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Near-Infrared pH Sensor based on SPEEK-Polyaniline Polyelectrolyte Complex Membrane

Nedal Y. Abu-Thabit*

Department of Chemical and Process Engineering Technology, Jubail Industrial College, Jubail Industrial City 31961, Saudi Arabia;
Correspondence: abuthabit_nidal@yahoo.com; Tel.: +966-13-340 5418

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Abstract: Polyelectrolyte complex (PEC) membrane based on sulfonated poly(ether ether ketone) and polyaniline (SPEEK-PANI) was developed for pH sensing application. Aniline was polymerized in the presence of SPEEK membrane by using in situ chemical oxidative polymerization to yield an ionically crosslinked SPEEK-PANI membrane. The fabricated membrane exhibited sensitivity in the physiological pH range of 2-8. The PEC membrane pH sensor showed good absorption properties in the near-infrared region (NIR). The membrane showed fast response during de-doping process (≈ 90s), while longer response times are essential for doping process from alkaline/ neutral pH region to acidic pH region, which is attributed to the presence of highly acidic sulfonic acid groups with high buffering capacity in PEC membrane. SPEEK-PANI membrane exhibited slightly higher water uptake as compared to neat SPEEK membrane. The membrane exhibited good stability as it was stored in 1M HCl solution for more than 2 years without physical or visual deterioration. A preconditioning step in 1 M HCl ensures obtaining reproducible results and allows for the pH sensor to be used repeatedly. The PEC sensor membranes are suitable for applications that start at low pH values and move upwards to higher pH values in the 2-8 pH range.

Keywords: Polyelectrolyte complex; pH sensor; Near-Infrared; polyaniline; SPEEK; Membrane; Optical

1. Introduction

Polyelectrolytes are charged macromolecules with positive or negative charges, which termed as cationic polyelectrolytes and anionic polyelectrolytes, respectively. When two oppositely charged polyelectrolytes mixed, a polyelectrolyte complex (PEC) forms due to the gained entropy upon release of counter ions [1]. PEC can be formed by different techniques such direct polyelectrolyte titration [2], jet mixing [3], direct mixing with required substrate [4], layer-by-layer assembly (layered PECs) [5-7] and in situ polymerization of a suitable monomer onto a preformed macromolecule which is known as “template” or “matrix” polymerization [8, 9].

PECs have been employed in a variety of applications such as self-healing coatings [10], sensors [11], biosensors [12] and biomedical applications [13-15]. PEC membranes is considered to be a special class of PECs which can be prepared using LbL assembly [16] or by direct mixing of polycations and polyanions followed by casting process [17]. PEC membranes are pH-responsive due to the presence of physical ionic crosslinks that can be altered by pH change in the surrounding environment [18]. The swelling/ de-swelling behavior of pH-responsive PECs enables their use for optical pH sensing applications [11, 19, 20]. In this paper, we employ in situ chemical oxidative polymerization to prepare an optical pH-responsive PEC membrane by polymerizing aniline monomer onto a solid SPEEK membrane.

2. Experimental:

2.1. Materials:

Ammonium persulfate (APS) (ACS reagent, 98.0%), $NaH_2PO_4 \cdot 2H_2O$ (ACS reagent, 98%–100.5%), Na_2HPO_4 (ACS reagent, 98%–102%), NaCl (>99.5%), Na_2CO_3 (ACS reagent ≥99.5%), and $NaHCO_3$ (ACS reagent ≥99.7%), N,N-Dimethylacetamide (anhydrous, 99.8%) were received from Aldrich (Milwaukee, WI, USA). Sulfonated poly(ether ether ketone) (SPEEK) having a degree of sulfonation (DS) = 75 was acquired from Fumatech (Germany). Aniline was distilled twice and stored in the dark at 5 °C before use. The PBS buffer system was prepared as reported in our previous work [21].

2.2. Preparation of SPEEK-Polyaniline PEC Membrane

SPEEK membranes were casted from 5 wt. % N,N-Dimethylacetamide solutions using glass Petri dishes to yield membranes with thicknesses of ≈50 μm. PEC membranes were prepared by using in situ chemical oxidative polymerization as following: Dried SPEEK membranes were immersed in 500 mL of 1M HCl solution for 30 minutes. After that, 0.5 mL aniline monomer was added to the reaction vessel and stirred for 30 minutes. Finally, 10 mL solution of a pre-dissolved 1.45 g APS/1 M HCl solution was added to the reaction mixture. After a certain period of reaction time, the resulted greenish color SPEEK-Polyaniline PEC membrane was removed and washed repeatedly with distilled water ensure the removal of unreacted materials. The membrane was stored in 1M HCl solution for further analysis.

