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Polyaniline fibres as electrodes. Electrochemical characterisation in acid solutions

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Abstract

Polyaniline fibre microelectrodes prepared from a doped solution of polyaniline protonated with 2-acrylamido-2-methyl-1-propanesulphonic acid in dichloracetic acid were characterized electrochemically for the first time. Low scan rate cyclic voltammetry was used for characterisation in different acid electrolyte solutions, hydrochloric, nitric, perchloric, sulphuric and phosphoric, at low pH values with varying positive potential limits. Electrochemical impedance spectroscopy was also utilised. The electrochemical behaviour of polyaniline (PANI) fibres was found to be similar to that of PANI films obtained by electropolymerisation on metallic electrode substrates. The conduction potential window was found to be from +0.20 to +0.60 V versus SCE, with small variations in the different acid solutions as well as with pH. The standard electrochemical redox couple hexacyanoferrate(III), was found to behave quasi-reversibly in the conduction potential region and rate constants were evaluated.

Keywords: Polyaniline; Fibre; Cyclic voltammetry; Electrochemical impedance spectroscopy

1. Introduction

Polyaniline (PANI) has been regarded as an attractive conducting polymer for a long time. The importance of chain length and branching in determining electronic, magnetic, optical, structural and mechanical properties of polyaniline have been stressed [1], and which are important for its application. Such applications include a number of fields: for sensing pH [2–4], gases [5], and some relevant biological molecules [6] and for the development of biosensors [7,8].

PANI was prepared in the form of membranes for the first time in [9] and used to study charge transport [10–13], electromagnetic effects [14], and water adsorption [15] as well as for the investigation of memory effects [16]. Other strategies have involved the incorporation by deposition of micro- and nanoparticles of heavy metals [17–19]. Further potential uses are as protection against corrosion [20], for which a commercial product was developed [21]; for the development of electrochemical capacitors [22] and for lithium batteries [23].

The physical and chemical properties of PANI depend on the method of synthesis, chemical or electrochemical, as well as on different precursors and temperatures [24–28] and, for electropolymerisation, on the experimental deposition conditions for film formation at different substrates [23,29–32]. Concerning electrochemical applications, a conducting form is required—protonated polyaniline exhibits higher conductivity and is best synthesized in acidic media [24–28].

Conductive polyaniline fibres are a new and interesting alternative to films or membranes, as well as their potential use as microelectrodes. They have been synthesised in several different ways—by chemical deposition onto cotton, silk or wool [33], by drawing [28], by one-step wet spinning [25,28], by air-gap spinning [26], and simply spun [27,34] leading to different physical properties of the fibres.

The aim of this work was to investigate electrochemical properties of PANI fibres prepared by one-step wet spinning using different electrochemical methods in order to explore

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new applications of these materials for microsensors and biosensors.

2. Experimental

PANI fibres were prepared from a doped solution of polyaniline protonated with 2-acrylamido-2-methyl-1-propanesulphonic acid in dichloracetic acid; the procedure is described in Ref. [27]. High molecular weight PANI powder, concentration 9%, was mixed with 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPSA) powder and the mixture added to dichloracetic acid and stirred under nitrogen for 10 min. The solution was poured into the stainless steel dope pot of a spinning rig. A nitrogen gas supply was used to force the solution through an in-line 140 μm filter and through a single 150 μm spinneret orifice, just submerged in the coagulation solvent, so as to have no air gap. The fibre was spun into the coagulation solvent and removed when all fibres were spun. Fibres were dried in air for 24 h. "As-spun" fibres had Young's moduli up to 2 GPa, density 1.6 g cm^{-3}, specific tensile strength dN tex^{-1} and conductivity from 600 to 1000 S cm^{-1} depending on the temperature at which fibres were aged.

Solutions of 1.0, 0.1, and 0.01 mol L^{-1} HCl, $HClO_4$, HNO_3, and 1.0, 0.5, 0.05 and 0.05 mol L^{-1} H_2SO_4, and 1.0, 0.3, 0.03, and 0.003 mol L^{-1} H_3PO_4 were prepared from concentrated hydrochloric, perchloric (Merck, Germany), nitric, sulphuric, and phosphoric acids (Riedel-de-Haën, Germany), respectively. Acetate buffer solutions, concentration 0.2 mol L^{-1}, were prepared from sodium acetate (Riedel-de-Haën, Germany) and concentrated (99.8%) acetic acid (Riedel-de-Haën, Germany). Millipore Milli-Q nanopure water (resistivity >18 MΩ cm) was used for preparation of all solutions. Experiments were performed at room temperature (25 ± 1 °C).

Electrodes were made from 20 μm diameter as-spun polyaniline fibres. Approximately 3 cm of a fibre was cut and glued to copper wire 0.5 mm in diameter and 15 cm length with conducting silver paint, and left to dry for 1 h at room temperature. The electrode was sheathed into a 7 cm long plastic tube and both ends (with a PANI fibre at one end and with Cu wire at the other) were carefully sealed with epoxy resin, and left for 24 h to dry. The exposed fibre was cut to 3 or 7 mm length (depending on the purpose) such that the total surface area was 3.8×10^{-4} or 8.8×10^{-4} cm^2 (Fig. 1).

