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Title : "AN IMPROVED PROCESS FOR MAKING SILVER SENSING ION-SELECTIVE COATED FILM ELECTRODE"

Applicant : COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, xRafiBx Rafi Marg, New Delhi-110001, India an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

Inventor(s) : G.P. RAO, S.JAYA& T.P.RAO.

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

166148

This is an invention by GOLLAKOTA PRABHAKARA RAO, SAMBAMOORTHY JAYA and TALASILA PRASADA RAO, all of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens and relates to an improved method of making silver ion-selective coated film electrode (CFE).

Potentiometric methods of analysis offer a simple and direct solution to the analysis of a variety of inorganic and organic species. In recent years ion selective electrodes (ISE) have emerged as simple, rapid and reliable potentiometric sensors particularly useful in field studies and on-line analysis.

A number of ion selective electrodes have been reported in literature for the determinatioon of silver. These can be broadly classified as (i) membrane based and (ii) metal based electrodes. Of these, the latter type of electrodes offer distinct advantages over the former whose 'method of making' besides being quite involved and time-consuming imposes stringent demands in the preparation of membranes for their successful and reliable performance. Important among the advantages are:

i) the simplicity of making the metal based electrodes;

ii) their easy regeneration after repeated use;

iii)lower cost of their production; and

iv) their low impedance characteristics that confer them with the desirable compatability with ordinary millivolt meters for the recording of their response.

A few reports are available in literature on metal based silver sulphide electrodes. The usual procedures involve the exposure of the silver wire to a deaerated solution of sulphide anti-oxidant buffer (SAOB-II--) supplied by them for as long a period

as 2 days. A very recent report that appeared in 1984 in open literature Anal. Chem., 56 (1984) 297 brings to light the inherent difficulties in getting a reproducible silver sulphide coating with the above said procedure. It advocates the use of impure silver wire and asserts that deaeration of the SAOB-II plays a critical role. According to this report silver sulphide cannot be coated on to pure silver wire or without deaeration of SAOB-II solution, even after 6 days exposure of the wire to SAOB-II. The procedure finally recommended by these authors involves the use of silver wire containing 6% copper and its exposure to deaerated sulphide solution for 2 days. Another procedure described for formation of silver sulphide coating involves the exposition of silver to sulphur or hydrogen sulphide vapours at 40-60^{0}C for about 1/2 hr.

With these diverse reports existing, increased attention is being currently paid on the efficient method of making metal based electrodes.

The main object of the present invention is to develop a method for making a silver ion-selective CFE which can be used for the determination of silver ions present at trace levels in solution, based on a simple treatment procedure that is free from the drawbacks listed above.

Silver wire in the form of a protruded wire from a teflon holder, or a silver disc embedded in teflon is polished with emery papers of increasing fineness (1/o to 4/o). It is then kept immersed in a stirred solution containing suitable concentrations of sodium sulphide and sodium hydroxide for about 15 to 20 minutes

The film of silver sulphide formed over silver by the above treatment is violet in colour when formed as thin film which slowly turns to bluish violet or blue on further reaction. Once the film fully covers the surface (confirmed by the absence of any bright spots of silver metal exposed). CFE is ready for the measurement of silver ion activities. The potential of the silver ion-selective CFE obtained above is measured with respect of NCE as reference electrode using either a low or high impedance multimeter that could read precisely upto $\pm$ 1 mV. Studies on the response characteristics of the electrode shows that the electrodes exhibit a Nernstian response over wide ranging pHs (pH 2 to 9) both in aqueous and aqueous mixtures of miscible solvents (eg. alcohol) for concentrations of silver ions doen to 10-6M in the analyte solution

The following are the main advantages of the invention:

1. This invention for the first time offers a simple, rapid and reliable chemical deposition procedure for obtaining silver sulphide coating over silver metal substrate.

2. The chemical deposition procedure described in this invention does not involve either deaeration or heating. Further, silver sulphide coating can be obtained in reasonable and practical times and could serve as reliable sensor for silver.

Dated this 24th day of Month 1986

N R Subbaram

(N.R. SUBBARAM)
JOINT ADVISER (PATENTS)
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

166143

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

Title : "AN IMPROVED PROCESS FOR MAKING SILVER SENSING ION-SELECTIVE COATED FILM ELECTRODE"

Applicant : COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-110001, India an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

Inventor(s) : G.P. RAO, S. JAYA & T.P. RAO.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Gollakota Prabhakara Rao, Sambamoorthy Jaya and Talasila Prasada Rao, all of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens and relates to an improved process for making silver sensing ion-selective Coated film electrode.

Potentiometric methods of analysis offer a simple and direct solution to the analysis of a variety of inorganic and organic species. In recent years ion selective electrodes (ISE) have emerged as simple, rapid and reliable potentiometric sensors particularly useful in field studies and on-line analysis. Further the silver ion-sensitive electrode finds widespread use in analytical control laboratories.

A number of ISE have been reported in literature for the determination of silver. These can be broadly classified as (i) membrane based and (ii) metal based electrodes. Of these, the latter type of electrodes offer distinct advantages over the former whose 'method of making' besides being quite involved and time-consuming imposes stringent demands in the preparation of membranes for their successful and reliable performance. Important among the advantages of metal base over membrane based electrodes are:

i) the simplicity of making the metal based electrodes

ii) their easy regeneration after repeated use

iii) Lower cost of their production, and

iv) Low impedance characteristics that confer them with the desirable compatability with ordinary millivolt meters for the recording of their response.