2.3. Sensor characterization and pH measurements

A double beam spectrophotometer Cintra 2020 (GBC Scientific Equipment, Australia) was used for recording the absorbance in the range of 400-1000 nm. The reference cell holder was filled with the desired pH buffer solution, and the sensor membrane (6 cm long x 0.6 cm wide) was placed and fixed in the sample cell holder filled with the same pH buffer solution and the measurements were performed in a batch mode. All the measurements were done as triplicates and the standard deviations were calculated accordingly. To calculate the pH values based on the detected absorbance, the optical pH sensor membrane was calibrated using a Four Parameter Logistic (4PL) nonlinear regression model, with sigmoidal curve fitting according to equation (1):

$$\boldsymbol{A} = d + \frac{a - d}{1 + \left(\frac{pH}{c}\right)^{b}} \qquad (1)$$

where, A is the measured absorbance; a is minimum asymptote; d is the maximum asymptote; c is the inflection point; and b is the hill's slope.

This enables the measurement of pH over a wide proton concentration range, as the pseudolinear part of the calibration curve is not the only part used. From the constructed calibration curve, the pH can be calculated as shown in equation (2):

$$\boldsymbol{pH} = cx\ \frac{(\boldsymbol{A} - d)}{(a - \boldsymbol{A})}^{(1/b)} \qquad (2)\ (2)$$

3. Results and Discussion:

Chemical oxidative polymerization is simple and rapid method for preparation of polyaniline-coated substrates for a variety of applications [22]. In this study, the PEC membrane was prepared by chemical oxidative polymerization of aniline in the presence of solid thin film of SPEEK. The transparent SPEEK membrane changed into green color upon completion of the reaction. Polyaniline is a pH-responsive polymer that has a positive charge on its backbone. The presence of strong sulfonic acid groups (pKa < 1) allows SPEEK to: (1) act as anionic polyelectrolyte dopant for the cationic polyaniline, Figure 1; and (2) swell fast due to the solvation of $-SO_3H$ groups by the surrounding water molecules [23]. Table 1 displays the swelling properties of the neat SPEEK and SPEEK-PANI PEC membranes. Both membranes have reasonable water uptake values which ensure the wettability of the membrane's surfaces for fast ion-exchange process during switching through different pH values. The slight extra water uptake for SPEEK-PANI membrane could be attributed to the higher hydrophilicity of the polyaniline matrix.

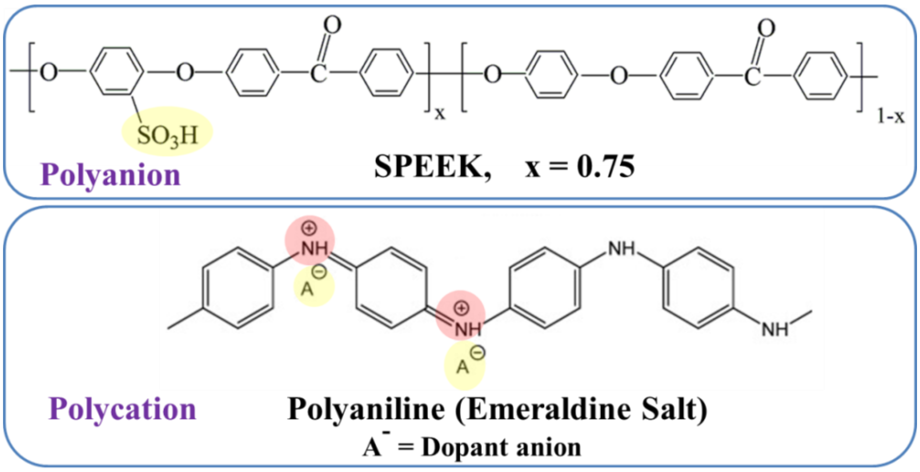

Figure 1. Chemical structures of SPEEK with degree of sulfonation =75% (top), and polyaniline (bottom).

Table 1 Water uptake values at room temperature.

Membrane type	**Water uptake (%)**
SPEEK	35.2
SPEEK-PANI	35.8

Polyaniline is a conductive polymer which has been utilized for pH sensing applications due to its pH-responsive nature [24-27]. The pH sensing property of polyaniline arises from the swelling-deswelling equilibrium upon pH change during the doping/ dedoping process. The obvious advantage of using polyaniline is the chemical stability of the macromolecular indicator compared to the leachable indicator molecules. The former property allows for preparation of reusable sensors with extended life time and reproducible results [21].