The three-electrode electrochemical cell contained the PANI fibre working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference. Before measurements the PANI fibre was pre-treated electrochemically in 1 M $HClO_4$ by cycling the potential at 50 mV s^{-1} between −0.20 to +0.60 V versus SCE for not less than five cycles until stable cyclic voltammograms were obtained. Measurements were performed using a computer-controlled μ-Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Eco Chemie, The Netherlands).

Electrochemical impedance measurements were carried out in the same electrochemical cell with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical). A sinusoidal voltage perturbation of rms amplitude 10 mV was applied, scanning from 65 kHz to 0.1 Hz with 10 points per frequency decade, integration time 120 s. Fitting to electrical equivalent circuits was performed with ZView 2.4 software.

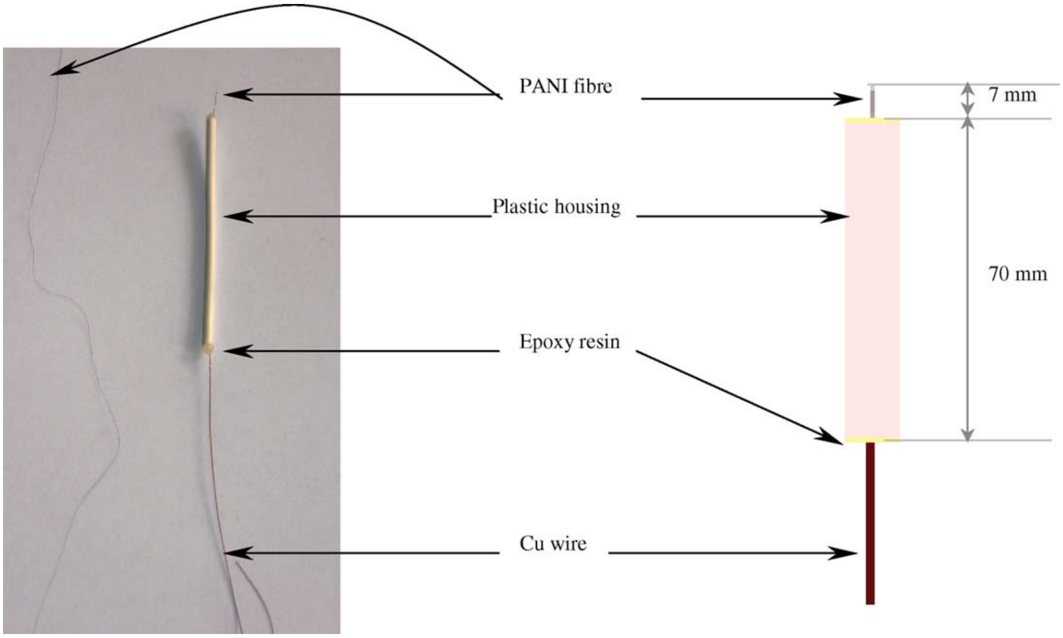

Fig. 1. Construction of polyaniline fibre electrode.

3. Results and discussion

3.1. *Cyclic voltammetry of PANI fibres in different electrolytes*

Fig. 2 shows steady-state cyclic voltammograms at PANI fibres in different electrolytes recorded between potential limits of −0.20 V and +0.60 V versus SCE at various values of pH, with a sweep rate of 10 mV s^{-1}. A quasi-reversible oxidation peak of polyaniline was observed at +0.37 V in the positive-going scan and a smaller reduction peak at +0.05 V in the negative going scan in 1 M $HClO_4$ solution. The other acid solutions shown, sulphuric and hydrochloric acids, led to smaller peak currents but similar peak positions. The polyaniline fibre electrode is thus seen to exhibit slightly different voltammetric behaviour from the electrochemically polymerised polyaniline films [35] suggesting that the fibre has a different surface structure, which depends on the precursor compounds and their ratio in the synthesis of polyaniline [6]. It is also shown in Fig. 2 that an increase in solution pH causes a larger separation of the redox couple and a decrease in the peak currents, until no peak was observed in the potential region studied at pH 3.2 in acetate buffer. This behaviour, i.e. that the conductivity of PANI decreases due to deprotonation of the polyaniline at higher solution pH agrees with what was found for PANI films on electrode substrates [32,35,36].

