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Author(s)	Do, Phuc Quan; Vu, Thi Huong; Pham, Bien Cuong et al.
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POTENTIOMETRIC SENSOR FOR HYDROGENE ION BASED ON NEUTRAL CARRIER IN A POLY (VINYL CHLORIDE) MEMBRANE WITH POLYANILINE SOLID CONTACT

Do Phuc Quan, Vu Thi Huong, Pham Bien Cuong, Tu Vong Nghi, Pham Hung Viet*

Research Centre for Environmental Technology and Sustainable Development, Hanoi University of Science, Vietnam National University, Hanoi, 334 Nguyen Trai Road, Thanh Xuan District, Hanoi, Vietnam,

ABSTRACT

In view of development of miniaturized sensors array, a potentiometric sensor for hydrogen ion with polyaniline solid-state contact has been investigated. A thin polyaniline film was cyclic voltammetry deposited on a solid electrode surface such as glassy carbon electrode and used as an internal solid-contact layer between the solvent polymeric sensing membrane and solid electrode surface. The important parameters of electropolymerisation affecting the stability of an electromotive force response of the solid-contact potentiometric ion sensor are thoroughly studied. The performance of potentiometric sensors for hydrogen ion based on tridodecylamine (Fluka hydrogen ionophore I) and N,N-dioctadecylmethylamine (Fluka hydrogen ionophore III) carriers in a poly(vinyl chloride) membrane was verified in the steady-state. In this study, it was found that adding polyaniline film by electropolymerisation as solid contact layer, significantly improved the potentiometric stability of the resulting solid-state potentiometric ion sensors. The increased stability is thought to be the result of a better defined interfacial potential between the sensing membrane and the solid electrode contact.

The designed sensors showed similar electrochemical behavior to conventional glass membrane electrode. They exhibited excellent selectivity for the hydrogen ion and a linear response over the pH range from 2.5 to 11.3 with a slope of 57 mV.decade⁻¹. The developed sensors showed fast response and a relatively high durability, during 2 months.

Keywords: Conducting polymer, electropolymerisation, pH sensor, solid-contact sensor.

INTRODUCTION

Over the past two decades, the development and applications of chemical sensors and biosensors have grown rapidly [1-14]. Among all sensors, pH sensors have received the most attention because of the importance of pH measurement in various scientific research and practical applications. Although the glass bulb pH electrode is a well-established tool in the measurement of pH, there are some disadvantages with this type of electrode. Glass pH electrode provide very high electrochemical impedance and difficult of miniaturization.

Optical and fiber-optic pH sensors complement the glass electrodes for pH measurement [19] and offer numerous advantages such as immunity from electrical interference, feasibility of miniaturization, and possibility of remote sensing and in environmental measurement. However, measurement with fiber-optic pH sensors often suffers from instabilities resulting from decrease in the concentration of pH indicator due to leaching and photobleaching, fluctuations in the intensity of light source, and variations in light attenuation through the optical fiber due to changes in the degree of bending. Certain conductive polymers change their colors as a function of pH and thus can be used for pH sensing.

Polyaniline and polypyrrole have been used in the development of optical and fiber-optic pH sensors based on their absorption in both the visible and near-IR regions [20]. These pH sensors offer several advantages: simple fabrication of the sensors since the polymers are intrinsic sensing reagents, a wide dynamic range since these polymers are basically polyelectrolytes with multiple pKa values, and measurement in the near-IR region, where there is less spectral interference and smaller degree of light scattering compared to the UV and visible regions. However, they also suffer from some shortcomings such as the long

response time due to slow diffusion in the polymers, the interference from other ions, reducing and oxidizing agents, and the need for pre/reconditioning (e.g. in 0.1 M HCl) before each measurement, which is to overcome the hysteresis due to conformational change in polymer chains occurring upon pH changes.

The first neutral carrier based solvent polymeric membrane pH electrodes have been developed in Simon's laboratory, where tridodecylamine and other compounds containing basic nitrogen groups have been discovered as selective membrane compounds for hydrogen ion [7]. This pH sensor offers great advantages, which include, ease of preparation, relatively fast response, reasonable selectivity, and wide linear dynamic range. Furthermore, solvent polymeric membrane pH ISE offers the possibility of miniaturization and maintenance-free ion sensors based on development of all-solid-state-contact sensors, in which, the transfer from ionic to electronic conductivity is provided by a solid contact layer having mixed ionic and electronic conductivity between the inner reference element and the sensing membrane.

