Fabrication and Characterization of Solid-state Electrochemical Sensor for the Determination of Ni(II)

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Abstract

An electrochemical sensor was prepared by using solid state electrode membrane based on NiS/Ag_2S by using nitrate of nickel dissolving in appropriate amount of sodium sulfide with silver nitrate by co-precipitation method. The sensor electrode prepared based on the NiS/Ag_2S at the ratio of 1:2 moles was prepared. The prepared sensor electrode can be used for the determination of trace amount of Ni(II) ions. The Nernstian slope for the sensor electrode was -6.1429 mV/decade. Then this was improved by using $NaNO_3$, ascorbic acid and methanol and Nernstian slope was improved to be -27.114 mV/decade. The prepared electrode can be used within long pH range between 2 to 7. In a reliable storage, the life time of sensor electrode was six months with which fast response was observed. Thus, prepared sensor electrodes can be used for the determination of Ni(II).

Key words: *sensor, nickel, potentiometry, pH range, selectivity coefficient.*

Introduction

Although Nickel is found in trace in quantity, environmentally it is so important in environment protection that it is highly toxic element[1]. It is present in the environmental sample of water as a contaminant coming from urban or industrial waste pollution. It is highly toxic even at low concentration and interference with various matrix, the determination of accurate, precise and selective for Nickel determination is required.

Different modern methods and precise technique such as inductively coupled plasma atomic emission spectrometric (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrometry (FAAS) have been developed for the determination of Nickel[2,3]. These methods are very expensive for the determination, therefore cannot be afford easily for developing countries and need more training, knowledge and sample pretreatment is required; also, onsite determination is not possible with these instruments[4]. On comparison with other techniques, electrochemical sensors are very attractive, ease of preparation, stability of their response, low ohmic response and no need internal solution[4].

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Among these methods, potentiometric electrochemical sensor using specific ion sensor are simple, more precise, high rate, more accuracy, low cost and non-destructive and can be used as in-situ technique. In the construction of these sensors, various design can be constructed depending for precise and more economic technique. Among various constructions, solid back contact can be the best design in the sensor; working and accuracy of sensor can be improved[5]. Similarly, on using solid back contact, the efficiency, precision and sensitivity of sensor can be enhanced. It reduces the changing the concentration of internal solution which is directly proportional to the potential given by the sensor electrode[6,7].

In this technique, the ion selective electrode NiS/Ag_2S was prepared by the co-precipitation method at the ratio of 1:2 moles. The sensor membrane is characterized by X-ray diffraction pattern[6,8]. A conventional sensor electrode is modified by removing internal solution by solid back contact. Here, solid back contact was used to remove internal solution from the conventional ion selective electrode which removes the problem created by the changing in the concentration of the internal solution. The ion selective electrode prepared by solid state back contact and used for the determination of nickel in environmental samples. The investigation of effective parameters was done and good selectivity towards nickel ion was observed. Thus, prepared electrode can be used for fast simple method for the determination of nickel content in environmental samples with low concentrations.

Experimental Methods

Reagents and solutions

All reagents and solutions were of analytical grade and used without any further purification. Nickel nitrate, silver nitrate and sodium sulfide were purchased from Merk company. All solution prepared were from deionized distill water.

Preparation of ion selective membrane

For the synthesis of NiS/Ag_2S ion selective membrane, 0.8589 g of nickel nitrate was taken in a 50 ml distilled water, 2.008 g of silver nitrate was taken in other 50 ml distilled water and 1.037 g of sodium sulfide taken in 50 ml distilled water. $Ni(NO_3)_2$ solution and $AgNO_3$ solutions from two separate burettes were added to Na_2S solution containing beaker at constant rate on stirring constantly by magnetic stirrer maintained at 50 ^{o}C to 60 ^{o}C in a water bath for about an hour to obtain the complete precipitation of NiS and Ag_2S.

$$Ni(NO_3)_2 + 2AgNO_3 + 2Na_2S \rightarrow NiS\downarrow + Ag_2S\downarrow + 4NaNO_3$$

Thus, obtained black precipitate was filtered with 4G sintered glass crucible and washed several times with distilled water for free from sulfide. The precipitate was dried in hot air oven at 110 °C followed by grinding and sieved over 150-micron sieve to obtain the fine powder of uniform sized particles. The formation of NiS/Ag_2S was confirmed by XRD analysis. About 1.5 g, 1.5 mm thickness and 1 cm diameter NiS-Ag_2S pressed pellet was prepared by IR pellet making die on giving pressure of 10 tones/cm^2 for about 15 minutes and dried over hot air oven at 100 °C for about an hour to remove the trapped air. The pellet was polished in different grades of SiC abrasive paper and finally in 2000 grit sized paper in order to make the surface smooth.

