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Polypyrrole membranes containing chelating ligands: synthesis, characterisation and transport studies

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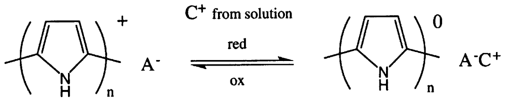
Abstract

Conducting polymer membranes consisting of polypyrrole (PPy) doped with either 8-hydroxyquinoline-5-sulfonic acid (HQS) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (bathocuproinedisulfonic acid, (BCS)) were prepared electrochemically using aqueous solutions of pyrrole and the respective chelating ligands. The ratio of pyrrole to dopant in the resulting PPy/HQS and PPy/BCS free-standing membranes was found to be 9:1 and 6:1, respectively, whilst the conductivities were comparable (1.13 and 3.40 S cm^{-1}, respectively). Cyclic voltammetry studies using electrodes coated with thin films indicated that both polymers undergo reversible oxidation/reduction processes in aqueous solution that are influenced by the nature of the supporting electrolyte. Electrochemically controlled transport of metal ions was demonstrated using laminated membranes (either PPy/BCS or PPy/HQS was deposited onto platinum sputter-coated polyvinylidene filters). Transport of Co^{2+}, Ni^{2+} and Zn^{2+} was demonstrated for the first time across PPy/BCS/Pt/PVDF membranes, which also proved permeable to K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+} and Cu^{2+}. By contrast PPy/HQS/Pt/PVDF membranes proved permeable to a smaller number of metal ions under the same conditions, with only K^+, Co^{2+} and Cu^{2+} transported to a significant extent. The flux of copper across membranes containing PPy/BCS was approximately 10 times greater than that observed using membranes containing PPy/HQS, and 50 times greater than for polypyrrole membranes containing other types of dopants. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polypyrrole; 8-hydroxyquinoline-5-sulfonic acid; Bathocuproinedisulfonic acid

1. Introduction

Conducting electroactive polymers (CEPs) exhibit a number of useful properties including electrical conductivity and electroactivity. When first prepared the backbone of a conducting polymer such as polypyrrole (PPy) exists in a conducting, oxidised state. The overall charge of the polymer is neutral due to the presence of anions (A^-) which are incorporated during the polymerisation process. When PPy is reduced the conducting polymer backbone becomes neutral and the overall polymer acquires a net negative charge. In order to maintain overall electrical neutrality either cations (C^+) must be incorporated from the surrounding solution (Eq. (1)), or the anions previously incorporated must be expelled (Eq. (2)). When the PPy is subsequently re-oxidised, cations previously incorporated are expelled (Eq. (3)) or anions present in the surrounding solution (B^-) are incorporated (Eq. (4)). By cycling between its oxidised and reduced forms it is possible, therefore, to force the conducting polymer to act as both a cation and anion exchanging material. The relative amounts of cation and anion movement depend on the size and mobility of the dopant initially incorporated [1–6].



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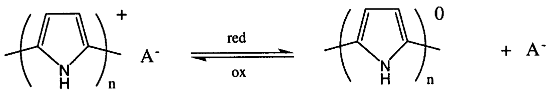

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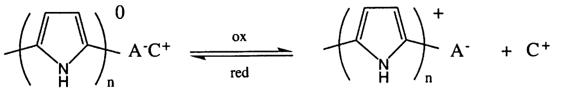

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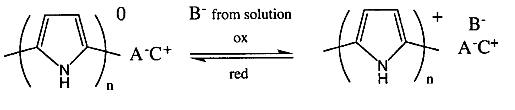

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Previous work in our laboratories has demonstrated that it is possible to electrochemically induce movement of electroinactive metal ions from one solution to another

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across free-standing and composite PPy and polyaniline membranes [7–14]. Transport of electroactive metal ions, such as copper, has also been demonstrated [10]. In the majority of cases the dopants initially incorporated into the conducting polymer were simple aromatic sulfonated anions. These were chosen in view of the favourable electrochemical and mechanical properties displayed by conducting polymers containing these dopants [15]. The flux of alkali metal ions across PPy membranes containing these dopants was found to increase as the size of the hydrated metal ion decreased [13]. These results suggested that the degree of compatibility between the size of the hydrated metal ion and the pores present in the polymer significantly influence the rate of metal ion transport. Varying the size of the dopant has been shown to produce significant variations in the flux of metal ions across conducting polymer membranes. For example, the membrane selectivity (flux K^+/flux Ca^{2+}) was found to decrease from 240 for PPy doped with benzenesulfonic acid, to 37 for the much larger naphthalenedisulfonic acid [7].