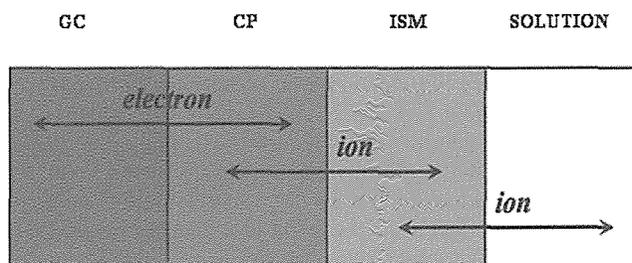


Fig. 1. Schematic description of charge transport occurring in a solid-contact ion-selective electrode. GC: Glassy carbon; CP: Conducting polymer; ISM: Ion selective membrane.

Miniaturization of a pH electrode will bring improvements in determination pH values in clinical, medicals field, industrial process and environmental monitoring. Recently, we reported on the highly stable response of the conducting polymer based solid-contact ion-selective electrodes for ammonium, nitrate, nitrite, potassium ions [15-18] with an electropolymerized polypyrrole film. These solid-contact electrodes can be easily miniaturized. Schematic description of charge transport occurring in a conducting polymer based solid-contact ion-selective electrode showed in the Fig. 1.

In the present work, the solid-contact pH sensor employing electropolymerized conducting polymer film as an internal solid-contact layer between the reference element and the pH membrane, instead of the conventional design with internal filling solution, have been investigated.

The potentiometric response characteristics of conducting polymer based solid-contact pH-sensor were evaluated using a steady-state measurement.

EXPERIMENTS

Materials

Tridodecylamine (TDDA), and N,N-dioctadecylmethylamine (DODMA), bis-(2-ethylhexyl) sebacate (DOS), bis(1-butyl pentyl)decane -1,10 - diyl diglutarate (ETH 469), Potassium tetrakis(4-chlorophenyl)borate (KTP-CIPB), high molar mass poly(vinyl chloride) (PVC), and tetrahydrofuran (THF) were Selectophore reagents from Fluka. Pyrrole and aniline purchased from Fluka was redistilled under vacuum prior to use. All other chemicals were analytical-reagent grade. Nanopure water (Barnstead Ultrapure water system, 18.2 MΩ) was used to prepare all solutions.

Electropolymerisation of conducting polymers

Conducting polymer (CP) synthesis and characterization were performed in a conventional three electrodes system consisting of a 2 mm i.d. glassy carbon (GC) disc working electrode (6.1204.110 GC, Metrohm, Switzerland), a platinum wire gauze auxiliary electrode and an Ag/AgCl (3M NaCl) reference electrode. An Autolab 30 general purpose electrochemical system (AUT30.FRA2-AUTOLAB, Eco Chemie, B.V., The Netherlands) was used for the electropolymerisation.

Before polymerization, the surface of the glassy carbon working electrode was polished on a polishing cloth with alumina slurry (0.05 μ m) and then cleaned with double distilled water and finally in a water-filled ultrasonic bath for 30 seconds.

Polyaniline (PANi) was prepared by cyclic voltammetry in 0.5 M aniline and 0.5 M H₂SO₄ onto the electrode surface. The monomer solution used for polymerization was deoxygenated with nitrogen for 5 minutes to remove any trace of oxygen from the solution, before the polymer synthesis. For electrochemical polymerization of aniline, the potential was swept between -0.4 and 0.8 V versus SCE at scan rate of 50 mV s⁻¹. The potential cycling was repeated up to 30 cycles.

Polypyrrole dodecyl sulfate (PPy/DS) was prepared by galvanostatic electrochemical polymerization from an aqueous solution containing pyrrole (0.2 M) and dodecyl sulfate (0.2 M). A current density of 1mA.cm⁻² for 600 seconds was used to achieve electropolymerisation.

After electrodeposition, the resulting conducting polymers were washed with distilled water and then dried for 2 h in desiccator.

Preparation of cocktail solution and solid-contact pH sensors

Solid-contact ISEs were prepared by coating GC/CP electrodes with ion selective membrane solution. The membrane compositions (see Table 1) were dissolved in 1 ml THF and applied by a micropipette (50 μ l of cocktail solution) on the electrode to cover the conducting polymer layer, then dried for overnight in desiccator, and conditioned overnight in pH buffer prior to any measurements.

Table 1: Compositions of the pH membrane mixtures prepared in this study.

