



International Journal of Chemistry and Pharmaceutical Sciences

IJCPS, 2013: Vol.1(8): 492-496

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Preparation and Characterization of Home-Made Silver Sulphide Based Chloride Selective Electrode

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Available Online 27 December 2013

Abstract

Mixed silver sulphide-silver chloride solid state ion selective electrode (ISE) with four different mole ratios of $\text{Ag}_2\text{S}:\text{AgCl}$: 9:1, 2:1, 1:1 and 1:9 have been fabricated and characterized. The membrane material was obtained by co-precipitation of silver sulphide and silver chloride from aqueous solution. The material was characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM). X-ray diffraction study showed the presence of Ag_2S and AgCl in separate crystalline phase. The electrode surface of these electrodes is found to become smoother and lustrous with increasing percentage of silver sulphide in the mixture. The ISE's 2:1 and 1:1 in presence of Cl^- ions showed Nernstian response with slopes of about 56 mV per decade change in chloride ion concentration in linear range of 1×10^{-1} M to 1×10^{-5} M while ISE 9:1 and 1:9 showed Nernstian behavior only upto 1×10^{-4} M range. The response of these ISE's were found to be very fast.

Key words: Chloride selective electrode, Nernstian Response

Introduction

A number of works on cationic sensors have been reported in literatures [1] but less attention has been given towards the development of anionic sensors though there is a need for analysis of varieties of anions in different environmental, biomedical, industrial as well as chemical samples[2-3]. Anion sensors are simple, low cost, convenient, portable and provide quick response towards selected ions. Silver sulphide based ion selective electrodes (ISE) are among well known ISE's for being well behaved electrodes in terms of their sensitivity and selectivity in analysis of anionic species and have been in operation for long [4-5]. In the previous study, preparation and characterization of silver sulphide based iodide selective electrode was reported [6]. Present study is concerned mainly on preparation and characterization of silver sulfide based chloride selective electrode. Silver sulphide based chloride selective electrodes ($\text{Ag}_2\text{S}-\text{AgCl}$ electrodes) have been fabricated in the laboratory by varying the composition. The phase composition, surface morphology of $\text{Ag}_2\text{S}-\text{AgCl}$ electrodes are studied. The electrodes are characterized in terms of their sensitivity and selectivity.

Experimental

Preparation of membrane material and electrode

The membrane materials were prepared by co-precipitation of Ag_2S and AgCl in different mole ratios as detailed in **Table 1**. Desired mole ratio of $\text{Ag}_2\text{S}:\text{AgCl}$ membrane was obtained by taking appropriate moles of aqueous solution of Na_2S and KCl in which slight excess of aqueous solution of AgNO_3 was added. The Reaction is given in equation¹

$$\text{KCl} + \text{Na}_2\text{S} + 3 \text{AgNO}_3 \rightarrow \text{Ag}_2\text{S} + \text{AgCl} + 2\text{NaNO}_3 + \text{KNO}_3 \dots \dots \dots (1)$$

The co-precipitate of $\text{Ag}_2\text{S}-\text{AgCl}$ thus obtained, was filtered and washed 5 times with distilled water and then with acetone. Then material was dried at 110°C for 6 hours and pulverized in an agate mortar. The powder was again heated to about 60°C for 15 minutes and then the membrane was prepared by pressing its powder (about 1.5 gm) under a pressure of 10 tones cm^{-2} pressures for 15 minutes in a KBr pellet making die. The pellet after heating for one hour at 200°C , was mounted in a polypropylene tube with the help of Araldite (Ciba-Geigy) and the back contact was made with silver epoxy conducting paint with silver disk in which a copper wire was soldered. The electrode was abraded successively with 1000 to 2000 grit sized silicon carbide paper and finally sonicated in distilled water carefully.