Despite the favourable properties displayed by conducting polymers containing simple sulfonated aromatic dopants, these anions do not exhibit great affinity or selectivity towards metal ions. In order to produce conducting polymer membranes which display greater metal ion fluxes and selectivity, the effect of incorporating chelating agents into conducting polymers has been investigated. Previous work by ourselves and others has shown that it is possible to use conducting polymers doped with dyes or chelating agents for electrochemical detection of cations [16–26]. We report here the synthesis, characterisation and metal ion transport properties of composite membranes containing PPy doped with either 8-hydroxyquinoline-5-sulfonic acid (HQS) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid (bathocuproinedisulfonic acid, (BCS)) (Fig. 1). Both ligands are commercially available and contain one or two sulfonic acid groups, which are known to confer good mechanical properties on polymer membranes [15]. Furthermore both ligands contain functional groups which allow them to coordinate bifunctionally to metal ions. Like their precursors 8-hydroxyquinoline and 1,10-phenanthroline, HQS and BCS form stable complexes with many transition metals.

2. Experimental

2.1. Reagents

Pyrrole was obtained from Merck and distilled before use. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid and 8-hydroxyquinoline-5-sulfonic acid were obtained from Aldrich. All other inorganic reagents were obtained from Ajax Chemicals. Solutions were prepared using deionized Milli-Q water (18 MΩ cm).

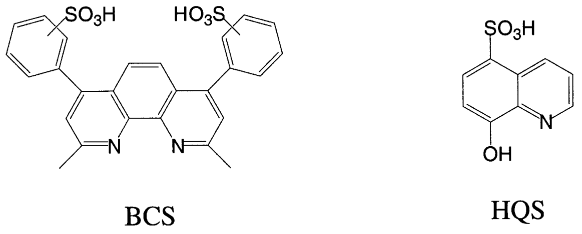

Fig. 1. Structures of the dopants used in this work.

2.2. Preparation of polymers

Electropolymerisation was performed in aqueous solutions containing 0.20 M pyrrole and either 0.01 M BCS or 0.10 M (sat) HQS, using an EG and G Princeton Applied Research Model 363 Potentiostat/Galvanostat. All solutions were deoxygenated using nitrogen before use. A three electrode system consisting of a working electrode, Ag/AgCl (3 M NaCl) reference electrode, and either a platinum mesh (100 lines $in.^{-1}$) or reticulated vitreous carbon (RVC) auxiliary electrode, was used in conjunction with a conventional one compartment electrochemical cell for all polymerisations. All experimental data were collected using a MacLab A/D and D/A data collection system (AD Instruments).

Growth of thin films composed of either polymer was initially performed using potentiodynamic, potentiostatic and galvanostatic methods. Potentiodynamic methods (cyclic voltammetry; 0.0– + 1.00 V, 100 mV s^{-1} scan rate for PPy/BCS and −1.00– + 1.00 V, 50 mV s^{-1} scan rate for PPy/HQS) were used to determine the minimum potential required for polymer growth under potentiostatic conditions. Subsequently a constant potential of +0.80 V was used for growing PPy/BCS potentiostatically, while +0.70 V was used for PPy/HQS. During galvanostatic growth a current density of 2 mA cm^{-2} was used for both polymers.

Synthesis of larger free-standing polymer membranes for microanalysis, conductivity measurements and morphological examination was accomplished galvanostatically (current density = 2 mA cm^{-2}). The concentrations of monomer and dopant used for preparing larger membranes were the same as those described above for preparing thin films. However, stainless steel electrodes measuring 6 × 2 cm or larger were used as the working electrodes. Galvanostatic growth under the same conditions was also used to produce membranes for metal ion transport studies, except that the polymer was deposited onto platinum sputter-coated polyvinylidene fluoride (PVDF) membranes (Millipore).

2.3. Techniques and instrumentation

Elemental analysis of free-standing membranes was carried out by the Microanalysis Unit at the Research School of Chemistry, The Australian National University.