Membrane Components	pH-1	pH-2	pH-3	pH-4
TDDA	1.0	1.0	-	-
DODMA	-	-	1.0	1.0
PVC	32.5	32.5	32.5	32.5
KT ₄ CIPB	0.5	0.5	0.5	0.5
ETH469	66	-	66	-
DOS	-	66	-	66

E.M.F. Measurements

Steady-state potentiometric measurements were made while stirring at a constant rate and with the electrodes immersed to the same depth in the solution to be tested. In all the experiments, the pH measurements of the sample solutions were determined with a Metrohm 6.0228.000 glass electrode. The potentials were measured against a double junction Ag/AgCl reference electrode (Orion 90-02-00) using a 692 pH/Ions meter (Metrohm, Switzerland).

The calibration curve was obtained by a standard addition method. A buffer solution (10.0 mM Na₂HPO₄, 10.0 mM NaH₂PO₄, NaOH) was adjusted by the addition of 1 M HCl solution in the pH range 2.0–12.0. The standard deviation arising from this measuring equipment was

± 0.1 mV for a single determination. Selectivity factors were determined by the fix interference method using solutions that were added 0.01 M LiCl, 0.01 M NaCl, 0.01 M KCl, 0.01 M CaCl₂, 0.01 M BaCl₂, respectively, into buffer solutions.

Electrochemical impedance measurements

Electrochemical impedance spectroscopy (EIS) was performed by using an Autolab general-purpose electrochemical system and Autolab frequency response analyzer system (AUT30.v AUTOLAB, Eco Chemie, B.V., The Netherlands). Impedance measurements were performed by using a one compartment three-electrode cell where the electrode under study was connected as the working electrode. The reference electrode was an Ag/AgCl with a salt bridge containing 1 M NaCl and auxiliary electrode was a platinum wire gauze electrode. The impedance spectra were recorded in the frequency range 100 kHz-10 mHz by using a sinusoidal excitation signal with amplitude of 10 mV. The measurements were done in a solution of 0.1 M HCl at room temperature.

RESULTS AND DISCUSSION

Electropolymerisation and pH sensitivity of conducting polymers

Since the conducting polymer plays the role for the transfer from ionic to electronic conductivity in the solid-contact pH sensor as can be seen in the Fig. 1, the estimation of the electropolymerized conditions such deposition time, concentration of counterion in electrolyte solution, and incorporation of various counterions into the polymer film are important to the development process.

A polypyrrole film was deposited on the glassy carbon electrode surface by oxidation of monomer from an aqueous solution containing the dodecyl sulfate (PPy/DS) as supporting electrolyte. Chronopotentiogram was recorded during film growth. Relatively constant potential was observed throughout the polymerization, indicating the formation of a conductive polymer layer.

Cyclic voltammograms recorded in NH₄Cl solution after growth of PPy/DS were conductive in analyte solutions of counterion. Counterion injection and release to accompany the redox cycling of electropolymerized polypyrrole films in electrolytes were observed.

Since PANi has a variety of oxidation states, cyclic voltammetry method for electrochemical growth of PANi was employed. In the literature, the acidity of the solution has significant influence on the synthesis of polyaniline. It is evident that the incorporation of each aniline molecule to the growing polymer chain results in the release of two protons. So, if the medium is not buffered, the local pH may decrease dramatically in the vicinity of the growing film and the polymerisation reaction could actually take place in an acidic medium. Fig. 2A shows cyclic voltammograms recorded during the oxidation of 0.5 M aniline on a GC electrode in a 0.5 M H₂SO₄ solution. The film growth of PANi is slow at the beginning of the polymerisation, but increases considerably from cycle to cycle after approximately the first 10 cycles. The growth can be easily perceived because of the increase of the voltammetric peaks related to polaron and bipolaron waves.

In order to estimate the possibility of conducting polymer employing as solid-contact layer in solid-contact pH sensor, pH sensitivity of different polymer electrodes were measured over pH range between 2 and 12. As can be seen in Fig. 3, the potential responses of all conducting polymer modified electrodes were a Nernstian slope of 55 mV.dec⁻¹ in linear part between 5 and 12. However, PANi modified electrodes can establish equilibrium response faster than Ppy modified electrodes. Further additions, the PANi modified electrode, which is electropolymerized for 30 cycles, exhibit the best potentiometric response in pH solution in comparison with other conducting polymer electrodes.

