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Conducting polymer based pH detector: a new outlook to pH sensing technology

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The development of a new pH sensing technology using conducting polymers is addressed. Three different polymers have been examined as new pH sensor materials. The resistance of polypyrrole and polyaniline have been found to be pH dependent. The composite made of these two polymeric systems suggest a promising supramolecular structure for pH sensor applications. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: conducting polymers; resistance; pH sensor)

INTRODUCTION

The monitoring of the pH of solutions is widely required in laboratories, clinics and industries as many chemical processes are pH dependent. 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 electrodes do not provide accurate data at very high and very low pH values because of alkaline error and dehydration, respectively[1,2]. The electrode also needs special care and treatment before and after use[2]. Improvement of pH measuring techniques to overcome existing problems may be achieved by exploration of new sensing materials. Nata and co-workers have introduced pH sensitive microelectrochemical transistors based on WO_3[3] and $Ni(OH)_2$[4]. In this work the use of conducting polymers to form the basis of new pH sensors has been considered. In acidic media, polyaniline (PAn) can be oxidized and reduced from a more conductive (oxidized) to a less conductive (reduced) form; deprotonation of the polymer at high pHs results in decreased conductivity[5,6]. The conductivity of polypyrroles (PPys) in the oxidized form is also known to be pH dependent with resistance increasing dramatically above pH 12[7,8].

In this paper the sandwich electrode already described[9,10] has been employed. The effect of pH on polypyrrole chloride (PPy/Cl), polypyrrole vinyl sulphonic acid (PPy/PVS), polyaniline chloride (PAn/Cl) and PPy/PVS–PAn/Cl composite is discussed in a stationary cell. We then point out the practical utility of the conductive polymer electrodes in monitoring solution pH in a continuous flow system.

EXPERIMENTAL

Reagents and standard solutions

All reagents were of analytical grade purity unless otherwise stated. Pyrrole was obtained from Aldrich and aniline was obtained from BDH. All salts were also obtained from Aldrich and all acids were supplied by BDH. All aqueous solutions were prepared in deionized (Milli-Q) water.

Procedure

Voltammetric data were obtained using a BAS CV 27 Voltammograph. Data were collected using a Maclab (Analog-Digital Instruments, Sydney, Australia) interface or Electrolab and an Apple computer. Pulse resistometry measurements were facilitated by the use of a resistometer developed at the CSIRO Division of Mineral Products, Melbourne, Australia. A 10 mV d.c., home made, power supply was employed for applying voltage, and a multimeter model HP 3465B was used for recording currents.

Polymerizations were carried out potentiostatically in a three-electrode electrochemical cell. All polymers were grown at constant charge and constant potential (for PPys $E = 0.75\,\mathrm{V}$ and $Q = 100\,\mathrm{mC}$, for PAns $E = 0.80\,\mathrm{V}$ and $Q = 20\,\mathrm{mC}$). The working electrode was a platinum sandwich electrode, and the reference and auxiliary electrodes were Ag/AgCl and a platinum plate, respectively. Solutions of different pHs were prepared from HCl and NaOH by dilution with 1 M NaCl to keep the ionic strength almost constant. The polymer resistance was recorded in different solutions when the values had stabilized. This varied from 1 to 3 min. The time response of each polymer during its metallic/insulator transition was measured by immersing the polymer in a solution of higher pH and then lower pH. The current was then recorded at each time the changes were observed. The resistance was then calculated and the curves of R *versus* time were plotted.

RESULTS AND DISCUSSION

It has been discussed that pulse resistometry is a useful technique for the characterization of conducting polymers, and d.c. resistometry is a simple and helpful technique for applying conducting polymers in sensing technology[11–15]. Initially, pulse resistometry was used to

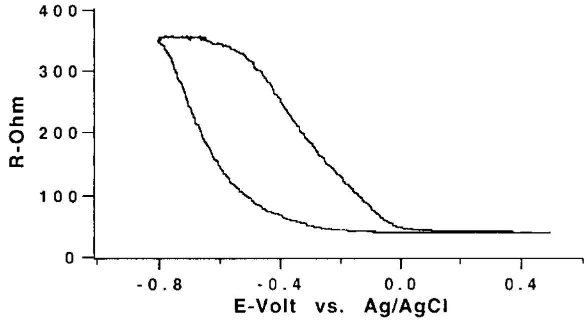


Figure 1 *R*/*E* response during oxidation/reduction of PPy/Cl in 1 M NaCl using the pulse resistometry method. Scan rate = 100 mV s^{-1}

