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CHARACTERIZATION OF CADMIUM (II) SELECTIVE ELECTRODE BASED ON CHALCOGENIDE GLASS

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This work relates characterization of sensor based on chalcogenide glassy CdS-AgI-Ag_2S-As_2S_3. The composition and analytical characteristics have been determined. Ageing study is described according to the soaking time in a cadmium (II) nitrate solution. The chalcogenide membrane/solution interface has been investigated using X-ray photoelectron spectroscopy (XPS) in order to understand the sensing properties. The evolution of the electrode behaviour depending on time was observed by scanning electron microscopy (SEM) and potentiometrics measurements.

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1. Introduction

The presence of heavy metals in the environment has been a matter of major concern due to their toxicity to human. To date quality control of superficial and grounds waters results from reliable but expensive analytical measurements carried out in laboratory. Therefore reliable sensitive and low-cost on-line monitoring systems need still to be developed [1]. A rinsing interest in the possible use of electrochemical sensors based upon selective vitreous membranes for miniaturised devices has lead to their extensive study in recent years. Chalcogenide glasses with their flexible structure, enormous variations of properties and almost unlimited ability for doping and alloying have been proven to be very promising materials for chemical sensors [2, 3]. In many case chalcogenide glasses exhibit chemical durability better selectivity and reproducibility [4-5].

Chalcogenide-based sensitive materials are widely used in the mode of bulk sensors for the analysis cadmium species. For instance, Vlasov et al. [6] used with success CdS-Ag_2S-As_2S_3 for Cd^{2+} ion detection. Later on, Tohge et al. [7] showed that CdS-GeTeSe system was suitable for the determination of cadmium (II) ion in aqueous solution. In addition, solid-state electrodes based on CdI_2-Ag_2S-As_2S_3 [8] and CdS-AgI-Sb_2S_3 [9] are well established. At last, Cd-Ag-As-I-S system were used as membrane of cadmium (II) selective electrode [10]. It is well known that chemical ISEs are well investigated under laboratory conditions but only a few of them can really be widely applied for in situ monitoring.

The present paper reports some investigation of the chalcogenide membrane life time, with the composition 4CdS-24AgI-47Ag_2S-25As_2S_3 (mol.%), tested in water site conditions for the cadmium (II) detection. X-ray photoelectron spectroscopy technique, which was already tested and proved to be successful for such studies [11], 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.

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2. Experimental methods

$4CdS\text{-}24AgI\text{-}47Ag_2S\text{-}25As_2S_3$ (mol.%) electrode 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. Structural characteristics of the materials were checked by X-ray diffraction and scanning electron microscopy. To prepare electrodes, small discs were cut from the ingot. The two faces were polished with a very fine diamond paste. A silver layer was sputtered on one side and a wire was attached with a silver micro adhesive. Then the inner side was coated with and epoxy resin to produce a Cd-ISE.

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 ($Au4f_{7/2}$ = 83.9 eV, with reference to the Fermi level) the $Au4f_{7/2}$ 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 C1s 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.

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. ISE material was dipped in a stirred $Cd(NO_3)_2$ aqueous solution containing cadmium ion at various concentration. KNO_3 (10^{-1}M) was used as the supporting electrolyte. To avoid $Cd(OH)_2$ formation, the pH of the test solution was maintained at the same value (pH 6) for all measurement. The evolution of the sensor behaviour with time was investigated by potentiometric measurements.

3. Results and discussion

Bulk material was found to be amorphous. It is shown that the conductivity has a strong ionic character. Glass transition temperature is close to 160°C. All these data are reported elsewhere. The chemical composition of the chalcogenide material was checked by energy-dispersive X-ray spectroscopy (EDX). Due to a contamination, C is detected. EDX data (Table 1) show that sensing material contained 1.16 at% in cadmium, while the relative amount of all the elements was closed to the theoretical composition of the glassy matrix. On the whole the data obtained indicated that the membrane was homogeneous, had a surface of good quality and was poorly contaminated.