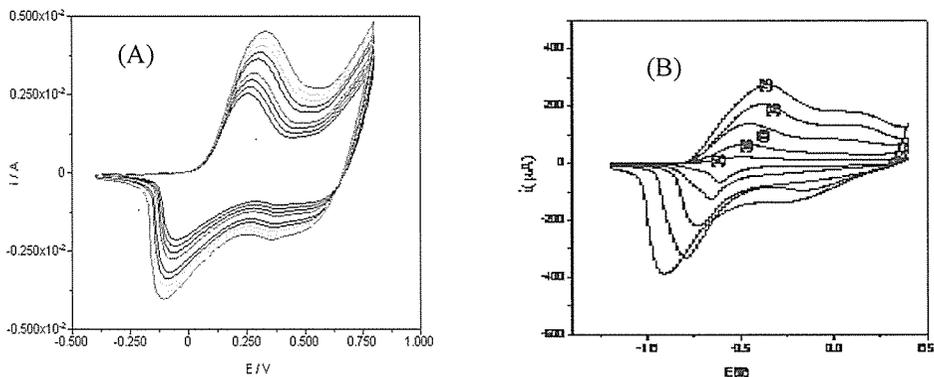


Fig. 2. Cyclic voltammograms of a conducting polymer modified electrode in an electrolyte solution. A) Cyclic voltammograms recorded during electrochemical polymerization of polyaniline by cyclic voltammetry; B) Cyclic voltammograms at different scan rates of the polypyrrole modified electrode recorded after galvanostatic electropolymerisation for 600s.

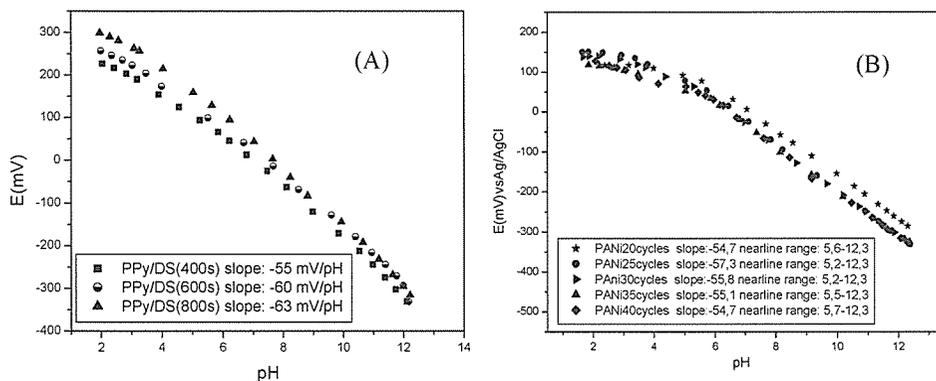


Fig. 3. The potentiometric response of a conducting polymer modified electrodes in an electrolyte solution with different pH values. A) polypyrrole modified GC electrode, and B) polyaniline modified GC electrode.

Potentiometric response characteristics of solid-contact pH sensors

Principle pH sensor characteristics, such as Nernstian slope, dynamic linear range, detection limit and selectivity depend on the composition of the ion selective membrane and potentiometric stability of ISEs depend on solid-contact layer based on conducting polymer film. In order to estimate the affect of conducting polymer film to the potentiometric response of solid-contact pH sensors, two pH sensors based on Ppy and PANi films incorporate with membrane pH-2 (TDDA/DOS/PVC) were prepared. The calibration plots were recorded over a pH range between 2 and 12. As can be seen in Fig. 4A, the potential responses of both solid-contact sensors were very stable in the linear part of pH from 2.3 to 11.5 of dynamic response curve with a Nernstian slope of $57 \pm 1 \text{ mV.dec}^{-1}$ ($n=4$) on the first day measurement. The stable potential response of the solid-contact pH sensors in the measured pH range is believed to be the result of a better-defined interfacial potential between the sensing membrane and the solid – contact layers.

However, the potential responses of two these sensors showed some different after 30 days conditioning in the pH buffer solution. The solid-contact pH sensor employing PANi films

showed no significant change in a Nernstian response and linear range, meanwhile, pH sensor employing Ppy/DS films exhibited significant decrease in potentiometric response and Nernstian slope of linear part calibration (see Fig 4B). The change of Ppy based solid-contact pH sensor was attributed the decreasing of capacity exchange of hydrogen ions at interface of Ppy/DS layer.