Apparatus

The electrode used was obtained at room temperature with the Ni(II) ion selective electrode and calomel electrode (Hg/Hg_2Cl_2) as reference electrode. In between working and reference electrode a high

impedance multi-meter (BK Precision model-389, Taiwan) was connected. For drying hot air oven was used (Narang Scientific Works Pvt. Ltd). The pH measurement made by pH meter (model-276) and the solutions were stirred with the help of the magnetic stirrer (Stuart Scientific,UK). The ultra-sonicator (Branson-2510) was also used for removing the loose particles and for preparation of the pellets out of the prepared co-precipitate, an IR-based machine was used manufactured in UK.

Preparation of nickel ion selective electrode

During the fabrication of the nickel ion selective electrode a PVC rod of 10 cm long and 1.5 cm diameter was used as outer body of the sensor in which a groove of about 1.1 cm wide and about 2.5 mm depth was made and for the electrical connection a hole was drilled at the center throughout the length of the polyethylene rod. For the electrical connection with the membrane sensor i.e. back contact with pellet, a thin copper tape of about 1.0 cm in width was made with about 12 cm long copper wire soldered to it. The copper disc was then inserted inside the polyethylene rod for copper back-contact and the pellet membrane was smeared very thin with silver paste on one side and then attached to the silver disc into the groove of the rod. The electrode with the membrane was left for 30 minutes for the silver paste to dry and the space around the sensor membranes were then fixed with the help of epoxy resin and left for overnight for the solidification.

Electrode conditioning and Emf measurement

The sensors were finally conditioned for 24 hrs. by soaking into a solution containing 1.0×10^{-3}M Ni(NO$_3$)$_2$ solution. The electrodes were rinsed by deionized distilled water then polished in 2000 grit sized SiC abrasive paper for smooth before potential measurements. In all solutions the potential was measured versus calomel electrode (Hg/Hg$_2$Cl$_2$) as reference electrode. The electrochemical cell assembly for potential measurements can be represented as:

Pt(Hg)/Hg$_2$Cl$_2$, (KCl) // Test solution (Ni^{2+}), ISBA / Ni(II) ISE
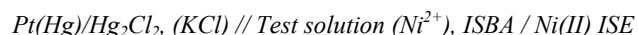
Sample preparation

For the purpose of carrying out the experiment, all the reagents in this work were of AR grade or of LR grade. The stock solutions were prepared using distilled water. The stock solutions were diluted at required concentration prior to the experiment.

Results and Discussion

Characterization of co-precipitate

The obtained compound was confirmed to be Ag$_2$S/NiS by matching all the peaks obtained in the XRD of Ni(II) ISE with the JCPDS data card no. 75 - 0613 for NiS and JCPDS data card no-14-0072 for Ag$_2$S. The JCPDS database showed the presence of binary phase of existing as separate phase of NiS and Ag$_2$S and obtained all peaks were assigned according to the JCPDS database. The peaks for NiS were obtained at 34.7(002), 37.88(220) and that for Ag$_2$S were at 29.01(111), 30.93(111) and. 31.7(101). This shows that the co-precipitates prepared were in pure state and polycrystalline in nature with metallic nickel.
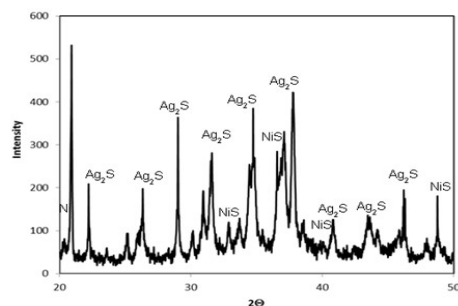
Figure 1: *XRD pattern of Ag₂S-NiS co-precipitate*

Working pH range of the electrodes

The working pH of the test solution having concentration of 1.0×10^{-3}M was determined at the room temperature. From the graph, it was observed that the potential response was not affected with in the pH range in between 2.0-7.0, beyond this pH range of the solution; the potential response of the electrode was seen deviating considerably and the potential drift occurred. Hence, this pH range of 2.0 to 7.0 was taken as the working pH range of the Ni (II) sensor as no interference from H^+ ions or OH^- ions was observed. The cause of considerable drift at the acidic solution i.e. at lower pH may be due to the fact that the membrane of the electrode could be protonated to some extent. It is noteworthy that in alkaline solution, the observed drift at higher pH values could be due to the hydrolysis of nickel in the test solution.
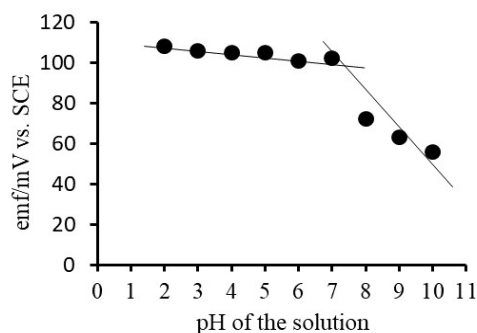