Table 1. Chemical composition of the fresh built membrane measured by EDX.

	at. % of elements	
	Theoretical composition	Experimental data
As	15.5	14.11
Cd	1.3	1.16
S	39.1	38.66
I	7.5	7.94
Ag	36.6	38.13
Total	100	100

The sensor has a Nernstian response with slope of 29 mV per decade and the limit of detection is close to 10^{-7}M. The potential of the chalcogenide glass-based sensor does not depend on the pH in a large pH range. The selective electrode showed good long term stability. The electrode potential is insensitive to variation in the concentration of solutions containing several species. Since the sensing device is not suitable for the detection of Cd^{2+} ion in solution containing Cu^{2+} it is important to know the additional contributions to the total measured activity that result from the presence of copper in the sample solution. The total measured potential is given by Nernst equation which takes into account the selectivity coefficients (1).

$$E = E_0 + \frac{RT}{nF}\log\left[\left[Cd^{2+}\right] + \sum_{j \neq Cd^{2+}} K_{Cd^{2+},j} \times a_j^{\frac{z_{Cd^{2+}}}{z_j}}\right] \qquad (1)$$

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

To determine the selectivity coefficients $K_{Cd^{2+},M^{n+}}$ (for an interfering ion M^{n+}), we used the fixed interference method [9, 12]. The out-put signal was recorded with solutions of constant level of interference (10^{-2} M) and a varying concentration of the Cd^{2+} ion. The sensitivity of the electrode was investigated in the presence Ca^{2+} and Cu^{2+}. Calibrations without foreign species were performed in order to check the Nernstian membrane behaviour versus cadmium (II) ion. Figure 1 shows typical copper calibration curves in the presence of considered ions. It should be noted that the selectivity limit occurs when a flat out-put signal versus Cd^{2+} concentration is observed.

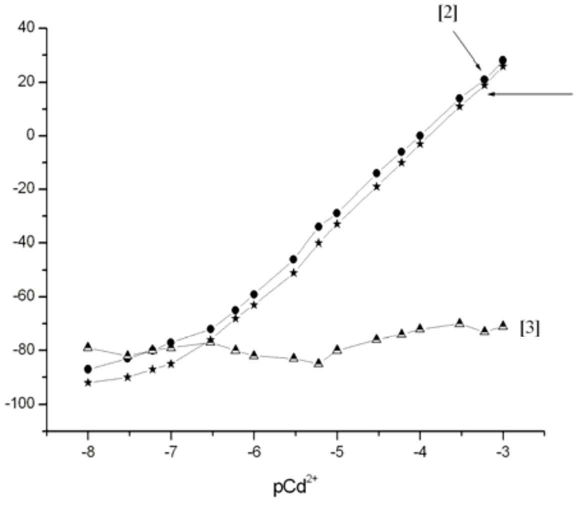


Fig. 1. Selectivity of the Cd-ISE in [1] no interfering ion; [2] 10^{-2} M Ca^{2+} solution; [3] 10^{-2} M Cu^{2+} solution.

