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All Solid State (ASS) Polymeric Membrane Sensor (PMS) for the Monitoring of Nanomolar Nickel Concentration

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A nickel(II) selective all-solid-state PVC membrane sensor (ASS-PMS) has been designed and constructed for the monitoring of nanomolar nickel(II) concentrations in various samples. The applicability of the sensor to real samples was proved through its use for the analysis of the target ion in waste water samples. The all solid state support and transducer was build through coating a nickel wire with a composite of graphite powder and an epoxy resin, and next it was coated with a nickel selective PVC membrane, with the optimal composition of 33% of PVC, 57% of Nitrobenzene, 2% RTIL (1-n-butyl-3-methylimidazolium hexafluorophosphate), 3% of KpClTPB, and 5% of ionophore L. The potential response of the ASS-PMS change with the concentration of the target ion at a slope of 29.5±0.3 mV/decade, which is indicative of a Nernstian behavior, and was linear in the concentration range of 1.0×10^{-8} to 1.0×10^{-3} mol L^{-1} of the nickel(II), reaching a lower detection limit as low as 5.0×10^{-9} mol L^{-1}. The response of the ASS-PMS was found to be almost independent from interference from different conventional ionic species. The ASS-PMS was successfully applied to the potentiometric determination of nickel(II) concentrations in ions electroplating waste water samples.

Keywords: All solid state, Nickel, Electroplating waste water, Sensor

1. INTRODUCTION

Low concentrations of nickel(II) are present in raw meat, saturated and on-saturated oils, chocolate products, cotton seed, dairy products and processed foods. The element is also found in many industrial dumps due to its application in various catalytic processes. The negative biological influences of the element include disorders of the respiratory system, including lung and nasal cavity cancers, asthma and acute pneumonitis, as well as damages to the central nervous system, which stress the importance of monitoring the concentration of nickel in environmental, biological, industrial and food samples. This is commonly done through cumbersome instrumental procedures like AAS, ICP, and the like, which clearly impose high time and financial costs [1-4].

Ion selective electrodes (ISEs), on the other hand, have found various applications in monitoring applications, and have been well established as simple, fast and yet accurate and precise tools for the analytical procedures. Advantages of potentiometric sensors include their being direct, fast and non-expensive, as well as their potentials for different applications arising from their miniaturizable dimensions and shapes. Many major applications of ISEs fall in clinical, environmental and process control analytical applications [5-7].

To enhance the possibility to miniaturize ISEs, which in turn provides a range of new possibilities for their applications and improved characteristics, the elimination of the internal reference electrode and filling solution (that are the major parts of symmetrical electrodes), which has been actualized in the case of all-solid-state (ASS) [8-12] electrodes provides great advantages, and their combination with polymeric membrane electrodes (PMEs) has given rise to a new class of ion selective electrodes with adjustable selectivity. Due to the elimination of the further limitations of using an inner reference solution, like the obligation to be used in vertical positions, evaporation and of the inner solution and the changes in the resulting response the lower detection limits of the ASS-PMEs as compared to those of the symmetrical equivalents, and their improved mechanical stabilities, ASS-PMEs have attracted great interest in the area of design and construction of potentiometric electrodes, which is well reflected by the publications made in the area [8-12].

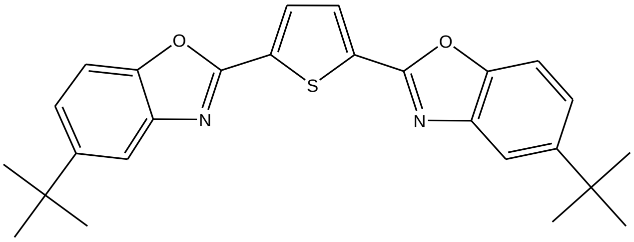
Regarding the need for the selective and accurate monitoring of traces Ni(II) in various aqueous samples, a range of chelating compounds have been tested and some have been found to act as suitable ionophores to be used in selective electrodes for the determination of this ion [13-24], and naturally benefitting the advantages of building nickel(II) ASS-PMEs, seem very enticing.