Figure 2: *Effect of the pH of the test solution of $1.0 \times 10^{-3}molL^{-1}Ni(II)$ ions on the potential response of the Ni(II) ion-selective electrode*

Direct potentiometry study

The potential response of the solid-state sensor of NiS/Ag₂S, acting as a working electrode, along with saturated calomel electrode was recorded as a function of change in the concentration of the test solution of Ni(NO₃)₂ of fixed pH of 6.5. Theoretically, the cell emf of the Ni(II) ion selective electrode can be related to the concentration of the Ni(II) ions present in the test solution as:

$$E_{cell} = E_{const} + 0.0292\log[Ni^{2+}]$$

The outcome of the direct potentiometry measurements with Ni(II) ion selective electrode for Ni(II) ions was - 6.1 mV/decade on plotting the experimental values of the emf of the electrochemical cell as a

function of different concentrations of $Ni(NO_3)_2$ solution. For the bivalent cations, theoretical Nernstian slope is 29.58 mV/decade as obtained by the Nernst equation. It seemed that without the presence of any anti-oxidants and ionic strength adjuster buffer the value of Nernstian slope of fabricated Ni(II) ion selective electrode was greatly affected and resulted in much less than the predicted theoretical Nernstian slope. The good outcome of the lower detection limit by the nickel nitrate solution and the significant improvement in the Nernstian slope with the addition of ascorbic acid to the test solution with sodium nitrate solution was obtained. The graphs show a good Nernstian slope which is very nearer to the theoretical value. In addition of these improvements, the experimental data were also found to have less scattering and all the points fell in a linear slope with coefficient of determination (R^2) value of 0.997.
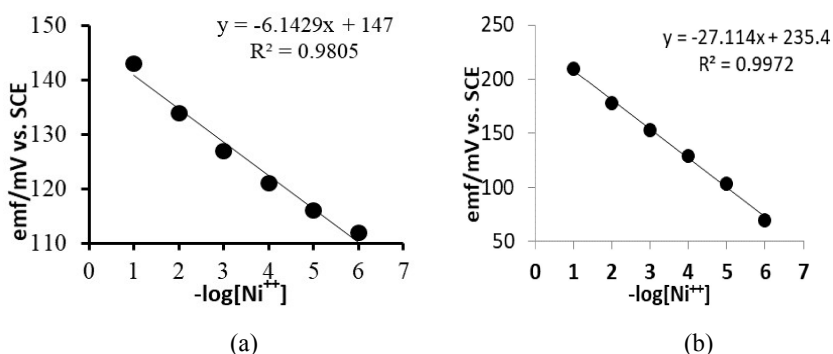

(a)	(b)

Figure 3: *Plot of potential vs. concentration (a) only $Ni(NO_3)_2$ solution and (b) in a mixture of $Ni(NO_3)_2$, ascorbic acid and $NaNO_3$ for electrode*

Comparing this electrode with the commercially available electrode, the Ni(II) ion selective electrode fabricated in this study seemed to perform as good as the commercially available electrode having the lower detection limit of 1.0×10^{-6}M and the Nernstian slope above 20mV/decade. Therefore, the solid-state sensor prepared in the laboratory worked well for the determination of Ni(II) ion concentration up to 1.0×10^{-6}M concentration.

Potentiometric titration

The applicability of the NiS/Ag_2S ion selective electrode, as an indicator electrode for the potentiometric titration, was examined by titration of 5mL of 1.0×10^{-2}M concentration of $Ni(NO_3)_2$ solution against 1.0×10^{-2}M concentration of EDTA. During titration, 20 mL of water was added to the solution and 1mL of EDTA solution was added to the nickel nitrate solution and the potential was recorded while stirring the solution.