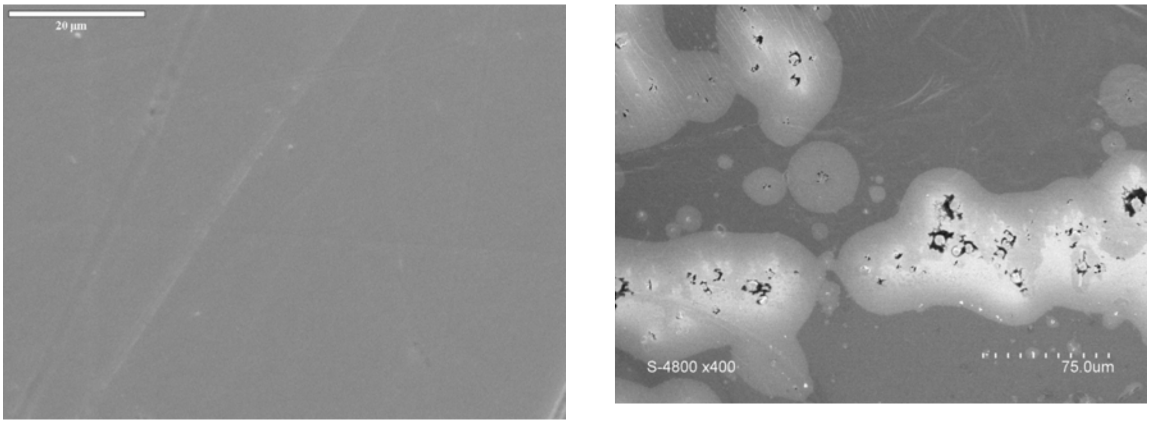
The value of $K_{Cd^{2+},Ca^{2+}}$ (10^{-6}) seems interesting, since the lower the coefficient, the smaller is the influence of the interfering ion. This result is in agreement with the good selectivity of chalcogenide based sensor in presence of alkali and alkaline-earth ions. It can be seen from the curves that the sensor give a worse response to cadmium (II) species in presence of Cu^{2+}. Therefore, the calculated selectivity coefficient for copper ion is somewhat larger ($<10^{-2}$).

Chalcogenide sensors are suitable for the determination of cationic species in solution at concentration lying in the ppm range. Anion-selective chalcogenide electrodes are less known.

Three main methods are commonly used for the determination of sulphide in solution (i.e. potentiometry, calorimetry and the iodometric method). The sensitivity of CdS-AgI-Ag_2S-As_2S_3 device to sulphide species in solution had been investigated. Calibration were performed by addition of a know volume of test solutions to supporting electrolyte (10^{-1} M potassium nitrate). Tests solutions were prepared by successive 10-fold dilution of 1M Na_2S, $9H_2O$ solution by the electrolyte. Experimental data showed a detection limit close to 6.10^{-7} M and a Nernstian slope of 58 mv per decade which correspond to the exchange of one electron.

The main goal was to understand the ageing process of the studied electrode. Then, additional experiments were carried out. In particular, surface modification of the membrane in function of the ageing time was observed by Scanning Electron Microscopy (SEM) using a HITACHI S-4500 I. Figure 2 presents SEM micrographs of the membrane surface before and after one week of soaking in a 10^{-1} M cadmium nitrate solution. It is shown that the fresh membrane surface does not present any defects and secondary phases. The microstructure is different from the structure reported for $Cu_{40}(Ge_{28}Sb_{12}Se_{60})$ thin film and $Cu_{10}(As_2S_3)_{90}$ bulk membrane where a columnar structure [13, 14] and a multiphase system exist [15]. 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 10^{-1}M $Cd(NO_3)_2$.