Consequently it is the object of the present work to design a new nickel(II) selective ASS-PME. In doing so a conductive polymeric composite (CPC) composed of a mixture of MWCNTs and an epoxy resin, which was used as the ASS transducer, was coated with a nickel(II) selective PVC membrane and the different parameters influencing the performance of the device were evaluated and optimized.

2. MATERIALS AND METHODS

2.1. Reagents

The solvents and chemicals used including 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), tetrahydrofuran (THF), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), *o*-nitrophenyloctylether (NPOE), oleic acid (OA), potassium tetrakis (pchlorophenyl) borate (KpClTPB) and sodium tetrapenyl borate (NaTPB), high-molecular weight polyvinylchloride (PVC), Epoxy (macroplast Su 2227), hardener (desmodur RFE), graphite powder with a 1–2 µm particle size and MWCNTs, were of analytical reagent grade and were procured from Merck, Fluka, Henkel and Bayer Ag, companies. The ionophore used L (Scheme 1), was prepared as described elsewhere [25].



Scheme 1. Chemical structure of the used selectophore

2.2. Preparation of the sensor

The ASS transducer of the devices were constructed through preparing the CPC of graphite powder and MWCNT-loaded epoxy resin, through admixing different portions of powdered graphite, MWCNTs, the epoxy, and hardener in THF solvent and giving the resulting mixture about 20-30 min to age in the air (to reach a proper viscosity), before they were coated on the polished section of a shielded nickel wire (0.5 mm diameter and 15 cm length) so as to act as the solid contact of the ASS-PMEs after completely drying after resting for 10 hours. The best ASS transducer behavior was observed at CPC concentrations of 30% w/w of the epoxy resin, 15% w/w of the hardener, 5% w/w of MWCNTs and 50% w/w of powdered graphite.

The ASS transducer prepared this way was next immersed the cocktail of the PVC membranes with different compositions 3 times, and allowed to dry in air for 24 h to yield the resulting ASS-PMEs which were then studied and evaluated. All ASS-PMEs were conditioned in a 10^{-3} mol/L solution of Ni(II) ions. The best sensing behavior was observed in the case of membranes containing 5%w/w of the L, 57%w/w of the best plasticizer (i.e. NPOE), 2% RTIL, 33% w/w of PVC powder, and 3% w/w of KpClTPB.

The overall routine for the preparation of the PVC membranes included admixing different amounts of L, with appropriate amounts of PVC, plasticizer and the ionic additive in tetrahydrofuran (THF). THE resulting mixture was next transferred into a glass dish of 2 cm diameter, and left in the air until an oily concentrated mixture was obtained, due to the evaporation of THF.

2.3. Potentiometric measurements

The ASS-PMEs were used as the indicating electrode in a glass cell further consisting of an Ag/AgCl double junction reference electrodes (Azar-Elelectrode Co., Iran) as the external reference electrode, and the two electrodes with in contact through a 250 pH/mV meter with ±0.1 mV precision, hence the resulting electrochemical cell can be illustrated as:

Cu wire/ASS layer/ion selective PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

All measurements were made using this cell assembly and using the well-known calibration method using standard solutions.

3. RESULTS AND DISCUSSION

Given the advantages of ASS based PMEs, it is interesting that the majority of Ni(II) selective electrodes so far are symmetrical devices, requiring the presence of an inner reference solution to develop a potential gradient across the membrane, which naturally suffer the inherent shortcomings of this class of electrodes [26,27]. Hence to have more robust, miniaturized devices, enjoying the above mentioned advantages the focus of the current work was on the construction of an ASS-PME for nickel ions [28].