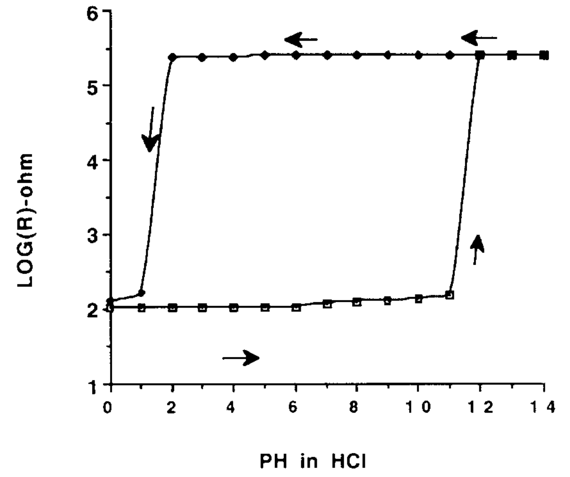


Figure 2 The resistance behaviour of PPy/Cl in solutions with different pHs prepared as described in the text. The polymer is the same as in *Figure 1*

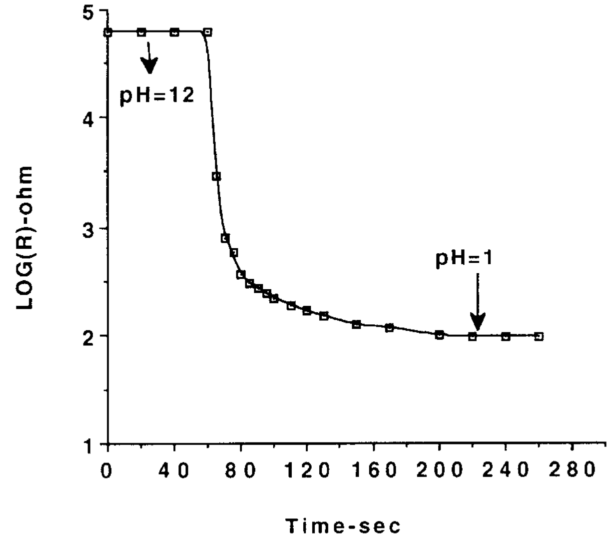


Figure 3 Resistance behaviour as a function of time for base/acid treatment of PPy/Cl. The same polymer was used in *Figure 1*

investigate the effect of solution pH on the polymers used in this work.

PPy/Cl

PPy/Cl was deposited on/in the sandwich electrode potentiostatically at $E = 750$ mV until the charge consumption was 100 mC. The pulse resistometry result (*Figure 1*) suggests that the polymer is very conductive at $E = 400$ mV. As other researchers[16] have pointed out, the conductivity of polymers decreases with increased pH of the solution in contact with the polymers. Therefore, it is better to use the polymer with the best possible conductivity in the study of the effect of solution pH on the resistance of the polymers. As illustrated in *Figure 1* the polymer has the best conductivity at $E = 400$ mV. Therefore the polymer resistance was determined, using the d.c. method, after application of $E = 400$ mV to the electrochemical cell for a sufficient time to allow the polymer to reach equilibrium at this potential (*Figure 2*). In this experiment the polymer was left in solutions of different pHs until no further resistance changes were observed.

The polymer remained very conductive ($R = 100\,\Omega$) from pH 0 to 11. It was at pH 11 that a sudden increase in the resistance of the polymer occurred. The surprising feature of this polymer is that when the solution pH was decreased the polymer remained resistive until pH 2. This suggests that a marked change in polymer properties occurs as a result of exposure to high pH. Pei and Qian[16] suggested that protonation and deprotonation of PPy occurred in solutions of different pH. They used *in situ* optical absorption spectra to study this process. They found that in a basic solution at pH 11, the absorption band which was around 460 nm for pristine PPy shifted to 390 nm, close to the value for the bandgap transition in neutral PPy^0. In acidic solutions this absorption band was shifted to 470 nm. They believe that this is probably due to the protonation of PPy chains.

In their studies[16] they published a very interesting plot which shows the dependency of the Cl$^-$ content of PPy/Cl films on the pH. The plot showed that with increasing pH from 0 to 13 two stages of Cl$^-$ expulsion from the PPy film exist: one in the pH range 2–4, the other in the pH range 9–11. They argue that the process involved in the latter pH range may be associated with the deprotonation of PPy. They supported their ideas by looking at the amount of H$^+$ in the polymer film. They have shown that the amount of H$^+$ increases with decreasing solution pH. This is in agreement with their protonation theory.