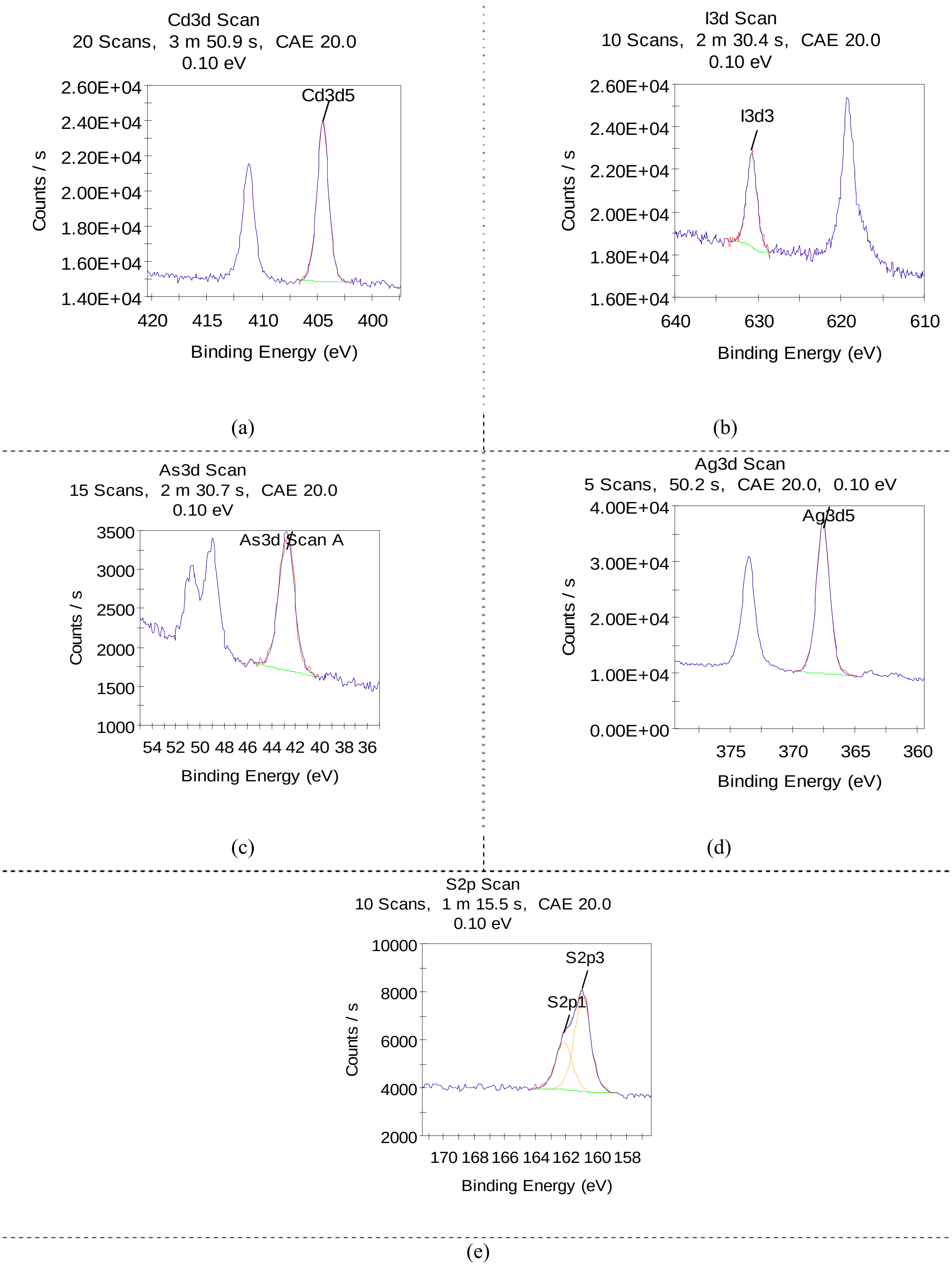
Due to the high resistance of the bulk material, the studied sensor is not suitable for electrochemical impedance spectroscopy (EIS) analysis. However, from an electrical point of view the low impedance of a thin film compared to that of the corresponding bulk material allows the analysis of thin layer. Therefore, films sputtered from target consolidated by spark plasma sintering technique [16] should be suitable for EIS analysis.



(a) (b)

Fig. 2. Untreated membrane surface (a) and micrographs of the membrane surface after one week of soaking in a 10^{-1} M cadmium nitrate solution (b).

A XPS analysis of the surface was undertaken in order to get information on the environment of the different elements of the sensing membrane. 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. The binding energies of the main peaks are reported in figure 3. For the analyzed area, surface or in-depth (UHV fracture), a single peak $Cd3d_{5/2}$ is observed, characterized by a binding energy (404.55eV) similar to the one observed in CdS. The $I3d_{3/2}$ peak reported at a binding energy of 630.16 eV characteristics of the AgI element. The $As3d_{5/2}$ (42.8 eV) core peak has the same characteristics as in the reference compound As_2S_3. It is shown that sulphur and silver are S(-II) and Ag(+I) type respectively. For instance, figure 3 show respectively $Ag3d_{5/2}$ peak at a binding energy of 367.5 eV and S $2p_{3/2}$ and $2p_{1/2}$ peaks at 160.94 eV and 162.10 eV. For each compound, an oxygen atomic percentage has been found at the surface, it decreases after fracture. The presence of trace carbon and oxygen in the XPS survey spectrum are attributed to surface hydrocarbons adsorbed upon storage in ambient condition before XPS analysis [17]. Again, we confirmed the absence of any other by-product such as Ag_2O from the Ag 3d core level spectrum, even on the top surface of the material.