The emf of the cell with respect to the concentration of Ni^{++} and S^{--} during potentiometric titration was shown by the equation below;

$$E_{cell} = E_{aggreg} + 0.0295 \log[Ni^{++}]/[S^{--}]$$

The emf of the cell depended on the concentration ratio of $[Ni^{++}]/[S^{--}]$. When Ni^{++}ion solution was titrated against EDTA solution from burette, observed emf of the cell decreased for every addition of EDTA solution. This was due to the decrease in free Ni^{++} ions in the solution. At the equivalence point,

there was dramatic decrease in observed emf because at that point nearly all the Ni^{++}ions were consumed by EDTA solution to form Ni-EDTA complex. The equivalent point of the reaction is confirmed by the sudden change in potential. The sharp break point and the fast response time in the potentiometric titration of Ni(II) salt solution against EDTA corresponded to Ni-EDTA stoichiometry which showed that this sensor can be used for the determination of Ni(II) ions by potentiometric titration methods. Hence, Ni(II) ion selective electrodes can be used as an indicator electrode in potentiometric titration for the determination of Ni(II) ions even in low concentration range.
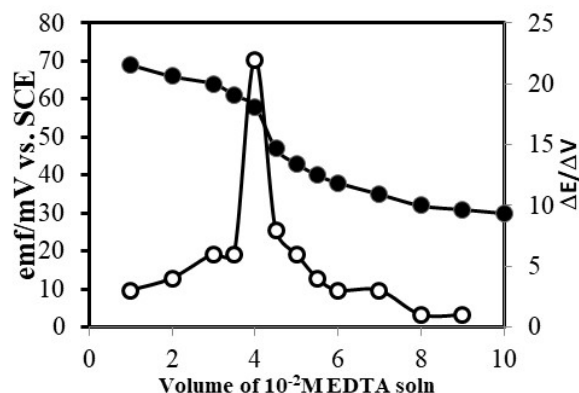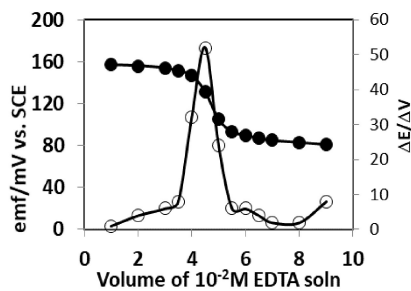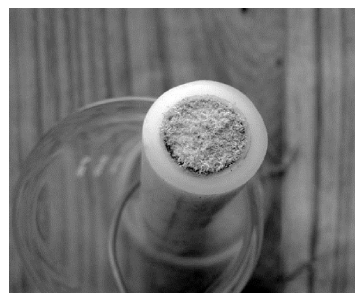

Figure 4: *A Potentiometric titration curve of 10ml Ni(II) ion solution(1.0×10⁻³molL⁻¹) with1.0×10⁻³molL⁻¹ EDTA using the proposed membrane sensor as an indicator electrode*

Determination of leaching behavior of the membrane

The leaching of the NiS/Ag₂S electrode can be studied by determining the amount of Ni²⁺ ions dissolved in the aqueous solution from the membrane sensor. For the determination of the amount of the Ni(II) ions leached from the sensor membrane, the electrode was dipped in 5 mL of $1.0×10^{-2}$ M nickel nitrate solution which was diluted to make 25 mL by adding distilled water containing $NaNO_3$ and ascorbic acid was added up to 3 hrs. Then, the test solution was titrated against $1.0×10^{-2}$ M EDTA solution.

(a)   (b)

Figure 5: *(a)Potentiometric titration curve of 5 mL Ni⁺⁺ion solution (1.0×10⁻² molL⁻¹) with 1.0×10⁻² molL⁻¹ EDTA using the fabricated sensors as an indicator. (b) Spontaneous leaching of the membrane sensor after long storage in the moist environment*

It can be estimated that for the consumption of 5ml of $1.0 \times 10^{-3} molL^{-1} Ni(NO_3)_2$ solution, exactly 5ml solution of $1.0 \times 10^{-3} molL^{-1} EDTA$ solution is required. But here, 1ml of excess volume of EDTA was consumed by the $Ni(NO_3)_2$ solution. This excess volume of EDTA consumed was proportional to the amount of Ni^{++} ions dissolved from the sensor membrane in the aqueous solution for 3hrs. Hence by calculation, 5.869×10^{-5}g or $(4 \times 10^{-5}$ M) of Ni^{++} ions of the Ni(II) sensor membrane has been leached into the diluted aqueous solution of $Ni(NO_3)_2$ after dipping the electrode for 3hrs. The leaching may be due to the setup of the concentration gradient of Ni^{++} ion solutions in between the membrane sensor and the test solution.