Table 1: Composition of home made electrode

Mole ratio of Ag ₂ S: AgCl	Mole % of AgNO ₃	Mole % of AgCl
9:1	90	10
2:1	67	33
1:1	50	50
1:9	10	90

Reagents

The analytical grade reagents (AgNO₃, KCl, Na₂S and KNO₃) and distilled water were used for preparing all aqueous solution. All the solutions were freshly prepared by accurate dilution of their 0.1 M stock solution with distilled water. Direct potentiometry was performed in a solution prepared by successive addition of chloride ion solution in 0.1 M KNO₃, used as the background electrolyte.

Instrumentation

Scanning electron microscopy (SEM) characterization of the surface was performed with a KEYENCE REAL 3D System, VE-series, Japan at 5 kV accelerating voltage. XRD analysis was performed to investigate the crystal phase of the electrode materials using an X'Pert MPD-OEC, Phillips X-ray diffractometer. The measurements were performed using Cu K α radiation at 40 kV and 40 mA. The cell assembly of the following type was used: Ag/AgCl, KCl (sat) // test solution /Cl-ISE ($\mu=0.1M$). All EMF measurements were made relative to a Ag/AgCl (sat) reference electrode. The performance of the electrode was investigated by measuring the emf of chloride solutions in the concentration range of 10⁻¹ to 10⁻⁵ M. Each solution was stirred and the potential reading was noted within 30 seconds, and then plotted as a function of -log [Cl⁻].

Results and Discussion

Characterization of the membrane materials

The smooth surface morphology of an ISE is essential for better response of electrode as solution trapped inside the rough surfaces may give erratic results. In this study, the surface morphology of Ag₂S-AgCl pellet was analyzed under scanning electron microscopy (SEM). SEM pictures of 1:1, 2:1, 9:1, and 1:9 Ag₂S-AgCl pellets were taken at 5 kV of accelerating voltage and are shown in **Fig. 1(a-d)**. The surface texture is found to change with changing mole percentage of Ag₂S in the membrane. In the ISE 1:1, 2:1, 9:1 the surface was found to be smooth and fine even if the percentage of Ag₂S was increased from 50-90 percent. The sample 1:9 having high percentage of AgCl however showed rough surface. So, it is obvious that high amount of AgCl in the membrane is not good for smoothness of the surface as it gives a rough surface.

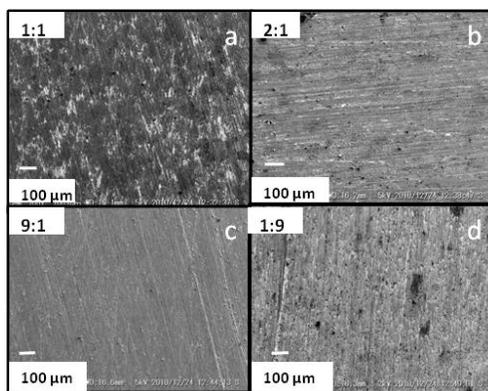


Figure 1a-d: SEM picture of Ag₂S/AgCl electrodes

XRD pattern of laboratory prepared Cl-ISE having 1:1 composition of Ag₂S:AgCl is shown in **Fig. 2**. The sharp diffraction peaks appeared at 2 θ of 27.85°, 32.25°, and 46.25°, were assigned for AgCl while those appearing at 31.46°, 37.6° were assigned for Ag₂S according to JCPDS data. In the figure, peaks for AgCl are represented by circles while peaks for Ag₂S are represented by triangle. The sharp intense peak of AgCl and Ag₂S showed that the

materials exist in separate phase state of Ag_2S and AgCl . No additional peak corresponding to the new phase could be seen in XRD-pattern.