The prepared sensor membranes were tested as an optical pH sensor across the visible and near infra-red (NIR) regions (400–1000 nm). SPEEK-PANI PEC membranes exhibit well-defined pH sensitivity in the pH range of 2–8, Figure 2. The experiments were conducted from pH 2 to 8, with 1 pH unit increments. After each experiment, the membrane was reconditioned by rinsing with 1M HCl. The absorption maxima was shifted from (λ = 810 nm at pH = 2) to (λ = 840 nm at pH = 8), which is attributed to the strong ionic interactions and hydrogen bonding between the sulfonic acid groups and the imine groups [28]. Hence, the absorption maxima in the NIR was selected in the middle range (λmax = 825 nm). As expected, the absorption decreases with increasing the pH due to gradual conversion of polyaniline from the conductive Emeraldin Salt (ES) into the non-conductive Emeraldin Base (EB) via the dedoping process. Regardless, at basic pH =8, the strong blue shift is not observed which means that the pKa of the polymer is above 8. This behavior could be attributed to the fact that the sulfonic acid groups with low pKa (<1) has a strong ionic interaction and cannot be exchanged easily due to the formation of strong hydrogen bonding with polyaniline [29]. In other words, the sulfonic acid groups tethered from the bulky macromolecule chains require more alkaline conditions (higher basicity) to be titrated and exchanged with small anions.

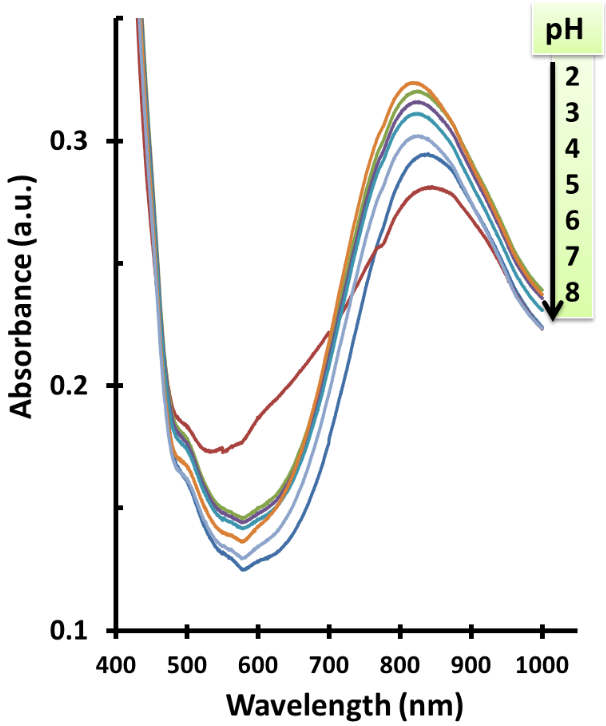

Figure 2 The absorption spectrogram in the visible and near-infrared region for the sensor membrane at different pH.

3.1. pH Measurements

The calibration graph for pH dependence of the absorptions at 825 nm is shown in Figure 3a. The measurements were done in triplicates with a standard deviation of the absorbance value over the calibration range less than 0.003 (a.u.). The obtained data were fitted by using the four parametric logistic equation (1), and the calibration curve (R2 = 0.996) was obtained for the absorbance change vs. pH, Figure 3b. This calibration graph, which has semi-sigmoidal curve character, can be used to find out the pH values of unknown solutions using equation (2), going from low to high pH (forward titrations). The backwards titrations (from high to low pH) were not feasible to be carried out (refer to the discussion of the next section).

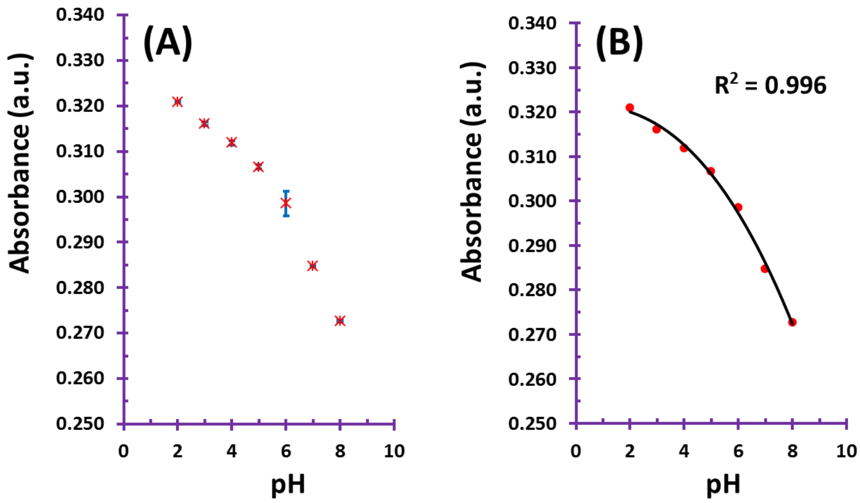

Figure 3 (A) Graph of the absorbance change vs. pH for SPEEK-PANI sensor membrane during forward titrations, pH 2 pH 8; and (B) the calibration curves for the pH dependence of the absorption at 825 nm.