There might also be a hydroxyl attack on the polymer chain in addition to the deprotonation process at high pHs. That is why it was very hard for the polymer to reach its initial conductivity at pHs between 10 and 3 while the acid/base treatment test was followed by base/acid treatment. In fact even by immersing the polymer in pH 2 solution, after being in pH 12 solution (*Figure 3*), the polymer requires a minimum of 200 s to attain its initial conductivity. In *Figure 3* the polymer was removed after 60 s from the solution of pH 12 and was immersed in a solution of pH 1. The changes in the resistance of the polymer were then recorded as a function of time until no further changes occurred. This means that there is hydroxyl ion attack of the polymer chain, but the effect is not enough to render the deprotonation process irreversible. This means that the attack does not change the structure of the polymer very effectively. However, there is likely to be hydroxyl ion attack because ion exchange and protonation are not slow processes and the polymer has been left in the solutions with different pHs for at least 4 min for each solution in the experiments shown in *Figure 2*. Therefore, it is better to suggest that

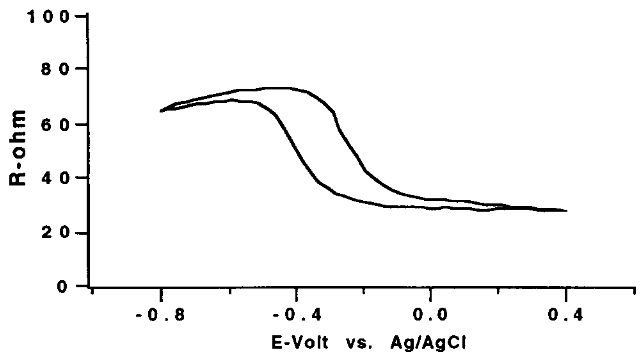


Figure 4 The R/E response for PPy/PVS in 1 M NaCl, with a scan rate = 100 mV s^{-1} using the pulse resistometry method. The polymer was electrochemically deposited as explained in the Experimental section

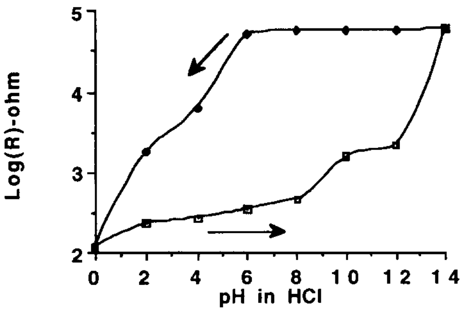


Figure 5 The resistance behaviour of PPy/PVS in solutions with different pHs using the d.c. resistometry method. The polymer is the same as in *Figure 4*

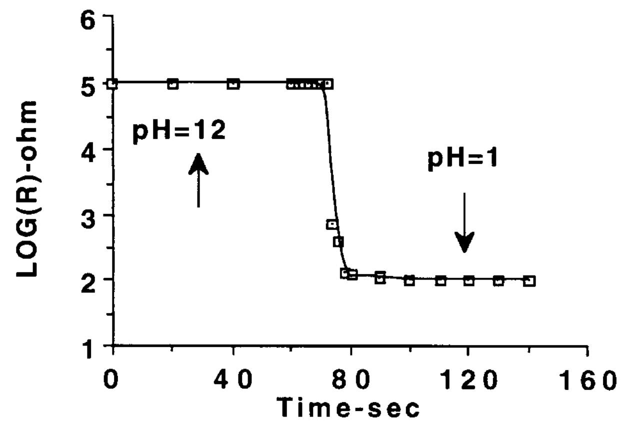


Figure 6 The resistance behaviour of PPy/PVS as a function of time and base/acid treatment. The same polymer was used in *Figure 5*