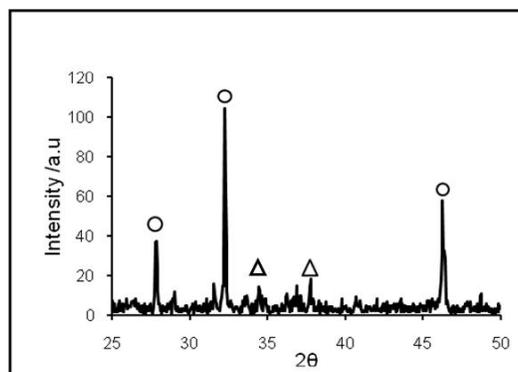


Figure 2: XRD pattern of Ag_2S - AgCl pellet. The sharp peaks of AgCl and Ag_2S are shown by circle and triangle symbols respectively

Potentiometric response of the electrodes

The potentiometric response of the home made ISEs were evaluated by measuring the known concentration of Cl^- ion in the concentration range of 10^{-1} M to 10^{-5} M. Appropriate spikes of chloride were introduced into the cell containing 0.1M KNO_3 as background electrolyte and corresponding potentials were recorded.

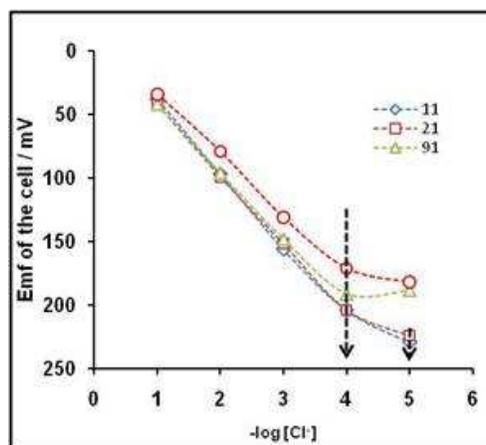


Figure 3: Calibration curves of 1:1, 2:1, 9:1, 1:9 ion selective electrodes

Figure 3 shows the potentiometric responses of Cl^- -ISE 9:1, 2:1, 1:1 and 1:9 to chloride ions. All measurements were carried out at constant stirring condition at room temperature. In the plot, the points are the experimental values and the line is the line of best fit computed from the regression analysis. All the ISEs gave a linear response with respect to $-\log[\text{Cl}^-]$ in the concentration range of 1×10^{-1} M to 1×10^{-4} M with slopes ranging from 50 to 56 mV. The ISE-1:1 and 2:1 showed a good response upto 10^{-5} M chloride solution, however, the performance of Cl^- -ISE 1:1 electrode seems to be more desirable since this electrode gives marginally larger useful range of determination of chloride ion. In the lower concentration range the curves however start to deviate from linearity for all electrodes. This is perhaps due to the release of Cl^- ions by the dissolution of membrane, since the solubility value of AgCl is ($K_{sp}=1.5 \times 10^{-10}$) at 25°C , the equilibrium concentration of Cl^- ion due to the dissolution of AgCl membrane can attain 1.22×10^{-5} M/L. It is obvious that the quantitative detection of chloride ions below this concentration could not be expected. The slopes and linear region observed for all the electrodes are tabulated in **Table 2**.

Table 2: Response characteristic of various electrodes.

Mole ratio of $\text{Ag}_2\text{S} : \text{AgCl}$	slope (mV)	Linear range
9:1	50	1×10^{-1} M - 1×10^{-4} M
2:1	54	1×10^{-1} M - 1×10^{-5} M
1:1	56	1×10^{-1} M - 1×10^{-5} M
1:9	46	1×10^{-1} M - 1×10^{-4} M

The response time of the electrode

The response time of the home made ISE was measured, in a 10 fold change in the Cl^- concentration, till a constant potential value was obtained. The time dependence curve of Cl^- -ISE 1:1 is shown in **Fig. 4** which shows that the response of the electrode with change in the concentration of the solution was rapid, and that the system attained equilibrium potential within less than 1 minute and the response time did not change on repetition of the experiment in the reverse order of this concentration. All measurements were made at constant temperature 25°C with constant stirring of the solution. It clearly showed that the response of the electrode to chloride ion in the concentration range of $1 \times 10^{-1} \text{ M}$ to $1 \times 10^{-5} \text{ M}$ is quite fast.