The membranes were grown galvanostatically (current density = 2 mA cm^{-2}) for 10 min in the case of PPy/BCS, and for 1 h for PPy/HQS. After growth, membranes were removed from the stainless steel electrode they were grown on, washed thoroughly with Milli-Q water, and allowed to dry at room temperature.

Absorption spectra (300–1100 nm) were obtained using a SHIMADZU Model UV-1601 spectrophotometer, and polymer films grown galvanostatically (current density = 2 mA cm^{-2}) on Indium/Tin/Oxide (ITO) coated glass. In the case of PPy/BCS growth was for 1 min duration, while for PPy/HQS a 3 min deposition time was used. Conductivity measurements were performed using the four point probe method and large, free-standing membranes grown galvanostatically as described earlier.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) studies of membranes were conducted using a Leica Cambridge 440 Scanning Electron Microscope and Digital Multitude Nanoscope 3, respectively, located within the Department of Materials Engineering at the University of Wollongong.

Cyclic voltammetry studies were conducted in a three-electrode electrochemical cell using a Ag/AgCl (3 M NaCl) reference electrode, platinum auxiliary electrode, and polymer coated platinum working electrode. The scan rate used throughout was 100 mV s^{-1}, and the scan range was +0.80– −1.00 V.

2.4. Metal ion transport studies

Metal ion transport studies were performed using a home-built transport cell [12]. The composite conducting polymer membrane was placed in the transport cell dividing it into two separate compartments (60 cm^3 each). The two compartments both contained a Ag/AgCl(3 M NaCl) reference electrode and Pt mesh auxiliary electrode, and were used to contain the feed and permeate solutions. A pulsed potential waveform with a 50 s pulse width, and potential range of +0.75 to −0.40 V was used for all experiments. During application of the pulsed potential the membrane was first subjected to the negative potential for 50 s, after which it was immediately switched to the positive value for a further 50 s. During transport studies 1 mL aliquots for metal ion analysis by atomic absorption spectroscopy (AAS) were removed every 30 min. Feed solutions contained 0.10 M metal ion in 0.01 M sulfuric acid for experiments involving transition metals, while for experiments involving Na^+, K^+, Mg^{2+} or Ca^{2+} the feed solution contained 0.10 M metal ion only. The permeate solution contained The permeate solution contained Milli-Q water in each case, except for experiments involving transition metals, when 0.01 M sulfuric acid was used. Most metal ion transport experiments were stopped after six hours. However, in some instances where significant deposition of elemental metal onto the auxiliary electrode in the permeate compartment had occurred, a final metal ion reading was taken after a further 24 h had elapsed to allow the deposited metal to redissolve in the acid.

3. Results and discussion

3.1. Polymer growth

It was found that thin films composed of PPy/BCS or PPy/HQS could be deposited on platinum electrodes using potentiodynamic, potentiostatic and galvanostatic techniques. The galvanostatic approach was found to provide greater control over polymer growth and was preferred for obtaining membranes used for characterisation and metal ion transport studies. It had been shown previously that the mechanical and electrochemical properties of PPy membranes obtained under galvanostatic conditions are superior to those obtained by other methods [12].

3.2. Chemical and physical characterisation of polymers

Elemental analysis indicated that the ratio of pyrrole to dopant in free-standing membranes composed of PPy/BCS or PPy/HQS was 6:1 and 9:1, respectively. This ratio is typically either 3:1 or 4:1 for PPys doped with small, singly charged anions [11,12]. Therefore, the ratio found for PPy/BCS may also be considered typical, since the dopant in this case can form a doubly charged anion, and would therefore compensate the charge on twice as many pyrrole groups. This has been observed previously with PPys doped with aromatic compounds containing two sulfonic acid groups, e.g. 1,3-benzenedisulfonic acid and 1,5-naphthalenedisulfonic acid [11]. For both these latter polymers the ratio of pyrrole to dopant was found to be 6:1, suggesting that the dopant was present in its fully deprotonated state. It is also worth noting that the level of doping present in PPy/BCS is typical despite the relatively low concentration (0.01 M) of BCS used for polymer synthesis. In contrast PPy/HQS was doped to a much lower extent than typically found, despite the use of a saturated HQS solution (~0.10 M) during polymer synthesis. Similar high monomer to dopant values have been reported previously for PPys containing bulky anions [27] or polyelectrolytes [14], reflecting the impact that variations in dopant size and shape can have on polymer structure. Further evidence of this was obtained when free-standing membranes composed of PPy doped with the closely related, but even bulkier 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid ($M_w = 503$) were prepared under similar conditions. Microanalysis of this material indicated a pyrrole to dopant ratio of 6:1, typical for a dopant that is a dianion [28].