3.1. Optimizing the PVC Membrane Composition

Table 1. Various membrane ingredients used in making ASS-PVC membrane sensor

No	**Composition%**					**Slope* (mV/decade)**	**DL (mol/L)**
	PVC	**Plasticizer**	**RTIL**	**L**	**Additive**		
1	33	65 NB	2	-	-	4.2±0.2	-
2	33	64 NB	3	-	-	4.3±0.3	-
3	33	62 NB	2	3	-	16.4±0.3	3.0×10^{-8}
4	33	60 NB	2	5	-	17.5±0.4	3.3×10^{-8}
5	33	59 NB	2	6	-	17.5±0.2	3.5×10^{-8}
6	33	58 NB	2	5	2 TPB	28.8±0.4	7.0×10^{-9}
7	33	57 NB	2	5	3 TPB	29.3±0.4	6.3×10^{-9}
8	33	57 NB	2	5	3 KpClTPB	29.5±0.3	5.0×10^{-9}
9	33	50 NB	2	5	10 OA	28.8±0.3	5.4×10^{-9}
10	33	45 NB	2	5	15 OA	29.4±0.4	5.5×10^{-9}
11	33	57 NPOE	2	5	3 TPB	29.3±0.2	6.2×10^{-9}
12	33	57 DBP	2	5	3 TPB	26.9±0.4	7.3×10^{-9}
13	33	57 BA	2	5	3 TPB	27.3±0.3	7.1×10^{-9}

*The results are based on five replicate measurements.

As it is clear the composition and the nature of the ingredients present in the PVC membrane has considerable influences on the function of any sensor based on such a membrane. The plasticizing solvent and the ionophore can be considered as the most important ingredients of a membrane sensor, since each play a significant role in the sensor response. The most important data gathered while optimizing the PVC membrane composition are shown in Table 1. In general a plasticizer/PVC ratio of about 2.0 is known to be the most suitable amount of the two ingredients [29-32], and since this ratio is observed in all compositions the amount of the PVC (i.e. 33%wt) is compromised in Table 1.

The major role of the water-immiscible plasticizer is facilitation of the mobility of the free ligand as well as the ligand-ion complexes inside the membrane. Such solvents should have specific properties like considerable boiling points, being inert toward the PVC and other membrane ingredients, and containing no chemically active, acidic or basic functional groups etc., which limits the number of compounds that can be used to this end. Conventionally dibutyl phthalate (DBP; Dielectric Constant (DC)=6.4), , nitrobenzene (NB; DC=35.7) and benzylacetate (BA; DC=5.7) and *o*-nitrophenyloctylether (NPOE; DC=24) are used as the plasticizing solvents in PVC membranes and this was no exception in this case [29-32]. The results showed that the very polar NB leads to better responses, which can be attributed to the rather high charge density that in turn leads to better extraction of the free or complexed Ni(II) ions into the PVC membrane phase. There is no need to mention that the plasticizer cannot provide all the requirements for the membrane to function properly and hence small amounts of ionic additives are added to the membrane composition to improve the exchange mechanism and also lessen the Ohmic resistance of the membrane.

A rather new approach in the preparation of PVC membranes is the application of water-immiscible room temperature ionic liquid (RTILs) in the membrane composition to decrease the Ohmic resistance and also the ion-exchange phenomenon [33]. Based o the data in Table 1, 2% the RTIL leads to best ASS-PME response.

The effect of the amount of the ionophore on the potential response of the sensor was depicted in Table 1. As it can be seen from Table 1, 5% L is the best amount of ionophore (membrane no. 4). The response of the sensor was also evaluated in absence of the ionophore. As can be seen, in a blank membrane, the membrane without the sensing ionophore, responds too poor (membrane no. 1 & 2). Hence, membrane no. 9 showed the best Nernstian slope (29.5±0.3 mV/decade) was selected for further studies.

