

# pH Electrodes Constructed From Polyaniline/zeolite and Polypyrrole/zeolite Conductive Blends

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**ABSTRACT:** A new type of solid state electrodes sensitive to pH changes is described, in which the chemical-sensitive layer consists of Pt microparticles deposited on a conducting polymer (polyaniline, polypyrrole) blend containing 22.7% w/w zeolite. These sensors are stable in aqueous electrolyte solutions of low pH value at temperatures up to 45°C with response time in seconds. At 25°C, sensor sensitivity was

$-310 \pm 40$  mV/pH and  $-1300 \pm 100$  mV/pH for polyaniline and polypyrrole blends, respectively. Interferences appear to be acceptably small. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1853–1856, 2006

**Key words:** conducting polymers; electrochemistry; charge transport; blends; surfaces

## INTRODUCTION

Electrochemical cells containing conducting polymers as electrodes permit the construction of miniature, compact detectors that cannot be damaged in highly corrosive environments.<sup>1–3</sup> A major impediment to the application of the conducting polymers for the construction of electrochemical devices has always been their processibility, as well as their mechanical properties. The development of polymer blends resulted in the improvement of their mechanical properties,<sup>4–7</sup> and the application of polyaniline (PA) and polypyrrole (PPy) in electrochemical devices has been reported.<sup>8–10</sup> In the present work, the behavior of a new type of solid state pH electrodes based on an electrochemical cell constructed of a Pt microparticles layer on a conducting polyaniline/zeolite and PPy/zeolite blend with 22.7% w/w in zeolite is studied. Zeolite with its pores, channels, and cages provides great effective surface for cations to be arranged by adsorption, intercalation, or cation exchange reaction. As a result, this has the minimization of the cell volume. Moreover, the acidity of the zeolite surface ensures the good adhesion with the conducting polymer and so the easy charge carrier transport through the cell, minimizing the internal resistance and maximizing its efficiency. Besides, the intercalation of a conducting polymer into a porous and leafy material, like zeolite,

protects the former from degradation, reducing its aging rate.

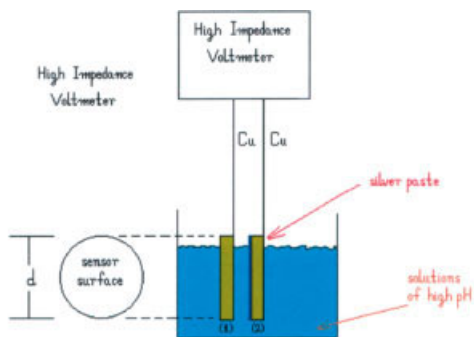
## EXPERIMENTAL

Clay mineral must be purified according to the following procedure<sup>11,12</sup>: first, it is dispersed in distilled water and the emulsion is stirred for 24 h. If the solution becomes viscous like a gel, water is added until the gel is dispersed. The suspension is then purified by sedimentation to collect  $<2\mu\text{m}$ , in diameter, fraction, washing with 1M  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOH}$  (pH = 5) to remove carbonate. Then washing with 0.3M sodium citrate, 1M  $\text{NaHCO}_3$ , and  $\text{Na}_2\text{S}_2\text{O}_4$  to remove free iron sulfide takes place. The precipitate is dispersed in 100 mL 1N NaCl and is stirred for 30 min. The emulsion is repeatedly centrifuged to obtain the same type of exchange cations.

Polyaniline and PPy blends were prepared by chemical polymerization at room temperature in 0.2N HCl aqueous solution (monomer: oxidant = 1:1 mol %) and in the presence of pure zeolite added prior of the monomer and oxidant addition.<sup>13,14</sup> The oxidant was  $\text{FeCl}_3$  (Ferrak, Analar). The precipitates were washed with 1N HCl and dried overnight under nitrogen atmosphere.

From these precipitates, PA/zeolite and PPy/zeolite blends disc-shaped specimens 13 mm in diameter and 1.5 mm thick were made in an infra red press with 22.7 and 22 w/w content in zeolite, respectively. The selection of the above concentrations is due to the best mechanical properties of the disc-shaped specimens in further handling and chemical deposition of Pt micro-

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- (1) Conducting Composite material (CCM)
- (2) CCM with Pt microparticles deposited over a two-day period by simply bathing of the composites in dilute aqueous solution  $\text{H}_2\text{PtCl}_6$ , 2% w/w, pH = 3.