The dependence of the anodic and cathodic peak potentials and of the anodic and cathodic peak currents are linear with the square root of the scan rate from 5 to 50 mV s^{-1} (Fig. 3); with a further increase in scan rate, the peaks become too broad and it is difficult to estimate their position. The oxidation and reduction reactions involve the electrode surface itself as well as species in solution. These results suggest that diffusion of species to the electrode surface is the rate determining step, which could be from within the electrode or from solution, but any observed differences between the acids are likely to be due to the negative counterion. For oxidation, the transport of counterions from solution is necessary to compensate the positive charge created. For reduction, the introduction of solvent molecules occurs when the counterions are released. The fact that both are observed to be diffusion-limited processes reflects the fact that the diffusion of counterions or solvent to the surface of the PANI fibres is important. The slopes of the linear plots are ∼64 (mV s^{-1})$^{1/2}$ and ∼22 Ω^{-1} cm^{-2} s$^{1/2}$ for the oxidation and ∼−35 (mV s^{-1})$^{1/2}$ and ∼−20 Ω^{-1} cm^{-2} s$^{1/2}$ for the reduction peak potentials and currents, respectively. The variation of peak potentials may therefore reflect the different rates of diffusion for oxidation and reduction. The slight variation in the slopes corresponding to the anodic peaks between perchlorate and the other two anions from the three acids can also be explained by a larger size of the hydrated anion.

Since the shape of the voltammetric peaks was most clearly evidenced at a sweep rate of 10 mV s^{-1}, this value was chosen for further investigations.

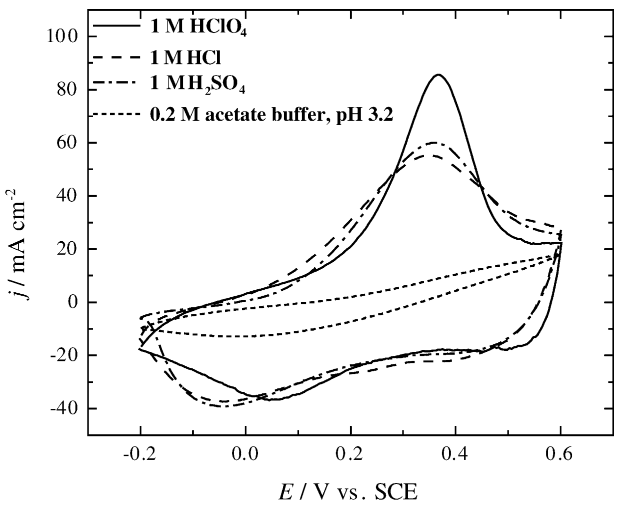

Fig. 2. Cyclic voltammograms at 7 mm length PANI fibres in different acid electrolytes at potential sweep rate 10 mV s^{-1}.

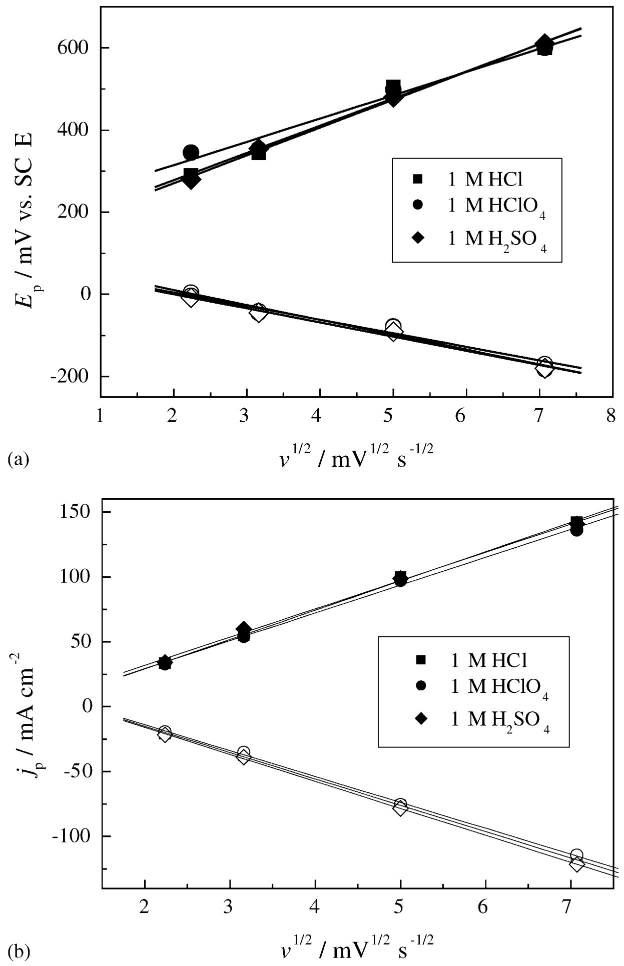

Fig. 3. Plots from cyclic voltammograms of (a) peak potential, E_p and (b) peak current density, j_p for oxidation (upper lines) and reduction (lower lines) vs. square root of scan rate at PANI fibres in different acid solutions. Data from cyclic voltammograms with potential limits as in Fig. 2.