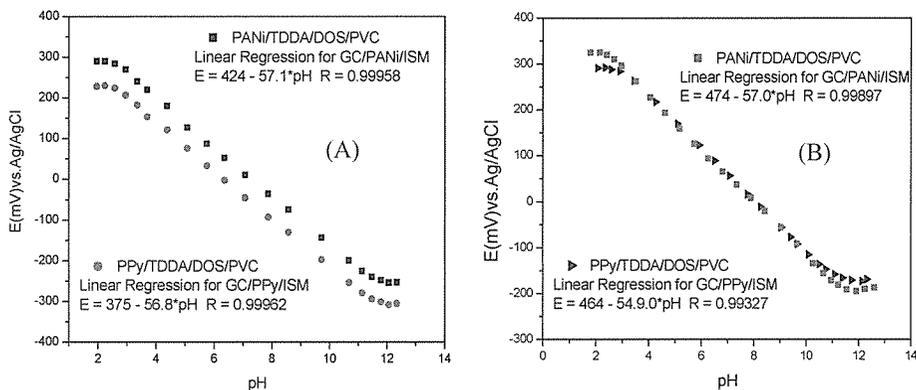


Fig. 4. Comparison of potential responses of solid-contact pH-sensors employing different conducting polymer films for a long-term. A) the first day of measurement; and B) after conditioning in pH buffer for 30 days.

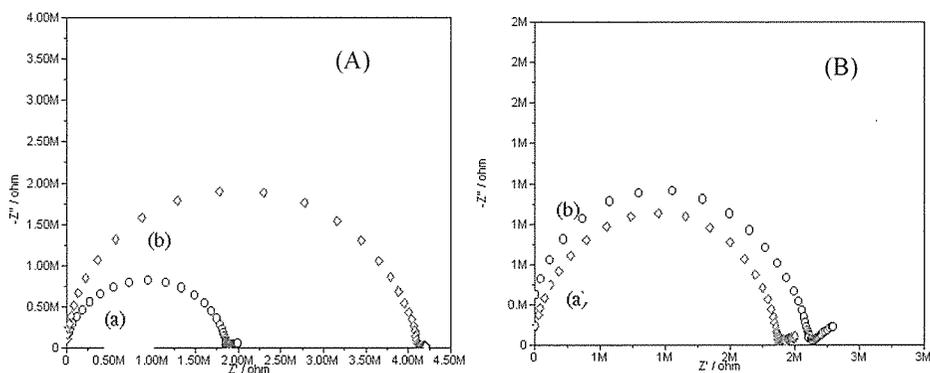


Fig. 5. Typical impedance spectra for solid-contact pH sensors employing conducting polymer as solid-contact layer.

Electrochemical impedance spectroscopy

Examples of impedance spectra of solid-contact pH sensors are shown in Fig. 5. The high frequency semicircle can be related to the bulk resistance (R_b) and geometric capacitance (C_g) of the plasticized PVC membrane, while the low frequency response can be related to interfacial charge transfer and diffusion processes in the ion selective electrode. The low frequency response also influenced by the solid-contact used as ion-to-electron transducer. As can be seen in Fig 5A, the PANi based solid-contact pH sensor employing membrane containing TDDA ionophore in DOS plasticizer shows the smaller bulk resistance ($1.89 \text{ M}\Omega \cdot \text{cm}^2$) than other pH sensor employing membrane containing DODMA ionophore in DOS ($4.1 \text{ M}\Omega \cdot \text{cm}^2$). Further additions, impedance spectra of pH sensors with the same ion-selective membrane (TDDA/DOS/PVC) and employing different conducting polymer membrane such as PANi and Ppy have been given in Fig 5B. Measuring results indicated that

bulk resistance of conducting polymer layers is insignificant to the bulk resistance of solvent polymeric membranes.