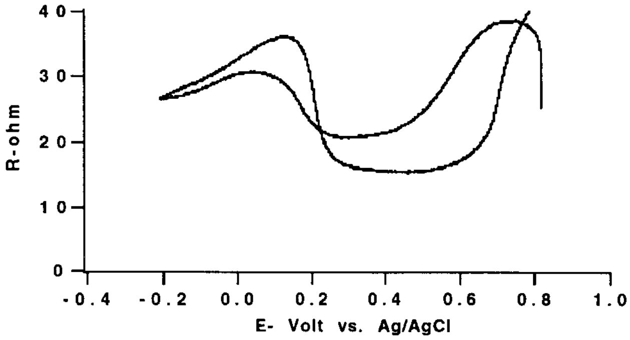


Figure 7 The R/E response for PAn/Cl in 1 M HCl using pulse resistometry (scan rate = 100 mV s^{-1}). The polymer was grown as explained in the text

there is a combination of ion exhange, protonation/deprotonation and hydroxyl ion attack in the interpretation of the results. Wegner *et al.*[17] suggest that the nucleophilic attack of hydroxyl ions on oxidized pyrrole units leads to the structure in which the π-system of the polymer chain is partially interrupted.

Munstedt[8] supports the idea that there is OH^- involvement in the sudden decrease in conductivity of PPys in solutions of pH around 12. He rejects the assumption of the insertion of OH^- as the process of retaining the electroneutrality of the polymer. However, he argues that there is another way of hydroxyl ion attack on the polymer. His hypothesis is that OH^- forms covalent bonds with PPy. In his view, this reaction decreases the conjugation length and following from that the conductivity becomes lower. Comparing this assumption with Pei and Qian's hypothesis[16] that the deprotonation process is a dominant process in changing the conductivity of PPys, I suggest that it is a combination of these processes that occur as a result of the effect of pH of the solution.

PPy/PVS

A very interesting and surprising feature has been found for electroactive and conductive PPy/PVS (*Figure 4*) in solutions with different pHs (*Figure 5*). According to *Figure 4* the resistance transition for this polymer begins at −0.2 V, and a 50 Ω difference in the resistance value between its oxidized and reduced forms was observed. As *Figure 5* illustrates, the polymer conductivity varies as a function of solution pH over the range 1–14. However, Munstedt's theory[8] about OH^- incorporation into the polypyrrole is not very clearly observed in this figure as the polymer remains very resistive from pH 14 to 6 during base/acid treatment, whereas in acidic media with pH less than 4 the polymer resistance becomes closer to its initial conductivity. This is perhaps an effect of a large size counter ion (under the same polymerization conditions) which prevents the insertion of OH^- into the bulk of the polymer. Therefore, it is easier for this polymer, compared with PPy/Cl, to regain its initial conformation during the protonation process as the OH^- can be easily removed by H^+ from the surface of the polymer film. The time response curve obtained for this polymer upon exposure to low pH solutions (*Figure 6*) suggests that the lag time is shorter compared to that of PPy/Cl.

PAn/Cl

The polymer was deposited on/in the sandwich electrode using a controlled potential ($E = 800$ mV) until 20 mC of charge was consumed. Therefore, this polymer was thinner than PPys. In fact our interest was in making the film on the electrode as thin as possible whilst filling the gap between the plates on the sandwich electrode. This makes the polymer more sensitive to pH. However, this also makes the comparison between the PPys and PAn more difficult. Thus, whenever the comparison is carried out it is based on the minimum thickness by which the plates are connected by the polymers. The post-polymerization resistogram result for this polymer in HCl is plotted in *Figure 7*. PAn/Cl was also made chemically using the method described previously[18].

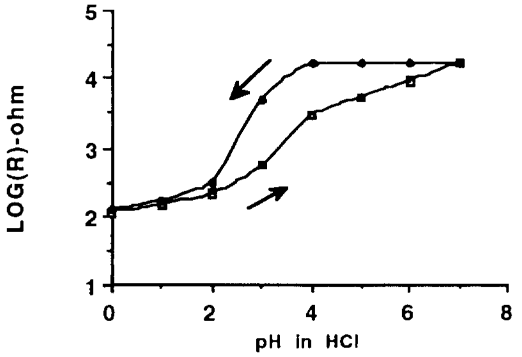


Figure 8 The resistance behaviour of PAn/Cl at different pHs using the d.c. method. The polymer is the same as in *Figure 7*

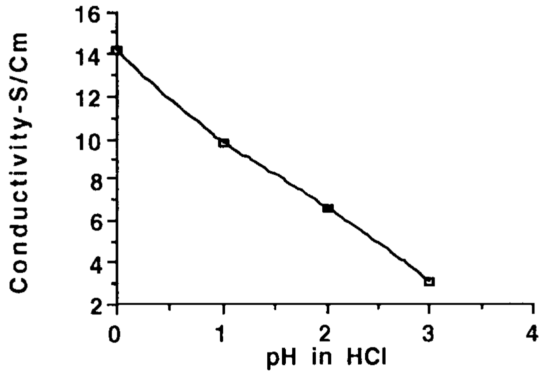


Figure 9 Plot of conductivity *versus* pH for PAn/Cl tape. The tape was made chemically