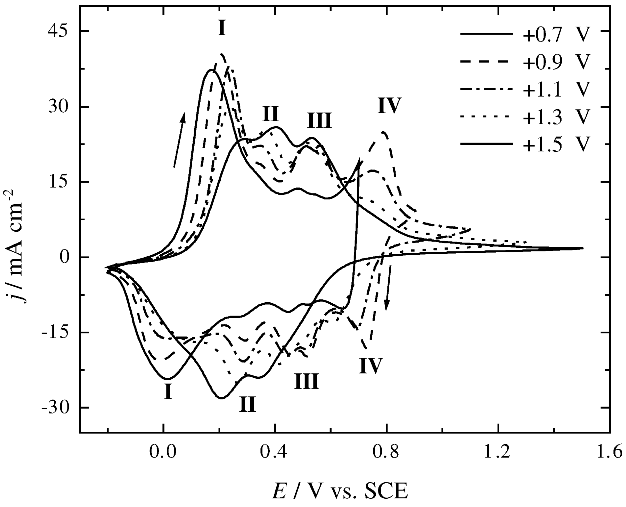

Fig. 4. Cyclic voltammograms at 2 mm length PANI fibres in 1 M H_2SO_4 at potential sweep rate 10 mV s^{-1} for different positive potential limits.

3.2. *Influence of potential window on electrochemical behaviour of PANI fibres*

The positive limit of the potential window in cyclic voltammetry was incremented in steps of 0.10 V up to a maximum of +1.50 V in order to investigate further oxidation processes occurring at the PANI fibres in 1 M H_2SO_4 (Fig. 4) and 2 M $HClO_4$ solutions (not shown). At a limit of +0.70 V, a quasi-reversible redox couple was observed with oxidation peak at +0.15 V (couple I) and two very small reversible double redox peaks appeared at +0.45 and +0.50 V, (couples II and III) which were not seen when the potential was inverted at +0.60 V. The first oxidation peak appears at a less positive potential than with a potential limit of +0.60 V demonstrating the effect of scanning until the beginning of the second oxidation peak on the steady-state response. In fact, the first scan was exactly like that obtained in Fig. 2.

When the potential was swept up to +0.90 V, another sharp reversible redox couple appeared at +0.76 V (couple IV in Fig. 4). On continuing to extend the potential range to +1.50 V no new peaks were seen, and the current of the first quasi-reversible redox couple decreased with increase in potential limit from +1.00 to +1.30 V and then disappeared. Meanwhile, the last redox couple, couple IV, shifted to less positive potentials as well as decreasing the peak current, demonstrating that the PANI fibres had been over-oxidised.

Some identification of the redox peaks can be achieved, based on previous work with PANI films on electrode substrates. The first quasi-reversible oxidation peak (I, Fig. 4) at +0.15 V indicates oxidation of the leucoemeraldine form to protonated emeraldine [37,38]. The last reversible peak (IV, Fig. 4) at +0.76 V result from oxidation of emeraldine and deprotonation of the polymer [37,38], while the nature

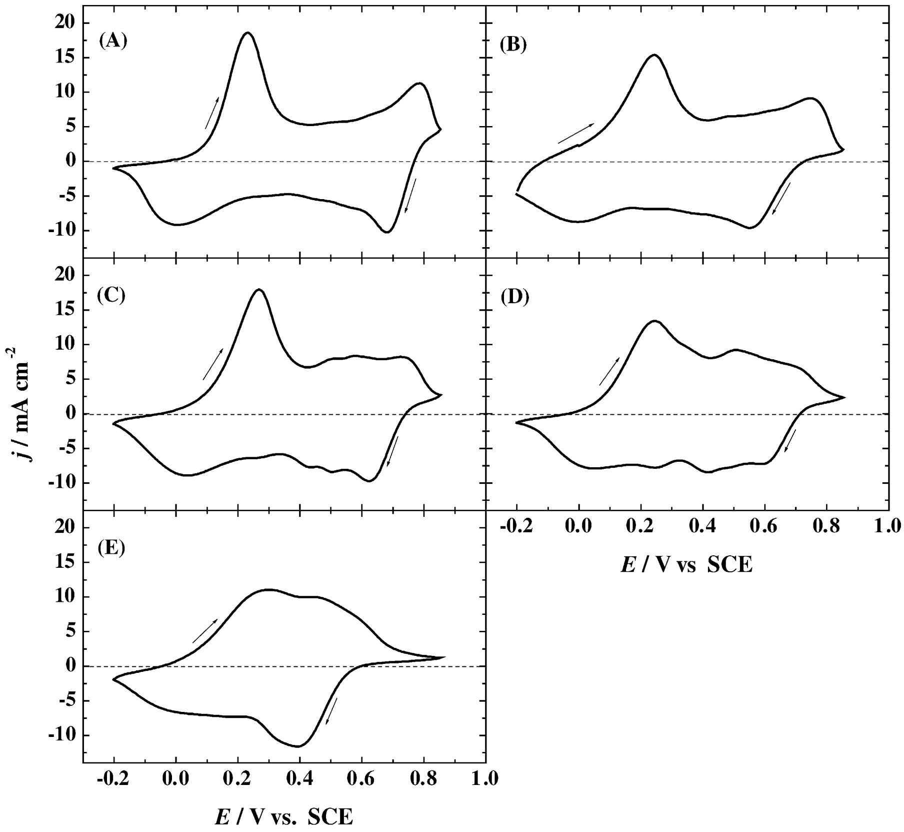

Fig. 5. Cyclic voltammograms at 2 mm length PANI fibres in different acid solutions: (A) 1 M HCl; (B) 1 M $HClO_4$; (C) 1 M HNO_3; (D) 0.5 M H_2SO_4; (E) 0.3 M H_3PO_4. Potential range −0.20 to 0.85 V vs. SCE at potential sweep rate 10 mV s^{-1}.