3.2. Calibration curve

To evaluate the response behavior of the ASS-PMEs the potential response of the electrochemical cells using the Ni(II) selective electrode as the indicator was recorded in different concentrations of the Ni(II) ranging from 1.0×10^{-9} to 1.0×10^{-1} mol L^{-1}, and the potential *vs.* –log [Ni(II)], (Figure 1) was found to follow a Nernstian pattern. Although in conventional symmetrical PVC membrane sensors, the response of the electrode is usually linear in the range of 0.1 to 10^{-5} or even 10^{-6} mol L^{-1}, the ASS-PMEs with the optimized compositions were found to have a linear range extending from about 10^{-8} mol L^{-1} of Ni(II), which is a marked improvement in the lower detection limit of the electrode. However, due to the smaller electrode surface and the easier saturation of the active sites the upper limit of the ASS-PMEs were more limited (i.e. 10^{-3} mol L^{-1}).

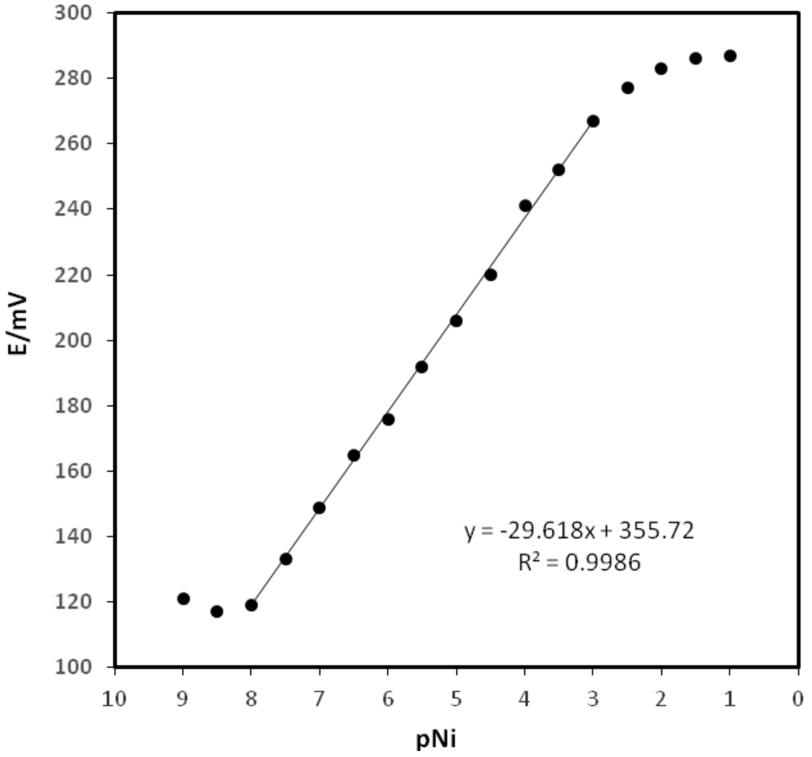


Figure 1. Calibration curve of Ni ASS PVC membrane sensor; the results are based on 5 replicate measurements.

The electrode response in the whole linearity range was 29.5 ±0.3 mV/decade of the Ni(II), which is indicative of the Nernstian behavior of the device. So, it was concluded that the designed ASS-PMEs have a near Nernstian response in the range of 1.0×10^{-8}-1.0×10^{-3} mol L^{-1}. By further extrapolation of the two linear parts of the calibration curves at its lower end, the lower detection limit of the electrodes were evaluated to be around 5.0×10^{-9} mol L^{-1}.

3.3 Response time and pH effect

The dynamic response time of the ASS-PMEs with the optimal composition were also evaluated. This parameter that is defined as the time span required for the device to reach responses within ±1 mV of its equilibrium potential upon a 10 fold concentration change [34-42], was evaluated by successive immersions of the ASS-PMEs in a range of standard solutions, with different concentrations ranging from 1.0×10^{-8} to 1.0×10^{-3} mol L^{-1}. During this tests the sensor quickly reached the equilibrium response in less than 10 seconds (Figure 2).