3.2. Response time

The sensor response time is defined as the time required for the sensor output to reach 90% of the change from its previous value to the final settled value [30]. Figure 4 displays the response diagrams for the membrane sensor during both doping and de-doping processes. The response time for the de-doping process, moving from pH 2 upwards to pH 8, was found to be ≈ 90 s, Figure 4a. However, moving in the reverse direction from pH 8 downwards to pH 2 (doping process) proved to be troublesome and requires long times that are not practical for sensing applications. This observation is evident from Figure 4b as there is a negligible increase in the sensor reading during the first five minutes. This behavior could be attributed to the presence of highly acidic sulfonic acid groups as dopants (pKa < 1) which have strong and broad buffering effect in the applied pH range. Regardless this shortcoming, SPEEK-polyaniline sensor membranes can be conditioned with 1 M HCl and used repeatedly for applications that start at low pH and move forwards to higher pH values in the optimized range.

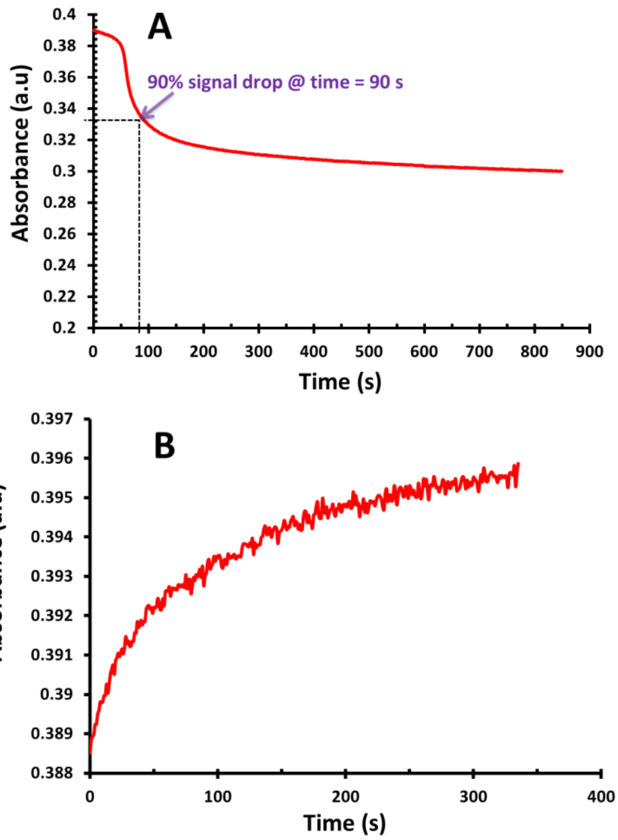

Figure 4 Response times for SPEEK-polyaniline membranes at wavelength = 825 nm for: (A) forward titrations (from pH 2 pH 8); and (B) backward titrations (from pH 8 pH 2). The membrane was conditioned initially with 1 M HCl, and then placed in the required starting buffer solution until a constant reading was obtained; this was followed by placing the membrane in the new buffer solution for measuring the absorbance. The process was repeated many times with the same membrane sensor.

3.3. Sensor stability:

The PEC membrane sensor was stored and preserved in 1 M HCl solution for more than 2 years without any observed physical deterioration of disintegration. The readings for the sensor membrane were checked during interval periods of 2 months and the variation in the obtained readings was found to be within the machine error (≤ 0.02 absorption units).

4.0. Conclusions:

The current study reports the fabrication of PEC membrane sensor based on SPEEK as anionic polyelectrolyte solid membrane coated with pH-responsive polyaniline as the cationic polyelectrolyte. The pH sensor membrane exhibited well-distinguished sensing in the pH range 2-8, and displays the maximum absorbance in the near-infrared region at λmax = 825 nm. The calibration curve for pH measurement was constructed using a Four Parameter Logistic (4PL) nonlinear regression model and resulted in semi-sigmoidal curve (R2 = 0.996). The response time for the sensor membrane was found to be about 1.5 minute during the movement from low pH to high pH environments (de-doping). The sensor required extended times for responding in the reverse direction. This phenomenon requires more investigations in the future. Regardless, the sensor membrane is stable, can be reconditioned using 1M HCl and is suitable for applications where the movement direction is from acidic to alkaline medium in the 2-8 pH range.

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