The polymer behaves as expected and according to published literature[19,20]. The polymer was left at $E = 400\,\text{mV}$ for the pH detection test because the polymer is very conductive at this potential. The electrode was then immersed in solutions with different pHs prepared immediately before use. The result is shown in *Figure 8*.

The polymer shows better sensitivity and reversibility in both acid/base and base/acid treatment compared with that observed for PPys. The trend of conductivity changes illustrated in *Figure 8* is the same as that reported by MacDiarmid *et al.*[19] in their investigations. They studied PAn conductivity in aqueous HCl at different pHs. They also found that the polymer is very resistive at pHs higher than 4. They believe that protonation and deprotonation of PAn results in increasing and decreasing of the polymer conductivity, respectively. They argue that by adding a proton, which interacts with the p system, the conductivity increases. They showed that this process is easily reversed by treatment with aqueous base. This is exactly what is suggested in *Figure 8*. In addition to MacDiarmid *et al.*'s studies[19], there have been other investigations using different analytical techniques to explain the transition occurring at pH 3. Bartonek *et al.*[21,22] have also been interested in investigating the transition from the insulating to the metallic state for PAn. They suggested that a critical protonation level is reached by equilibrium of polyemeraldine in a medium of pH 3.

It has been found that the polymer conductivity is more sensitive to pH while it is studied in a dry form. MacDiarmid *et al.*[19] showed that the degree of protonation decreases from nearly 50% at pH 0 to less than 10% at pH 3. This study was carried out while the dry PAn was used. In this investigation, it has been discussed that the sharp decrease in protonation between pH 2 and 3 suggests that a high degree of protonation are a prerequisite for low resistivity in the dry state. Later, Focke *et al.*[22] pointed out that the resistivity in the wet polymer is not as sensitive to the degree of protonation as the resistivity in the completely dry state. It would therefore appear that, for PAn in contact with electrolyte, a marginal degree of protonation is sufficient to induce the conductor–insulator transition. We also studied the effect of pH on the conductivity of dry PAn film using the four-point probe method (*Figure 9*). The polymer tape was made chemically and then it was prepared in standard sizes for dry conductivity measurements. The samples were immersed in different solutions prepared from HCl with different pHs for 2 h. They were then tested with the four-point probe in the dry form.

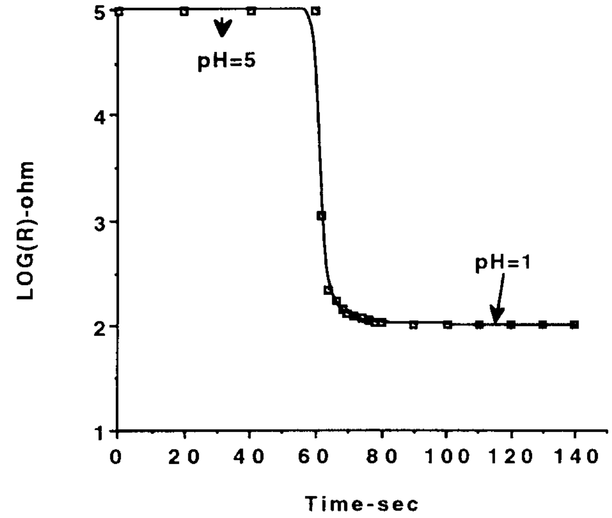


Figure 10 The resistance behaviour of PAn/Cl deposited on to the sandwich electrode as a function of time using DC resistometry. The polymer is the same as in *Figure 7*

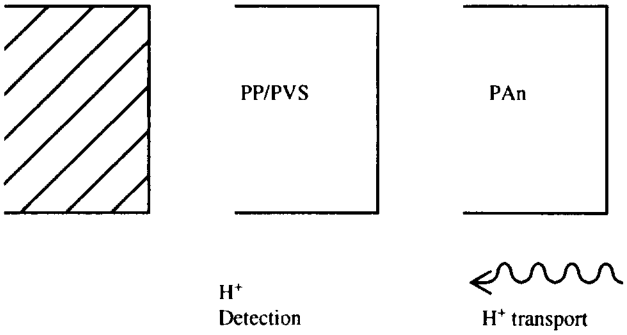
According to *Figure 9* the conductivity (conductivity = 1/resistivity) of the polymer decreases with increasing pH very sensitively. It is very difficult to compare the result obtained in *Figure 8* with that of *Figure 9* because two different methods were employed. However, it can be said that the tape configuration has shown better sensitivity in the way it was tested.