In summary, the NiS/Ag_2S ion selective electrode can be used as an indicator in the potentiometric titration for the determination of the Ni(II) ions dissolved in the test solution quantitatively and that such sensor should not be kept in nickel free solution for long time as it will lead to deterioration of the sensor membrane. The pellet of the Ag_2S/NiS sensor when kept in the moist environment for about 6-7 months without any use was gradually leaching. This happened due to the storage of the electrode in the moist environment that facilitated the aerial oxidative leaching of the nickel present in the crystal lattice of the pellet as well as the hydration of the sensor membrane to give the greenish crystal of the nickel.

Dynamic Response Characteristics

The curves for the dynamic response of a Ni(II) sensors are obtained by the concentration from 1.0×10^{-6}M to 1.0×10^{-1}M of the Ni(II) salt solution and the potential was measured at the interval of 30 sec. till the equilibrium potentials are obtained. The concentration of the test solution was usually changed by the addition of higher concentration of Ni(II) salt solution to the test solution. The potential of the cell was observed to increase with the increase in the concentration of the test solution and the potential was fluctuating unless the equilibrium potential between the membrane of the electrode and the test solution was maintained. it was observed that the equilibrium potential has been set up within 3 minutes after the electrode was dipped into the test solution. This was usually the average time required for the electrode to reach a potential within 1 mV or 2 mV of the final equilibrium value after successive immersion in a series of Ni^{++} ion solutions, each having a 10-fold difference in concentration. This was usually the average time required for the electrode to reach a potential within ± 2mV of the final equilibrium value after successive immersion in a series of Ni^{++} ion solutions, each having a 10-fold difference in concentration.

This may be probably due to the fast interaction kinetics of Ni^{2+} ions of the test solution with the membrane sensor at the test solution/membrane interface. Good polishing for the smooth and plane surface and optimum preconditioning of the membrane electrode may also be responsible for giving very short response time.
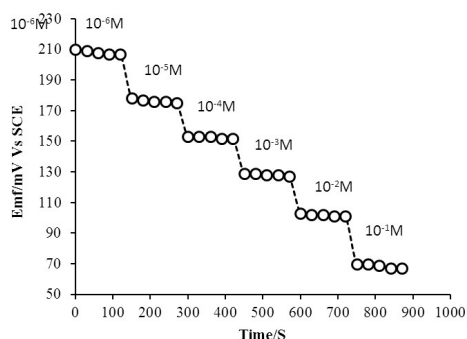

Figure 6: *Dynamic response time of the Ni(II) sensor for step changes from low to high concentration of Ni^{++} ions*

Selectivity coefficient determination

For the determination of selectivity coefficient of sensing electrode match potential method (MPM) is the recommended method for studying influence of interferences ion in the ion selective electrode by IUPAC. It is based on the measurement of specific activity of primary ion added to a reference solution. The selectivity coefficient for the Ni^{2+} ions was determined against the other interfering ions such as Na^{+}, K^{+}, Cu^{++}, Pd^{++} and Cd^{++}. For this, the first change in potential upon changing the concentration of $Ni(NO_3)_2$ from 1.0×10^{-4}M to 1.0×10^{-3}M was measured into a reference solution by the standard addition of high concentration of $Ni(NO_3)_2$ solution. Then in the separate experiment, the interfering ion was added to an identical reference solution until the same change in the potential was recorded. In the match potential method, the selectivity coefficient $K_{Pot,MPM}$ is given by the ratio of the resulting concentrations of the Ni^{2+} ions over the interfering ions. The selectivity coefficient $K_{pot, MPM}$ of the Ni(II) ion selective electrode is given by:

$$K_{Pot,MPM} = a_{Ni}^{++}/a_B$$

Where, a_{Ni++} is the activity/concentration of the primary ion.

a_B is the activity/concentration of the interfering ions.

The interference of Na^{+}, K^{+}, Cu^{++}, Pd^{++} and Cd^{++} was investigated and showed that they have no significant effect on the response to Ni(II) shown in table below.

Table 1: The selectivity coefficients of various interfering cations for Ni^{++} membrane sensors

Interfering ions	$K_{Pot,MPM}$
Na^{+}	0.9721
K^{+}	0.9732
Cu^{++}	0.9808
Pb^{++}	0.9723
Cd^{++}	0.9885

Method validation

For the validation of this method, different types of standard reference material were used[8-10]. The samples were treated as mentioned and the Ni(II) content were analyzed by this method. This method can be considered as the reliable and accurate method for the determination of nickel in the environmental samples.

Conclusions

A sensor membrane was fabricated for the determination of nickel ion. The electrode composition was NiS/Ag_2S at the ratio of 1:2 moles was prepared. Effect of pH on the electrode, potentiometric determination was studied. The electrode has a long-life time and a response time. A good selectivity among other ions to nickel ion was absorbed which makes the electrode a good candidate in environmental samples.

Acknowledgements

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