(a)

(b)

(c)

(d)

(e)

Fig. 3. X-ray photoelectron core-level spectra of the different element composed the fresh sensing device. Cd3d$_{5/2}$ (a), I3d$_{3/2}$ (b), As3d$_{5/2}$ (c), Ag3d$_{5/2}$ (d) and S2p (e).

On the other hand, XPS was used to investigate the modification of the membrane surface after soaking in solutions of $Cd(NO_3)_2$ (1.10^{-1} M) for different periods of time . 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, until the latter reaches two hours. 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 over this ageing time. XPS data are in agreement with $AgBr-Ag_2S-As_2S_3$ study [18]. It is shown that soaking the original membrane in $Hg(NO_3)_2$ solution results in appearance of mercury species at the surface and silver release from the sensor membrane to the solution.

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. 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 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.

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. This result is consistent with XPS observations.

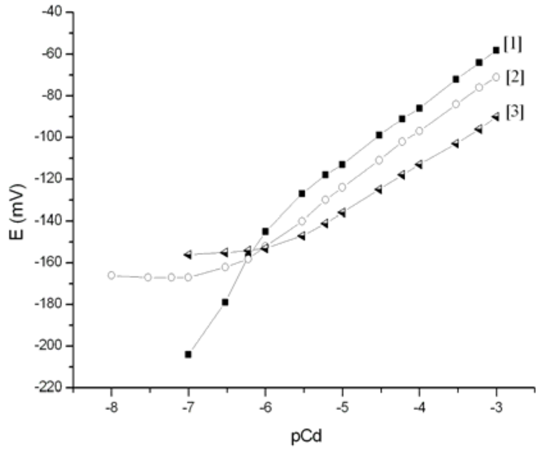


Fig. 4. Typical calibration curves versus Cd^{2+} ion after different period of ageing in a 10^{-4} M $Cd(NO_3)_2$ solution, [1] without ageing, [2] one night, [3] one week.

The evolution of the sensor response with time has been investigated. Potentiometric measurements of the ISE have been carried out after soaking in cadmium (II) nitrate solution. Figure 4 show the calibrations curves of the chalcogenide sensor. The result of the first calibration of the sensor differed from the subsequent ones. The fresh built electrode exhibits super Nernstian slope at low cadmium (II) concentration. The electrode was primary soaked over-night in a 10^{-4} M Cd^{2+} solution in order to activate it. Then, stable and Nernstian out-put signal was measured. The present measurements show clearly that the change in the chemical composition of the surface is necessary to reveal the sensing property of the membrane since a exposure to a $Cd(NO_3)_2$ solution is needed before the sensor displays a Nernstian response against Cd^{2+} ions. On the whole, these results point out for the presence of a ‘‘modified layer’’ needed for the membrane to get its sensing property. It is in agreement with some previous investigations on chalcogenide membranes, where the presence of such a layer was introduced to be the basis of the sensing mechanism [19, 20]. It is shown that the out-put signal slightly get damaged with time. After one week of ageing, sensitivity and detection limit decreased respectively to 26 mV per decade and 10^{-6}M. The ISE that has interacted with a cadmium nitrate solution during five weeks was found to be insensitive to Cd^{2+} ions.

4. Conclusions

The response of the CdS-AgI-Ag_2S-As_2S_3 device versus Cd^{2+} ion has been investigated. Experiments were carried out in order to checked structural changes of the sensor soaked in an ageing solution. XPS, SEM and potentiometry techniques were used to understand sensing mechanism of the studied sensor. It was shown that a modified layer formation is needed to establish the sensing properties of the membrane.

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