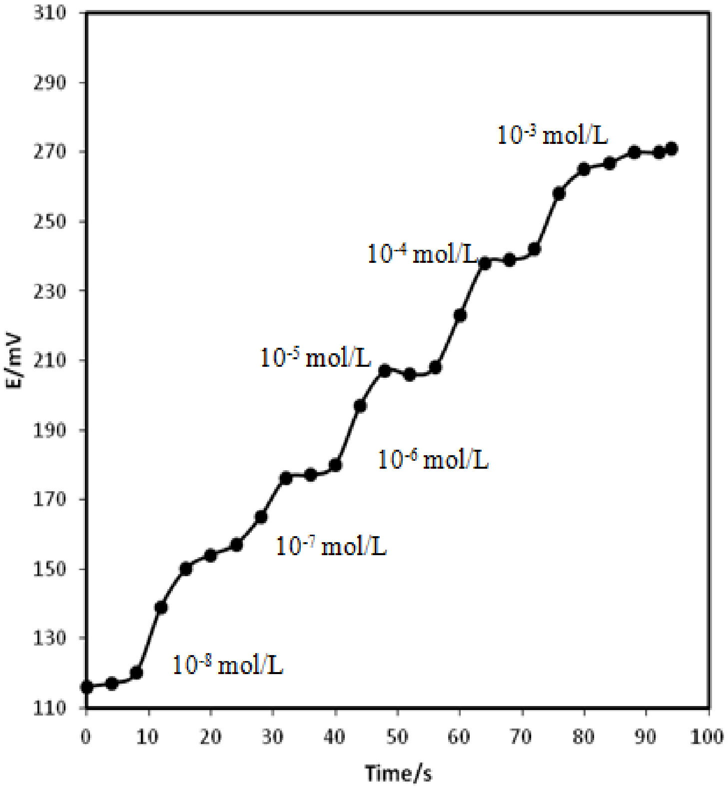


Figure 2. Dynamic response time of the Ni ASS PVC membrane sensor

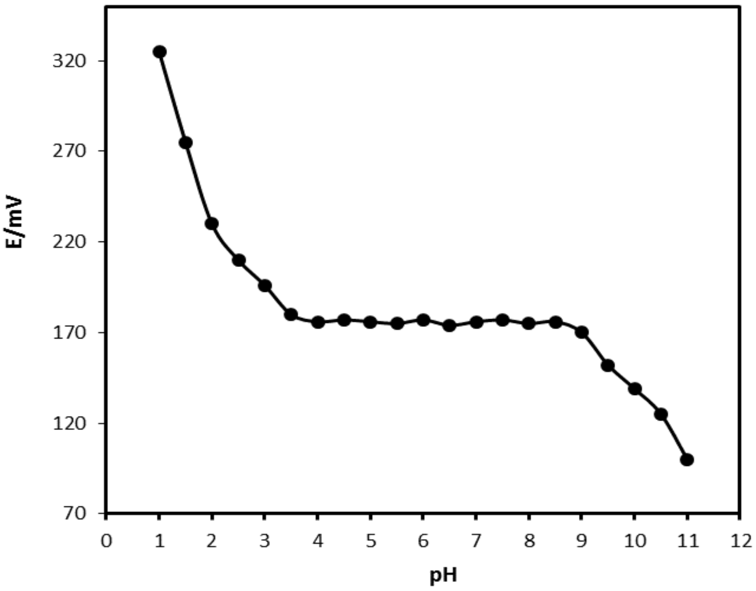


Figure 3. pH effect on the potential response of the sensor

Also the pH range in which the sensor response is independent from the pH changes was also evaluated and the results are illustrated in Figure 3. The study was performed at a fixed Ni(II) concentration (i.e.1.0×10^{-5} mol L^{-1}) while the pH was changed from 1.0 to 10.0 using concentrated NaOH or HCl solutions. As it is evident from Figure 3, the ASS-PME response is pH independent in the range of 3.5 to 8.50. The sharp changes in the potential response above 8.50 is due to the changes in the free Ni(II) concentration due to the formation of single charged or even neutral $Ni(OH)^+$ or $Ni(OH)_2$ species after this unset value. Below 3.5, the potential changes are due to the protonation of the nitrogen atoms present in L.