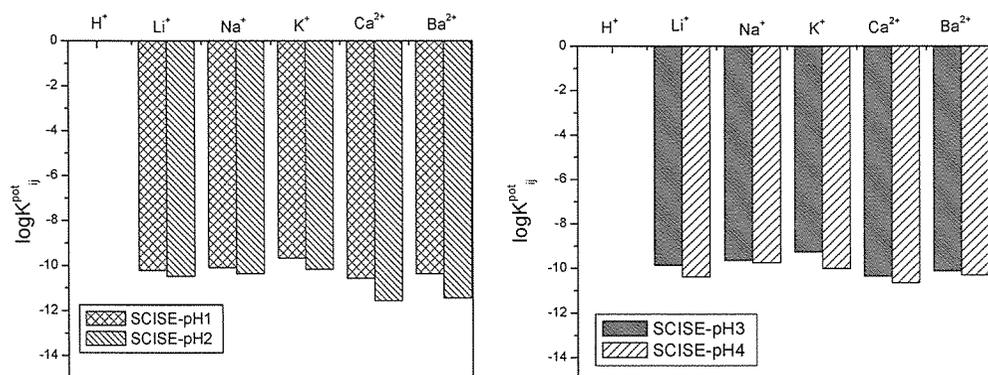


Fig. 6. Selectivity factors, $\log K_{ij}^{\text{pot}}$ for the PANi based solid-contact pH sensors employing different ion-selective PVC membranes: pH1: TDDA/DOS; pH2: TDDA/ETH469; pH3: DODMA/DOS; pH4: DODMA/ETH469.

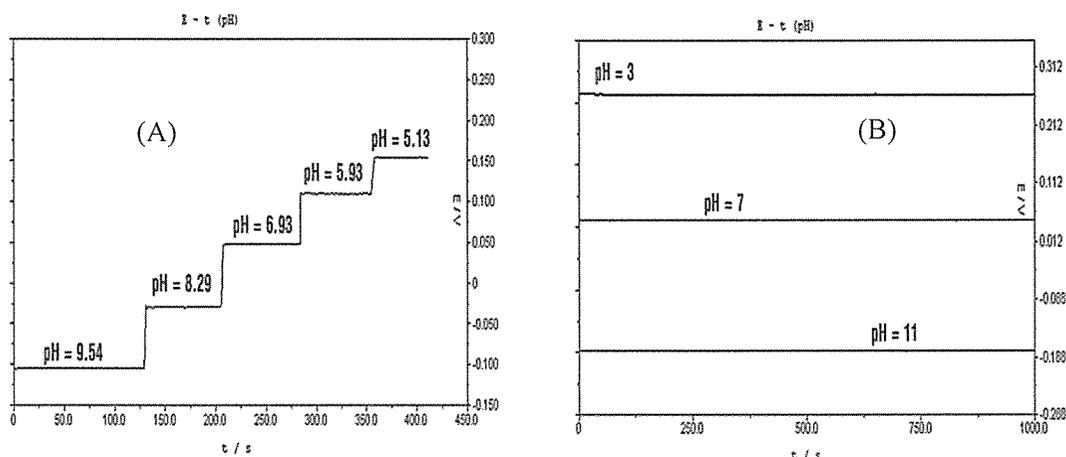


Fig. 7. A) Dynamic potentiometric response time; and B) stable potential responses of PANi based solid-contact sensor in the different pH solutions.

All the solid-contact pH sensor give the same geometric capacitance, i.e., the dielectric constant of the plasticized PVC membrane is not significantly influenced by the ionophore.

As can be seen in Fig. 5, all solid-contact pH sensors does not show significant Warburg diffusion line, indicating fast interfacial charge transfer and diffusion processes as well as a high capacitance of the solid contact where ion-to-electron transduction takes place.

The selectivity factor values of four PANi based solid-contact pH sensors employing ion selective membranes using hydrogen ionophores such TDDA and DODMA incorporate with different plasticizers such as DOS and ETH49 were obtained by the fix interference method (FIM). The selectivity coefficient values are given in Figure 6. The resulting values of $\log K_{\text{HM}}^{\text{pot}}$ for these pH sensors are almost below -10.0 for all testing cations such as Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+} . Furthermore, the selectivity factor values of pH sensors employing TDDA and/or DOS as plasticizer, exhibit higher selectivity than those containing DODMA and/or ETH469.

Response time of solid-contact pH sensors was also investigated, because it is an important factor in terms of the practical use of these sensors. The time taken for the pH sensors to attain 90 % of the steady-state response was typically a few seconds (see Fig. 7A)

The potential response of the PANi based solid-contact sensor was very stable in the measured pH range both in a short term and long term (see Fig. 7B) for more two months without decreasing of an initial slope.

CONCLUSIONS

The solid-contact pH sensor was successfully constructed by using a conducting polymer as ion-to-electron transducer in combination with a plasticized PVC based membrane containing proper plasticizer and ionophore. The resulting solid-contact ISEs showed excellent selectivity in concentration over the range of pH from 2.5 to 11.3 with a Nernstian slope of 57 mV.dec⁻¹. The PANi based solid-contact pH sensor employing PVC membrane containing DOS and TDDA exhibited a fast response (5 seconds) and relatively high robustness in steady-state measurement at least during two months without any loss of performance. This study will contribute to the design and construction of multi-sensors array.

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