The switching investigations between pH 5 and 0 (insulator–metallic transition) for PAn/Cl (*Figure 10*) also reveals the speed of the insulator–metallic transition for wet PAn film. This is so much quicker than that observed for PPy considering the pH range in which PPy shows insulator–metallic transition (pH values 12 and 1). The polymer was in the pH 5 solution for 60 s and then it was immersed in the pH 1 solution.

PPy/PVS–PAn/Cl composite

In the two previous sections we have shown that PPy/PVS and PAn/Cl are pH sensitive. Although PAn/Cl reveals better pH sensitivity over the range 0–5, it is not suitable for pHs greater than 5. In this section a novel layered structure electrode has been considered and the effect of solution pH on resistive properties investigated. The composite was made from PPy/PVS and PAn/Cl.

First, PPy/PVS was deposited on the electrode under the same conditions explained previously. PAn/Cl was then deposited on top of the PPy/PVS, as shown below, using the same monomer solution and conditions described in the Experimental section for electrodeposition of PAn.



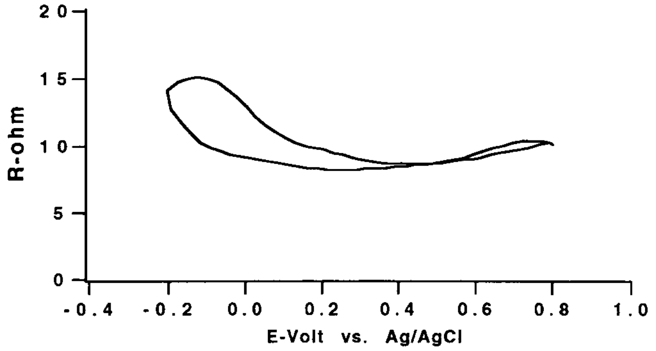


Figure 11 The R/E response for PPy/PVS–PAn/Cl composite in 1 M HCl using the pulse resistometry method (scan rate = 100 mV s^{-1}). The polymer was grown as explained in the text

As described, PPy/PVS was first deposited on the electrode and later was coated with PAn/Cl. Therefore, PAn/Cl is the first to make contact with the solution. The H$^+$ transport takes place through PAn/Cl and travels through PPy/PVS to reach the substrate electrode. Therefore, it can be illustrated as above that H$^+$ transport begins at the PAn/Cl layer and H$^+$ detection is carried out at the interface between PPy/PVS and the substrate electrode as a result of physical and chemical changes in the composite. In fact the H$^+$ is not detected directly but rather as a function of resistance changes in the electrode due to H$^+$ effects on the polymer. It is important to note that there is a possibility of direct connection between PAn and the platinum plates on the sandwich electrode as there might be some pores left on the PPy/PVS which can subsequently be filled by PAn during its polymerization on top of the PPy/PVS. This study needs further investigation by scanning electron microscopy (SEM). However, as the approach has been the resistometric examination of conducting polymers, it can be expected that the composite electrode shows a combination of PPy/PVS and PAn/Cl behaviour in solutions with different pHs.

Characterization studies were carried out in 1 M HCl to investigate the composite electroactivity and conductivity (*Figure 11*). The composite shows the best conductivity at $E = 400$ mV. Therefore, the electrode was equilibrated at this potential before resistance *versus* pH measurements were carried out.