3.4. Lifetime

The lifetime of the optimal ASS-PMEs were also evaluated by using three electrodes for 1 hour per day, within a 12 week period and recoding the response and detection limit data. The lifetime of the electrodes was within the typical 4–10 period week that is observed for PVC membranes [41-45]. It was observed that after 8 weeks of using the electrodes under the mentioned conditions some gradual decrease was observable in the slope of the calibration curves, while the lower detection limits gradually increased. This can be attributed to the well-known leaching of the plasticizer, sensing element, or ionic site from the PVC film. The application of RTILs in the composition of PVC membrane might be one of the reasons of the increased lifetime of the sensor, as compared to average symmetrical PVC membrane sensors.

3.5. Selectivity

Table 2. The selectivity coefficients of various interfering cations for Ni(II) ASS PVC membrane sensor

Cation	**Selectivity Coefficients**
Na^+	$<10^{-5}$
K^+	$<10^{-5}$
Mg^{2+}	$<10^{-5}$
Ca^{2+}	$<10^{-5}$
Cu^{2+}	5.3×10^{-4}
Zn^{2+}	6.2×10^{-4}
Co^{2+}	8.3×10^{-4}
Cd^{2+}	5.9×10^{-4}
Pb^{2+}	6.0×10^{-4}
Ag^+	2.0×10^{-4}
Fe^{3+}	4.5×10^{-4}
Hg^{2+}	5.0×10^{-4}
La^{3+}	4.2×10^{-4}
Al^{3+}	2.5×10^{-4}

Finally the most important characteristic of the ASS-PMEs, i.e. the selectivity to the target ion in the presence of conventional interfering ions, was evaluated using the well-known matched potential method (MPM) [43-46] and the results are summarized in Table 2. It is easy to conclude that, based on the acquired selectivity coefficients, the interferences of the tested interfering ions on the response of the electrodes is negligible.

3.6. Analytical performance

To evaluate the applicability of the ASS-PMEs in real analytical procedures, some tests were performed. Initially 3 standard synthetic samples were tested through the calibration method, to evaluate the repeatability of the responses obtained using the devices. The experiments proved the RSD of the response of the ASS-PMEs to be 2.55, 2.70 and 3.10%. The RSD values for the intra- and inter-day assays performed in the same laboratory by two different technicians revealed a maximum f 4.0%.

Next, the Ni(II) concentrations were evaluated in nickel electroplating waste water sample. The samples were only acidified with HNO_3, after being taken, and each sample was subjected to analysis three times, using the calibration method. The results were further validated through being compared with results of the analysis of the same samples using inductively coupled plasma optical emission spectrometry (ICP-OES), and were found to be in good agreement with them (Table 3).

Table 3. Results of nickel analysis in waste water samples

Sample	**Found by the sensor* (ppm)**	**Found by ICP-OES (ppm)**
Sample 1	11.5±0.3	11.4±0.2
Sample 2	24.6±0.7	24.1±0.5
Sample 3	3.2±0.2	3.1±0.1

* The results are based on five replicate measurements.

4. CONCLUSION

A Ni(II)-selective ASS-PME potentiometric sensor was designed and constructed using a CPC of graphite, MWCNTs, and epoxy resin as the coating of a nickel wire, to act as an ASS transducer. Next a thin layer of a PVC membrane containing 33% of PVC, 57% of NB, 2% of [bmim]PF_6, 3% of KpClTPB, and 5% of ionophore L, was coated on the ASS transducer to give and ASS-PME electrode. THE optimized compositions for the CPC and the PVC membrane were used to construct the devices. The optimal sensors had a linear response ranging from 1.0×10^{-8} to 1.0×10^{-3} mol/L of the Ni(II) and the lower detection limit of the device was found to be 5.0×10^{-9} mol/L. Apart from evaluating the response time, applicable pH range and selectivity coefficients of the sensors the device was practically used for the determination of Ni(II) concentrations is nickel plating waste waters through calibration curves.

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