of the peaks between I and IV has been found to depend on the experimental details of polyaniline synthesis, electrolyte and pH. These peaks are generally attributed to the formation of benzoquinone degradation products and formation of cross-linked polyaniline chains by direct reaction between parts of the polyaniline chain itself [38]. The results obtained suggest that for most purposes the highest positive potential limit that can be employed to avoid polyaniline overoxidation is at +0.80 to +0.90 V versus SCE.

3.3. *Influence of counter ion on electrochemical behaviour of PANI fibres*

In order to further observe the influence of the electrolyte and distinguish between the effects of the counter ion and that of pH on the electrochemical behaviour of PANI fibres, several acids were used as the electrolytes at pH close to zero, i.e. as 1 M H^+(aq.). The positive potential window used was up to a positive limit of +0.85 V to be able to follow changes in all the electrochemical processes occurring (peaks I–IV in Fig. 4). As can be seen in Fig. 5, the counter ion had the largest effect on peak IV, oxidation of protonated emeraldine, and on formation of the intermediate products (peaks II and III). An especially strong effect of the anion was observed in the solutions of acids having a counter ion with higher charge, i.e. SO_4^{2-} and PO_4^{3-}. The highest currents were found in the solution of HCl and HNO_3, while the lowest ones were in H_3PO_4 and H_2SO_4 at the same H^+(aq.) concentrations. The results obtained are in a good agreement with [35,39–43] and show that the electrochemical behaviour of the fibres depends not only on proton transport but also on nature of the counter ion. The size of the counter ions, which is in the sequence: $Cl^- < NO_3^- < PO_4^{3-} < ClO_4^- < SO_4^{2-}$ [44], is less important than the anion charge. This means that anion migration close to the electrode, i.e. anion mobility, is the most important factor.

3.4. *Influence of pH on the electrochemical behaviour of PANI fibres*

A systematic study showed that the pH has a more significant influence on redox couple I, as shown by the peak current and the bigger peak separation (Table 1 and Fig. 2). In all the acids redox couple I was observed down to pH 1 or 0 (except H_3PO_4). In these studies neutral electrolyte was added to keep the ionic strength approximately constant at 1 M: even when NaCl was added to 0.01 mol L^{-1} acid to keep the ionic strength constant, no leucoemeraldine oxidation peak was observed in 0.01 M acid, but the peak current increased and a reduction peak appeared at +0.19 V (not shown), which could be due to irreversible reduction of emeraldine oxidation products.

The conclusion is that only fully protonated polyaniline fibre exhibits the same electrochemical properties as polyaniline films [32,35–38].

Table 1
Influence of pH on peak current, I_p, and peak potential, E_p, for oxidation peak I at PANI fibres in different acid solutions

Acid	Concentration (mol L^{-1})	I_p (μA)	E_p (mV vs. SCE)
HCl	0.01	–	–
	0.1	3.7	237
	1.0	5.2	227
$HClO_4$	0.01	–	–
	0.1	7.4	239
	1.0	8.8	235
	2.0	8.3	202
HNO_3	0.01	–	–
	0.1	4.2	284
	1.0	13.6	264
H_2SO_4	0.005	–	–
	0.05	5.9	338
	0.5	11	239
	1.0	8.3	202
H_3PO_4	0.003	–	–
	0.03	–	–
	0.3	3.7	247
	1.0	5.2	227

3.5. *Electrochemical impedance spectroscopy*

Some electrochemical impedance experiments were carried out in order to make further comparison with electrochemical data obtained at polyaniline films. Fig. 6 shows complex plane spectra at PANI fibres in 2 M perchloric acid electrolyte at different potentials ranging from 0.0 to +0.80 V versus SCE in steps of 0.20 V. As can be seen, the spectra have a capacitive behaviour in the potential region corresponding to conduction (+0.20 to +0.60 V). The calculated values of capacity are in the range of 1.5 F cm^{-2}, a value larger than that obtained at polyaniline films, e.g. [32].

Outside the conduction potential region, a more complex response is observed. A mixed kinetics at high frequency and diffusion at low frequency behaviour was observed at 0.0 V, where electrochemical reduction of leucoemeraldine oxidation products takes place. The introduction of constant phase elements (CPE) into the equivalent circuit is necessary to fit the data at this potential. The over-oxidation of PANI fibres occurred at +0.80 V is reflected in the spectra, where no equivalent circuit model normally used for such systems could be applied because of the scatter in the spectra, and the impedance values increase by a factor of 10.