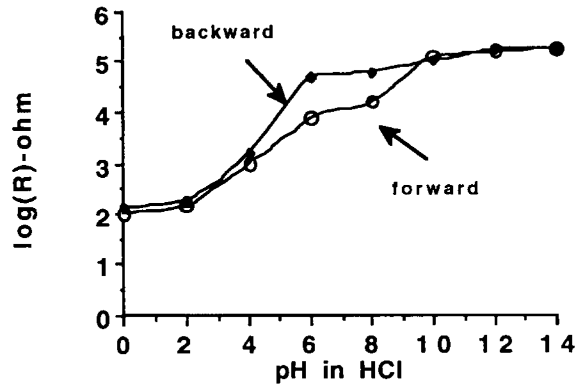


Figure 12 The resistance behaviour of PPy/PVS–PAn/Cl composite in solutions with different pHs using the d.c. resistometry method. The polymer was electrochemically deposited under the conditions explained in the text

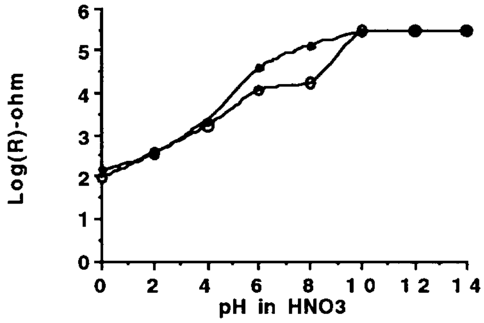


Figure 13 The resistance behaviour of PPy/PVS–PAn/Cl composite in solutions with different pHs using the d.c. resistometry method. The polymer is the same as in *Figure 12*

The pH study for this composite material was carried out over the range 0–14 (*Figure 12*). It was found that the pH–conductivity of both polymers could be induced using this layered structure. This figure demonstrates a PAn/Cl conductivity behaviour over the range pH 0–3 and a PPy/PVS conductivity behaviour over the range pH 4–14. According to *Figure 12* almost the same order of magnitude of resistance was observed for this novel composite as in *Figure 8* over pH 0–3. As discussed before, this suggests that the PAn connects directly to the plate and acts as a conducting pathway at lower pHs where PPy/PVS is resistive. Another very important point in this investigation is that the hysteresis is very small. This could also be due to the morphology of the composite. Therefore, any certain assumptions can only be made when detailed SEM studies are carried out. These experiments give us an idea about how different sensing materials can be easily made by using different conducting polymers and their composites.

Since this novel composite demonstrates interesting pH/R behaviour, it was employed for our investigations on the effect of ions in the acidic solution on the pH/R response. Two different acids, nitric and sulfuric, were used to examine the pH/R responses for the composite. The results are shown in *Figures 13* and *14*. It was found that the presence of SO_4^{2-} in acidic media creates more changes in the pH/R plot than in the presence of NO_3^-. Interesting differences were observed in the trend of

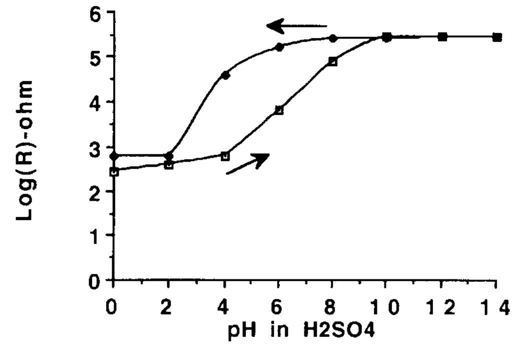


Figure 14 The resistance behaviour of PPy/PVS–PAn/Cl composite in solutions with different pHs using the d.c. resistometry method

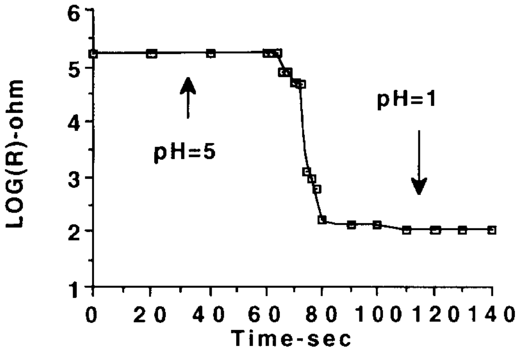


Figure 15 The resistance behaviour of the composite as a function of time and base/acid treatment

base to acid treatment. The decrease in resistance of the composite begins around pH 8 in HCl and around pH 9 and 6 for the composite in HNO_3 and H_2SO_4, respectively. The hysteresis in H_2SO_4 is also larger than in the two other acids. The time response of the composite in base/acid treatment was investigated (*Figure 15*) and it was found that the composite has a slower response compared with that of PAn/Cl.

CONCLUSION

An investigation into the effect of acid/base treatment on the resistivity of conducting polymers has been carried out. These materials perhaps may prove useful as new pH sensors. PAn/Cl and the PPy/PVS–PAn/Cl composite appear to be particularly useful in this regard.

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