A few reports are available in literature on metal based silver sulphide electrodes. Metal based electrodes supplied by Fischer Sci. Co., USA recommends the exposure of silver wire to a deaerated solution of sulphide by them for a period as long as 2 days. A very recent report that appeared in Anal. Chem. 56 (1984) 297 brings to light the inherent difficulties in getting a reproducible silver sulphide coating with the above said procedure. According to this report, silver sulphide cannot be coated on to pure silver wire, (either with or without deaeration of SAOB II solution) even after 6 days of exposure of silver wire to SAOB II. Hence, these authors recommend by the the use of silver wire containing 6% copper and its exposure to deaerated sulphide solution for 2 days. Another procedure described for formation of silver sulphide coating involves the exposition of silver to sulphur or hydrogen sulphide vapours at 40-60^{0}C for about 1/2 hr.

The metal base ISE approaches as described above involve time consuming processes similar to membrane based electrodes. The third procedure described above, on the other hand requires vapour deposition at 40-60^o and does not result in reproducible silver sulphide coating. With these diverse reports existing, increased attention is being currently paid on the efficient method of making metal based electrodes.

The main object of the present invention is to develop an improved method for making a silver sensing ion-selective electrode which can be used for the determination of silver ions

present at trace levels in solution, based on a simple treatment procedure that is free from the drawbacks listed in existing method as indicated above.

The main finding underlying the invention is the utilisation of suitable composition of chemical reactants which facilitate the obtainment of silver sulphide coated film in a few minutes instead of several days as in the case of existing methods. Moreover, the process prepared herein does not involve either deaeration or raising the temperature of the treatment solution.

The invention offers a simple, rapid and reliable procedure for obtaining a coating of silver sulphide onto silver surface.

Accordingly, the present invention provides an improved process for making silver sensing ion- selective coated film electrode which comprises embedding a silver wire or disc in a teflon rod, dipping the exposed portion of the silver wire or disc in a solution containing sodium sulphide and sodium hydroxide and stirring the solution to obtain a uniform coating of silver sulphide on the exposed portion of silver wire or disc.

According to an embodiment of the invention, the solution contains 10^{-3} to 10^{-1} M of sodium sulphide and 0.1 to 0.3M NaOH. According to a feature of the invention the silver sulphide deposited silver wire or disc is connected to the external circuit through a flexible shelded cable wire.

The following examples illustrate details pertaining to the making and response characteristics of silver ion selective

coated film electrodes. These examples should not be construed to limit the scope of the invention.

Example I

An 18-gauge silver wire force fitted in a teflon holder with about 1 cm of its length exposed is emery polished 1/0 to 4/0) and dipped into a solution (100 ml) containing sodium sulphide (0.01M) and sodium hydroxide (0.02M). The solution was stirred for 20 minutes. The electrode was then removed, washed and verified for completeness the coverage of silver surface by the silver sulphide film. The following table gives the response behaviour of the wire based CFE for the determination of silver ions where a (0.1 M) sodium nitrate solution serves to adjust the ionic-strength constant.

TABLE -I

Concentration of $[Ag^+]$, M taken in 0.1 M sodium nitrate		Potential vs NCE, mV
10^{-7}	..	176
10^{-6}	..	202
10^{-5}	..	260
10^{-4}	..	319
10^{-3}	..	379
10^{-2}	..	438
10^{-1}	..	498

Example - II

A 7 mm dia. silver rod of about 0.5 cm length was pressure fitted in a teflon holder so that its circular cross section is exposed as a disc. The surface of the disc was emery-polished, degreased with acetone and kept immersed in a stirred sodium hydroxide solution (0.2 M) containing 0.01 M of sodium sulphide for 20 minutes. On the completeness of the coverage of the silver sulphide film attained by the above treatment the electrode was removed, washed well with conductivity water and the response characteristics of this disc CFE are given in the following table.

TABLE -II

Concentration of $[Ag^+]$, M taken in 0.1 M sodium nitrate		Potential vs NCE, mV
10^{-7}	..	167
10^{-6}	..	202
10^{-5}	..	260
10^{-4}	..	319
10^{-3}	..	378
10^{-2}	..	438
10^{-1}	..	497

The main advantages of the invention achieved are:

i) Development of a simple, rapid and reliable chemical deposition procedure for obtaining silver sulphide coating over silver metal substrate.

ii) Chemical deposition procedure described does not involve either deaeration or heating and

iii) Silver sulphide coating is obtained within reasonable and practical times.

We claim: 166148

1. An improved process for making silver sensing ion-selective coated film electrode which comprises embedding a silver wire or disc in a teflon rod, dipping the exposed portion of the silver wire or disc in a solution containing sodium sulphide and sodium hydroxide and stirring the solution to obtain a uniform coating of silver sulphide on the exposed portion of the silver wire or disc.

2. An improved process as claimed in claim 1 wherein the silver wire or disc is kept immersed in 10^{-3} to 10^{-1}M of sodium sulphide solution in presence of 0.1 to 0.3 M NaOH.

3. An improved process for making silver sensing ion selective coated film electrode substantially as herein described with reference to the Examples.

Dated this 2nd day of June 1987.

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