**Figure 1** Schematic diagram of the sensor device. [Color Figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

particles. Furthermore, the Pt microparticles deposited on the surface of the polymer composites by simply bathing of the composites over a 2-day period in dilute aqueous solution  $\text{H}_2\text{PtCl}_6$  2% w/w, pH = 3. The deposited particles show excellent adhesion and are not removed by sonication. Pt particles may grow by an island mechanism and the metal Pt is in the zero oxidation state.<sup>1</sup>

The resulting conducting materials were characterized by scanning electron microscopy, (SEM, JEOL JSM 5200) equipped with surface microanalysis, Energy Dispersive X-ray Spectroscopy, EDS, (Philips, 1300/00, Cu-K $\alpha$  radiation), and chemical microanalysis.

For the conductivity measurements, a centered square four-probe array of electrical contacts, made by pressing platinum wires against the specimen, was employed.<sup>15</sup> Measurements of the d.c. conductivity against temperature were made in a cryostat cooled by liquid  $\text{N}_2$ .

The pH-measurements were done in a thermostated double-walled, water-jacketed Pyrex vessels, of 0.200  $\text{dm}^{-3}$  total volume. Solid reagent-grade (Merck) reagents and triply distilled  $\text{CO}_2$ -free water were used in the preparation of the solutions (Fig. 1).

Potassium hydroxide and hydrochloric acid solutions were prepared from concentrated standards (Merck, Titrisol). All solutions were filtered through membrane filters (0.22  $\mu\text{m}$ , Sartorius).

The solution pH was measured by a glass/saturated calomel pair of electrodes (Metrohm) standardized before and after each experiment by NBS buffer solutions (pH = 6.868 and 7.418 at 37°C).<sup>16</sup> The output voltage  $E$  (mV) was measured by a high impedance voltmeter (KEITHLEY 2000).

## RESULTS AND DISCUSSION

Many relations have been proposed to describe the temperature dependence of conductivity<sup>17–19</sup> for various conductive polymers and polymer blends, fresh or aged, in various temperature ranges.

The conductivity of the PA samples was thermally activated<sup>20</sup> and its dependence versus temperature follows the formula:

$$s = s_0 \exp[-(T_0/T)^{0.5}] \quad (1)$$

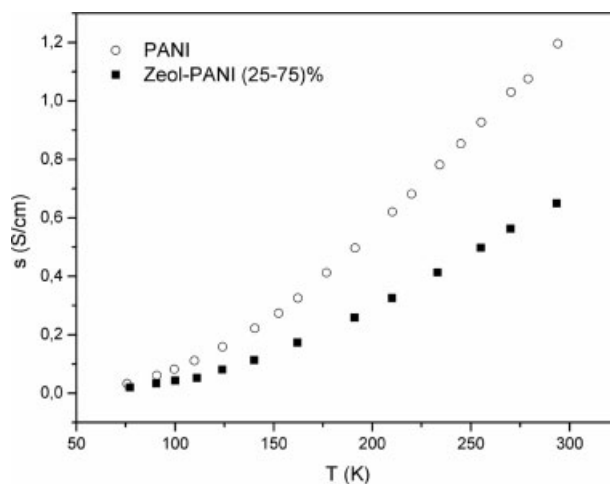
predicted by the Charging Energy Limited Tunneling model valid for a material with heterogeneous structure of the granular metal type.<sup>21</sup> In this model, conducting grains are randomly distributed into an insulating matrix and the conduction is due to charge carrier tunneling between the conducting grains. The same temperature dependence holds for the PA/zeolite blends too, as shown in Figure 2. The lower conductivity of the blend may be attributed to the trapping of charge carriers by the periodic zeolite framework.<sup>22</sup>

Polypyrrole exhibits a thermally activated conductivity,<sup>20</sup> which is described satisfactorily by the following equation:

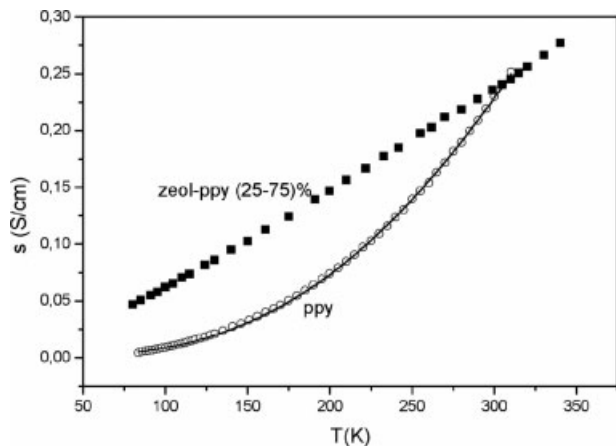
$$s = s_0 \exp[-(T_1/T + T_0)] \quad (2)$$

predicted by the Fluctuation Induced Tunneling model, which assumes conductive grains that are separated by insulating barriers<sup>23</sup> narrower than those in PA. The parameters  $s_0$ ,  $T_0$ , and  $T_1$  are related to intrinsic material characteristics.<sup>24,25</sup>

It is apparent from Figure 3 that though Fluctuation Induced Tunneling model successfully describes the temperature dependence of conductivity for both cases, one could also state that a linear law could also



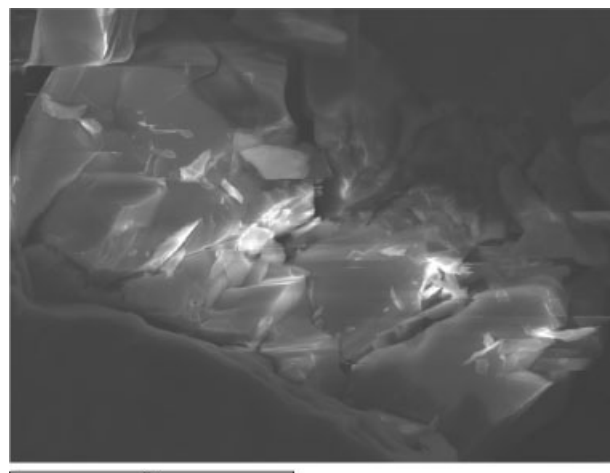
**Figure 2** Plots of the electrical conductivity as a function of temperature, (■) PA-zeolite blend, (○) PA.



**Figure 3** Plots of the electrical conductivity as a function of temperature, (■) PPY-zeolite blend, (○) PPY.

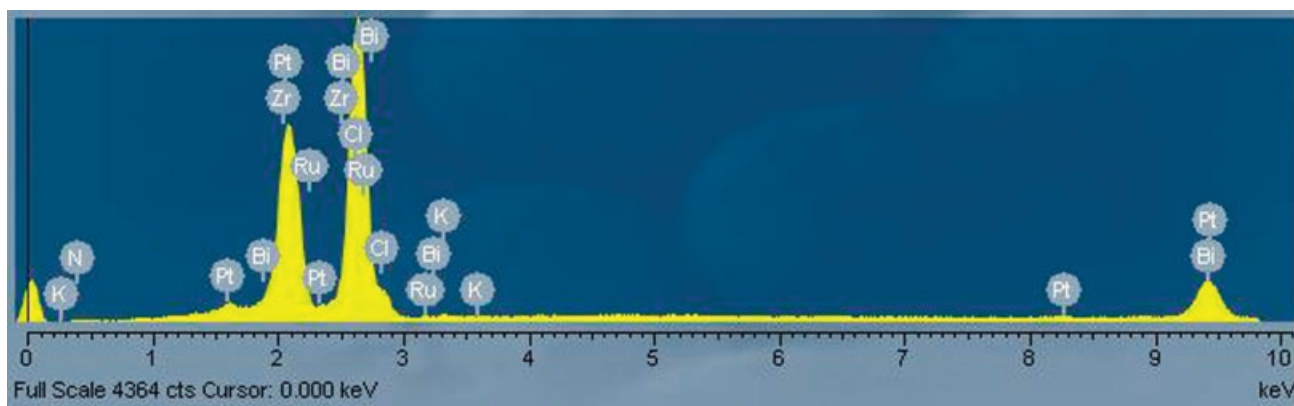
approximately describes the phenomenon. Kivelson proposed such a law according to which the interchain transport occurs by hopping between neutral and charged soliton or polaron states at isoenergetic levels.<sup>26</sup> The nanoscopic pores of zeolite favor a slight orientation of polymer domains which improves the electrical conductivity of the material.<sup>27</sup>