As was already found in the cyclic voltammetry studies, counter ions have a significant influence in the impedance spectra, and the same behaviour was found for all counterions studied in the conduction potential region at +0.40 V versus SCE (Fig. 7). Note that the concentration of acid is lower than in Fig. 6 and a diffusion-limited response becomes evident at high frequencies. Analysing the lower frequency range at this potential gives rise to the following values of capacity in F cm^{-2}: 7.3 (HCl), 2.1 ($HClO_4$), and 2.0 (H_2SO_4). Two points become clear from these results. First, regarding perchloric acid, the reduction in concentration leads to a slightly more effective charge separation and secondly, the acid with the smaller anion (HCl) has a higher capacity value, as would be predicted.

The general trends in impedance results are in good agreement with EIS carried out at, for example, polyaniline films on glassy carbon electrodes [35], at films of some substituted polyanilines [32,45], and at PANI membranes symmetrically bathed in the electrolyte solution [10]. However,

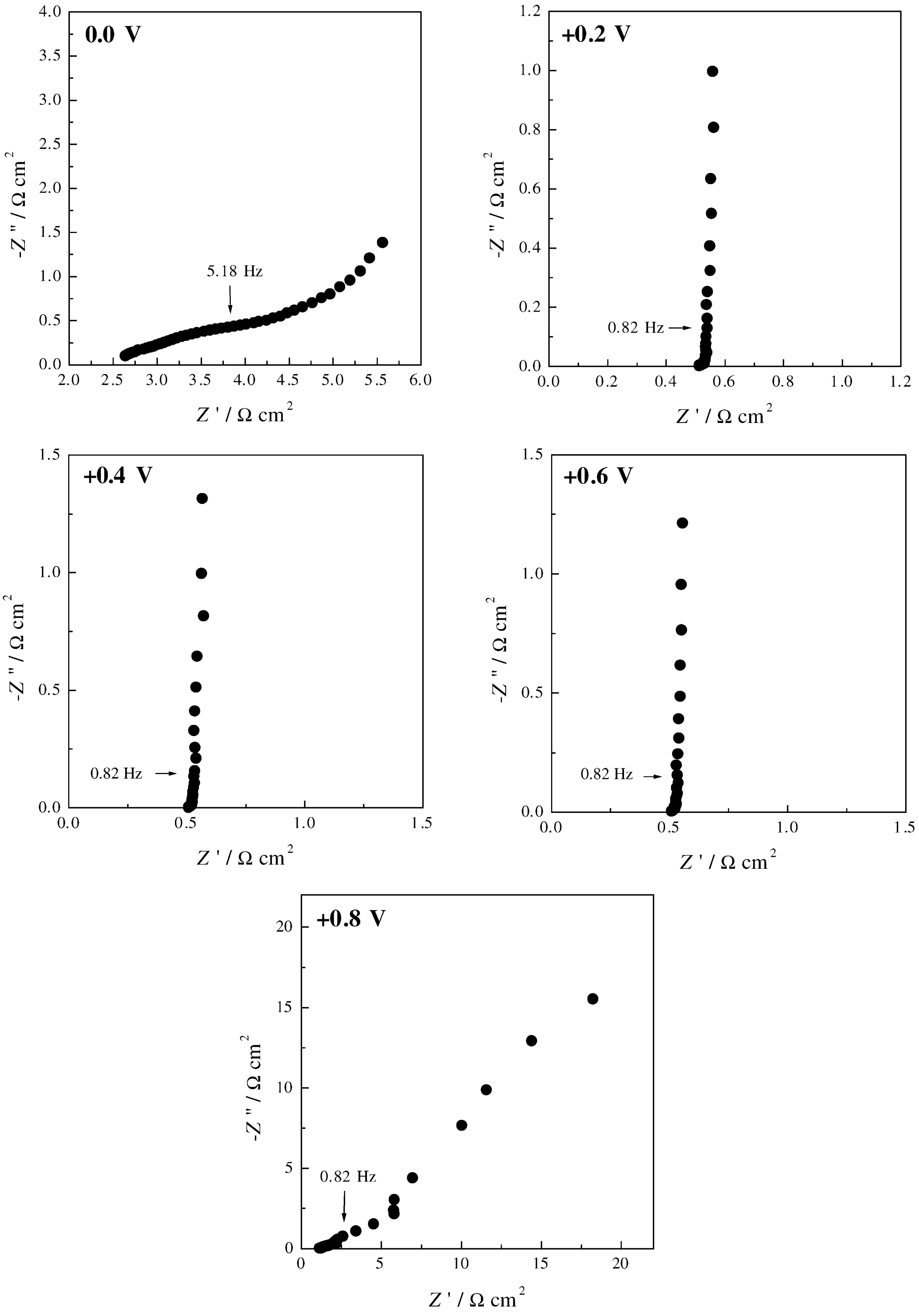

Fig. 6. Impedance spectra at 3 mm length PANI fibres in 2 M $HClO_4$ solution at different potentials. Integration time 120 s. All other conditions are given in the Section 2.

