the surface after exposure. Among them, one with a composition close to the stoichiometry and a phase with high cadmium concentration. This result is consistent with XPS observations. Further experiments are in progress in order to allow electrochemical impedance spectroscopy (EIS) analysis of low impedance thin films [9, 31]. Thin layers are sputtered from spark plasma sintering - prepared targets [32].
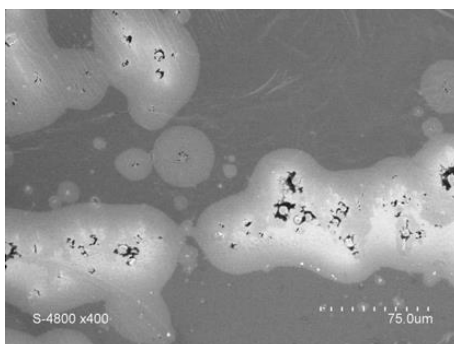
Fig. 5. Micrograph of membrane surface after one week of soaking in a 10^{-1} M cadmium nitrate solution.

The electrochemical characterisation of the Cd-ISE was done by means of ion-selective potentiometry. The sensor has a Nernstian response with slope of 29 mV per decade and the limit of detection is close to 10^{-7} M. Sensitivity measurements were performed stationary and the potential was found to be independent of change in pH in the range of $4 - 8$. The selective electrode showed good long term stability over the period of several weeks. However, a slight drift of about 9mV per day in absolute potential with time was observed. Fast response time within few seconds was observed, also with solution change from more concentrated to more diluted one. This result had shown the reversibility of the signal. High selectivity in the presence of alkali and alkaline-earth metal ions was observed, whereas the sensing device is not suitable for the detection of primary ion in solution containing Cu^{2+} and Fe^{3+}.

It is well known that ion-selective electrodes are studied for waste water monitoring, however only a few of them can really be widely applied for direct measurements in waste effluents because of an insufficient limit of detection [33]. Therefore, the aim of this second part is double: to remove polluting cations from diluted solutions and to concentrate them in order to obtain a solution allowing the detection of heavy metals by Cd-sensor. In this work the removal and concentration efficiency was investigated. The outlet flow rate of the solution was evaluated manually by measuring the time required to fill a graduated cylinder. The concentration of the product was measured by atomic absorption. The process efficiency was expressed in terms of concentration factor and elimination ratio. The concentration factor was calculated using equation (3). The elimination efficiency is the ratio of the number of cations extracted from the feed solution over the initial number of cations to be removed. The initial concentration of $Cd(NO_3)_2$ solutions used in the experiments was 10^{-5} M. Experimental data indicated that the concentration of Cd^{2+} ions in the dilution circuit was reduced with an average removal efficiency of 96%. This result is due to the membrane's characteristic.
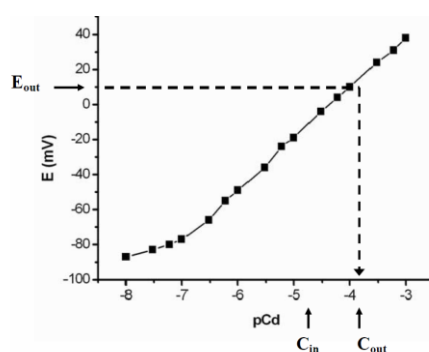

Fig. 6. Studied cadmium-selective electrode responses. E_{out} is the potential of the resulting concentration compartment solution.

IEC is one of the membrane characteristics and separation percentage is a function of IEC. IEC of the membranes are presented in Tab. 1. As seen, the result confirms that the higher the IEC of membranes, the higher desalination and ion removal rates [22]. This implies that membrane techniques such as ED are efficient processes for removing heavy metals from waste water, so as to reclaim this water for further uses. On the other hand, the potential of the resulting concentration compartment solution was measured with the studied Cd-sensor after one hour of pre-concentration process. Fig. 6 indicates the cadmium sensor out-put signal. It is observed that the resulting potential correspond to a 10^{-4}M cadmium concentration (dotted lines in the graph). Both experiments indicated that the pre-concentration module works properly in laboratory scale with a concentration factor equal to 10. At last, investigations were carried out with a model solution, e.g. a mono-cationic solution. Experiment concerned the conductivity measurements of a Na_2SO_4, $(10^{-3}$ M) electrolyte. Fig. 7 presents the evolution of the solutions conductivity with time, after pre-concentration experiment. Fig. 7 shows an increase with time in the conductivity of concentration circuit solution from the electrolyte room temperature conductivity (246 µS.cm^{-1}). A simultaneous decrease is observed in the conductivity of dilution compartment solution. Cell performance can be related to an increase of conductivity and consequently a decrease of solution resistance and also an increase of the diffusion constant through the membranes.
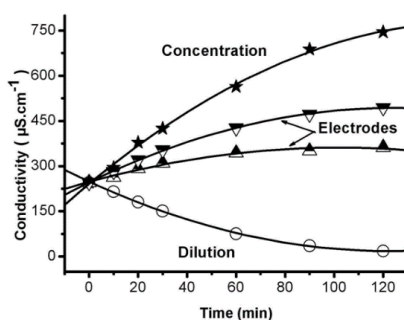

Fig. 7. Evolution of conductivity with time of a 10^{-3}M Na_2SO_4 solution circulating in the pre-concentration module

4. Conclusions

Cadmium-selective electrode based on CdS-AgI-Ag_2S-As_2S_3 has been developed. With respect to electrochemical results, sensitive membrane show satisfying behaviour against Cd^{2+} ion. XPS measurements were carried out to get some knowledge on the phenomena occurring at the solution/membrane interface and giving rise to the sensing properties of the membrane. It was shown that a modification of the surface with an accumulation of cadmium and a decrease in the silver content occurred when the membrane soaked in Cd^{2+} (II) solutions. This alteration of the surface is needed to establish the sensing properties of the membrane. On Laboratory scale, studied electrode can be used with a pre-concentration system to adapt the low polluted water to its working domain.

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