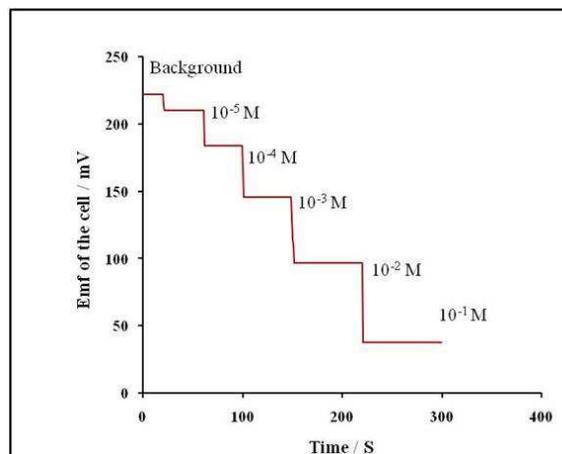
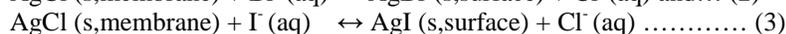


Figure 4: The dependence of response time of the electrode on the change of concentration

Selectivity Coefficient

Possible interferences due to iodide and bromide ions were studied by fixed interference method [7]. In this method, the concentration of chloride ion was varied from $1 \times 10^{-1} \text{ M}$ to $1 \times 10^{-5} \text{ M}$ while the concentration of the interfering ions was kept constant at 10^{-3} M . The selectivity coefficient ($K^{pot}_{A,B}$) values were found to be i.e. 48.9 and 10 for I^- and Br^- respectively. The selectivity coefficient values of 48.9 and 10 indicate that the response of Cl^- -ISE is adversely affected by the presence of iodide and bromide ions. As reported in previous study [6], I^- -ISE was not affected by chloride ions. This means, iodide ion is possible interference for Cl^- -ISE. The low solubility product values of AgI ($K_{sp}=0.9 \times 10^{-16}$) and AgBr ($K_{sp}=7.7 \times 10^{-13}$) than that of AgCl ($K_{sp}=1.5 \times 10^{-10}$), also is the strong evidence of possibility of interference due to iodide and bromide ions. Moreover, the similar crystal structures of silver bromide and silver chloride may be another possible reason for bromide interference. The interfering reactions can be represented as,



In these exchange reactions, the equilibrium will lie over to the right [8]. Thus, bromide and iodide ions interfere significantly with the determination of chloride.

Conclusion

Mixed silver sulphide-silver chloride solid state electrode with four different mole ratios of $\text{Ag}_2\text{S}:\text{AgCl}$, 9:1, 2:1, 1:1, 1:9 have been fabricated and characterized. Scanning Electron Microscopic studies indicated that the electrode surface has long term stability when the electrode surface is smooth. The smooth electrode surface is obtained when there is more than 50% of silver sulphide present in the membrane pellet. The electrode having 1:1 mole composition is found to be the best. The x-ray diffraction studies of $\text{Ag}_2\text{S}:\text{AgCl}$ pressed pellet showed the presence of Ag_2S and AgCl crystalline state with separate phases. All the electrodes are found to be well behaved having reasonable detection range. The result of direct potentiometric measurement is sufficiently precise and reproducible. The equilibrium potential is attained within 1 minute; the drift of the electrode potential is quite small. Estimation of chloride ion with $\text{Ag}_2\text{S}:\text{AgCl}$ membrane electrode is found to be interfered by presence of bromide and iodide ions which are quite reasonable.

Acknowledgements

A. Rajbhandari (Nyachhyon) thanks Tribhuvan University for granting study leave and to the Nepal Academy of Science and Technology (NAST) for providing PhD scholarship to carry out this work. The authors gratefully acknowledge Tsuru-Nishikata laboratory, Tokyo Institute of Technology, Tokyo, for providing facilities to record XRD, SEM of the material.

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