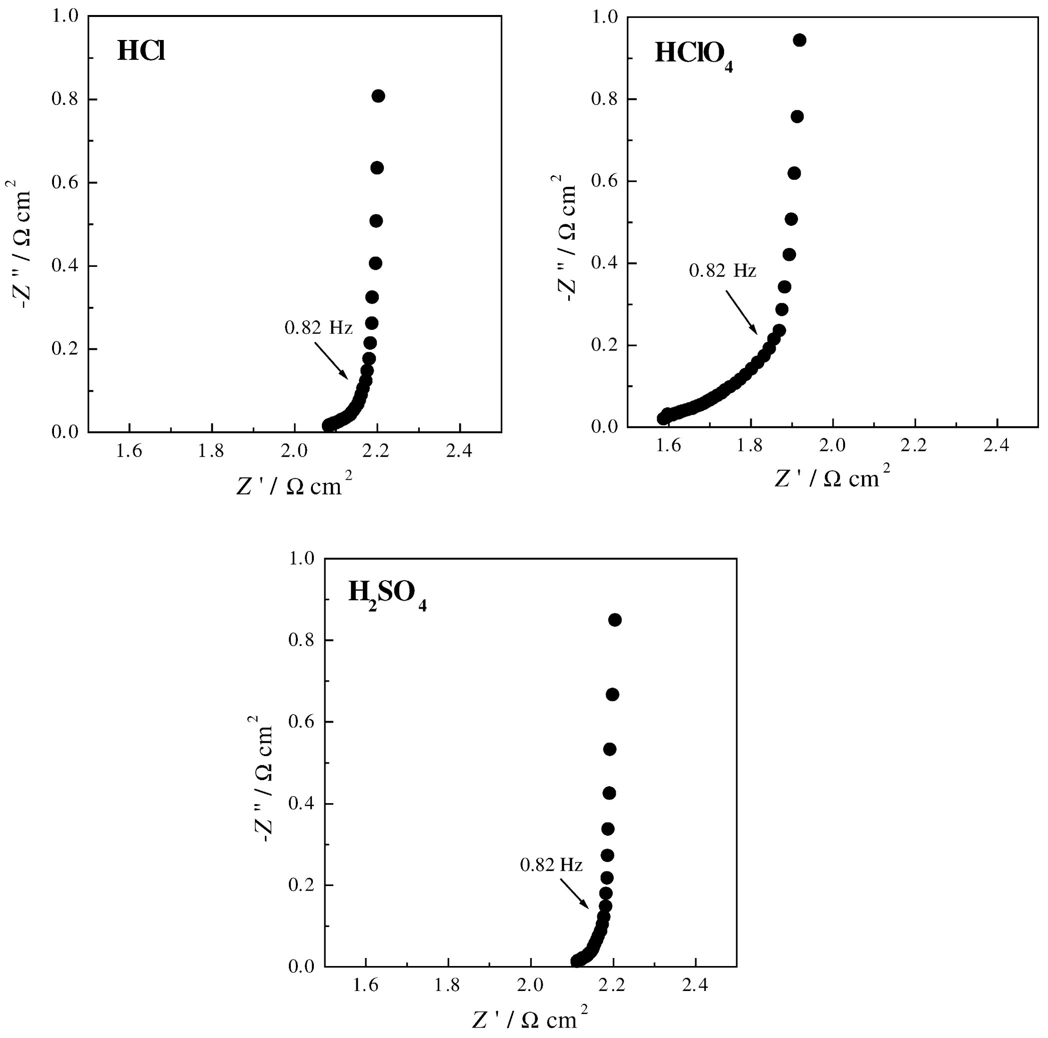

Fig. 7. Complex plane impedance spectra at 3 mm length PANI fibres at +0.40 V vs. SCE in different 1 M acid solutions. All the other conditions as in Fig. 6.

totally different results were obtained at free-standing polyaniline membranes made from emeraldine base by Benyaich et al. [40], who found ionic interfacial charge transfer to be negligible over a range of acidic pH and in different acid solutions. Nevertheless, their studies were done under applied dc current conditions, with two symmetric electrolytes were in contact, whereas we worked at ac current blocking conditions, i.e. asymmetric contacts. In any case, there is evidence that the morphology and interlocking of the polymer chains, which is certainly different in fibres, in free-standing films and electropolymerised films can significantly influence the polymer's electrochemical behaviour.

A more detailed analysis of electrochemical impedance spectra will be the subject of further work.