In Figure 4, a typical scanning electron microscopy micrograph of the PA-zeolite-Pt surface is shown. The deposited Pt particles show excellent adhesion and are not removed by sonication. Pt particles grow by a birth and spread mechanism<sup>28,29</sup> and after some hours form a continuous film as shown in the micrograph. The above is also confirmed by EDS analysis as shown in Figure 5. Control of particle size is possible through varying the time of bathing, temperature, and solution concentration. This new aqueous phase deposition, compared with complex and expensive vacuum deposition methods, is a simple technique for making interfaces between metal nanostructures and conducting polymers.

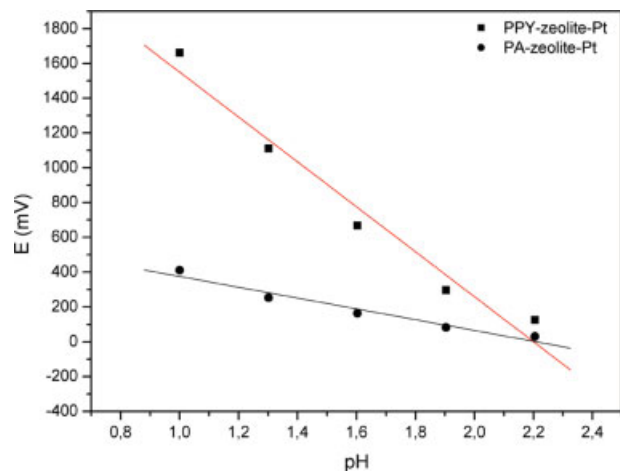


**Figure 5** EDS analysis of the surface of the PA-zeolite-Pt.

The electromotive force  $E$  versus the pH values for the conducting polymer/zeolite cells are shown in Figure 6. The slopes of the two straight lines determine the sensor sensitivities, which are  $-310 \pm 40$  mV/pH and  $-1300 \pm 100$  mV/pH for PA and PPY blends, respectively. The sensitivity of a PPY/zeolite sensor is about three times higher than the one of a PA/zeolite cell. This may be attributed to the fact that in PPy the conductive grains are amorphous and the chains enter easily the zeolite cages, though the crystalline nature of the PA conductive grains make this arrangement more difficult. The effect of dissolved  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ag}^+$  was essentially negligible at concentrations up to  $10^{-3}$  M. The reproducibility of the measurements was 7% (a mean of five experiments). As temperature increases, the slope of the sensors decreases to  $87 \pm 10$  mV/pH and  $390 \pm 32$  mV/pH for PA and PPy blends, respectively, at  $45^\circ\text{C}$ . There is a very complex sensing mechanism of the  $\text{H}_3\text{O}^+$  concentration in the solution because of the



**Figure 4** Scanning electron micrograph of the PA-zeolite-Pt surface. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** pH response of the (■) PPY-zeolite-Pt electrode and (●) PA-zeolite-Pt electrode. [Color Figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

conductive polymer blend construction. The conducting polymer itself was affected by the hydrogen cation concentration through the doping mechanism of these type of conducting materials.<sup>9,14</sup> Also, the zeolite content (83 meq/100 g cation exchange capacity) with its cavity structure affected by the  $H_3O^+$  concentration.<sup>10,11</sup> Redox reactions involving  $H_3O^+$  cations take place on Pt microparticles surface<sup>30</sup> as well as on conducting PA and PPy surface itself.<sup>6</sup> The above-mentioned interactions of the  $H_3O^+$  cations and the conductive blends resulted in a synergistic complex sensing mechanism with sensitivity of the blend electrodes much higher than the normal pH sensor (usually lower than 59 mV/pH).<sup>16</sup>

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