3.6. Reduction of hexacyanoferrate(III) at PANI fibres

One of the more interesting potential applications of PANI fibres is as an "inert", non-metallic conducting electrode material within the conduction potential range. To investigate

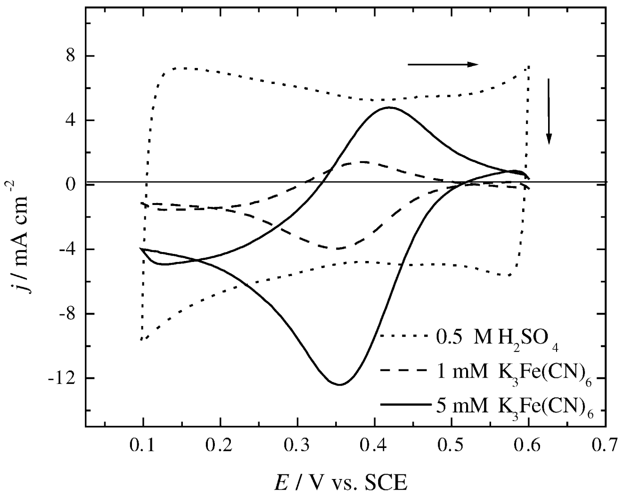

Fig. 8. Cyclic voltammetry of (- - -) 1 mM and (—) 5 mM $K_3Fe(CN)_6$ at 3 mm length PANI fibre electrode. The background current of the supporting electrolyte, 0.5 M H_2SO_4, (· · ·), has been subtracted.

Table 2
Rate constants, k^0, for electrochemical reduction of $K_3Fe(CN)_6$ at 3 mm length PANI fibre electrodes in different supporting electrolytes, calculated after background current subtraction

Supporting electrolyte	$[K_3Fe(CN)_6]$ (mmol L^{-1})	Peak separation (mV)	Peak current (μA)		k^0 ($\times10^{-3}$ cm s^{-1})
			Reduction	Oxidation	
1 M HCl	1	52	1.80	0.25	–
	5	75	5.90	0.85	0.33
1 M LiCl*	1	75	1.10	0.55	0.33
	5	113	3.68	1.15	0.077
1 M KCl*	1	75	1.12	0.38	0.33
	5	115	3.93	0.99	0.076
1 M KCl*	1	90	1.05	0.32	0.15
	5	130	3.85	0.90	0.058
1 M $HClO_4$	1	78	0.49	0.14	0.31
	5	141	2.43	0.59	0.049
0.5 M H_2SO_4	1	38	1.50	0.55	–
	5	75	4.68	1.85	0.33
0.3 M H_3PO_4	1	60	4.30	3.60	5.4
	5	90	8.50	4.90	0.15

* LiCl or KCl was added to HCl solution at the given pH to obtain ionic strength 1 mol L^{-1}.

this further the electrochemical behaviour of the standard redox couple $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ was studied in highly acid solution where the influence of deprotonation of PANI should have comparatively little influence. Some of the results obtained in 0.5 M H_2SO_4 electrolyte are shown in Fig. 8. Although the large background current could represent a significant disadvantage, the system behaved almost reversibly with some dependence on the supporting electrolyte and pH over the range tested, as well as on the concentration of hexacyanoferrate(III). Some of the smaller values of peak separation were such as to make clear the role of adsorption of the ions on the fibre surface and their possible role in doping/undoping reactions.

Rate constants, k^0, for the electrochemical reduction reaction in different media were calculated from the cathodic and anodic peak separation where possible, assuming species in solution, and are presented in Table 2, calculated from the peak separation using Nicholson's treatment [46]. The highest rate constants were found in phosphoric and sulphuric acids, probably determined by the higher charge of the electrolyte anion; and the lowest values were found in perchloric acid solution, probably due to the larger anion radius. The role of the cations with the different radii (Li^+ and K^+) was negligible, and pH had some influence in KCl electrolyte, while in other cases, when the pH was changed between different supporting electrolyte, the influence of the anion was much greater than that of pH. It is also interesting and of note that at the higher hexacyanoferrate(III) concentration the calculated rate constants are significantly lower, suggesting that the process is more complicated and there is accumulation of the anions near the surface due to doping/undoping interactions, as mentioned above, making charge transfer less easy to occur.

The electrochemical behaviour of the standard redox couple $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ at PANI films deposited on glassy carbon was found to be ideally reversible. Nevertheless, due to the porosity of PANI films the redox signal was partially obtained at the glassy carbon surface.

These results demonstrate the potentialities for the measurement of redox species using PANI fibre electrodes in situations where it is not possible to use conventional electrode materials.

4. Conclusions

PANI microelectrodes, made from fibres prepared from doped solution of polyaniline protonated with 2-acrylamido-2-methyl-1-propanesulfonic acid in dichloracetic acid exhibit good conductivity in solutions of high acidity (pH $\leq$1). The conduction region was found to be from +0.20 to +0.60 V versus SCE in 1 M H_2SO_4 solution, and varied slightly in the different acid solutions as well as with pH. The counter ion plays an important role in the oxidation process of PANI fibres, a particular effect being that anions with higher charge decrease the rate and ease of oxidation. Standard electrochemical redox couples, exemplified by hexacyanoferrate(III) reduction, were found to behave quasi-reversibly in the conduction potential region. A more detailed study of PANI fibres by electrochemical impedance is currently under way.

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