SEM was used to examine both sides of free-standing membranes composed of PPy/BCS or PPy/HQS. The membrane surfaces that were initially in contact with the electrode during polymer growth were very smooth in the case of both PPy/BCS and PPy/HQS. However, the surfaces that were in contact with the polymerisation solution both displayed the ‘cauliflower’ morphology typical of PPys [7,11,13,14]. More detailed analysis of the surface morphology of the solution side of both types of polymer membranes was provided by atomic force microscopy. For PPy/BCS a section of the membrane measuring 2500 μm^2 was found to have a true surface area of 3013 μm^2, reflecting a surface area difference of 20.5%. This may be compared to a value of 10.4% determined for the PPy/HQS membrane, indicating that the latter membrane has a significantly smoother surface. Further confirmation of this was provided by the results of section analysis of both membranes. For PPy/BCS the average distance between the peaks and valleys of nodes was determined by section analysis to be 1.7 μm, which is significantly greater than the 0.7 μm found for PPy/HQS. Overall the AFM results indicate that the surface morphologies of both membranes are comparable to those of other PPy membranes. For example, for PPy/pTS (pTS = *para*-toluene sulfonic acid) membranes the surface roughness was determined to be 9.5%, and the average peak to valley distance 0.9 μm [28].

The conductivity of a 19 μm thick membrane composed of PPy/BCS was found to be 3.4 S cm^{-1}, while for a 34 μm thick PPy/HQS membrane a value of 1.1 S cm^{-1} was determined. Both conductivity values are one to two orders of magnitude lower than what is typically found for PPys doped with other small molecules [11,12]. The visible absorption spectra of thin films composed of PPy/BCS or PPy/HQS deposited on ITO coated glass are illustrated in Fig. 2. Both spectra contain a relatively weak free carrier tail consistent with the low conductivities of these materials. In addition to the bipolaron band centred at 935 nm, the spectrum of PPy/BCS contained a weaker polaron band at 520 nm. The spectrum of PPy/HQS contained a peak at 454 nm (polaron band) in addition to the bipolaron band at 895 nm. Each band in the spectrum of PPy/HQS was therefore shifted significantly to higher energy relative to analogous peaks in the spectrum of PPy/BCS, which is consistent with the lower conductivity of the former system.

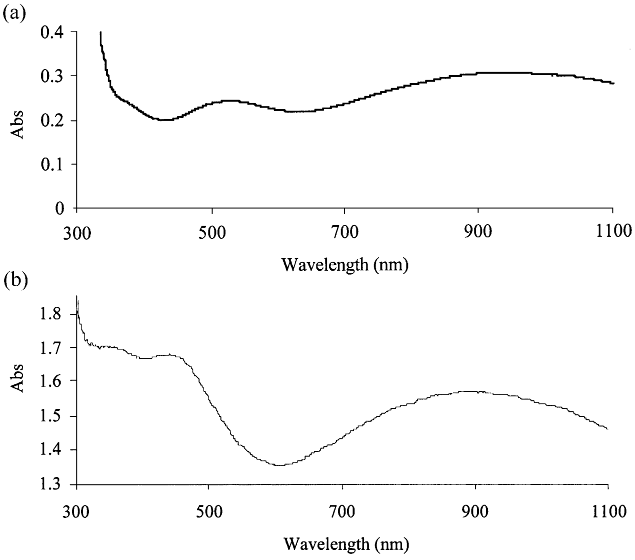

Fig. 2. UV–visible spectra of polymer films grown galvanostatically (2 mA cm^{-2} current density) onto ITO coated glass from solutions containing 0.20 M pyrrole and either 0.01 M BCS or 0.10 M (sat) HQS. (a) PPy/BCS, (b) PPy/HQS.

3.3. Electrochemical characterisation

Cyclic voltammetry studies were performed using platinum electrodes coated with either PPy/HQS or PPy/BCS, and solutions containing different metal nitrate salts. These studies were performed in order to confirm that the polymers prepared were electroactive, and investigate whether their electrochemical responses were markedly dependent on the nature of the cation in the surrounding solution. Fig. 3

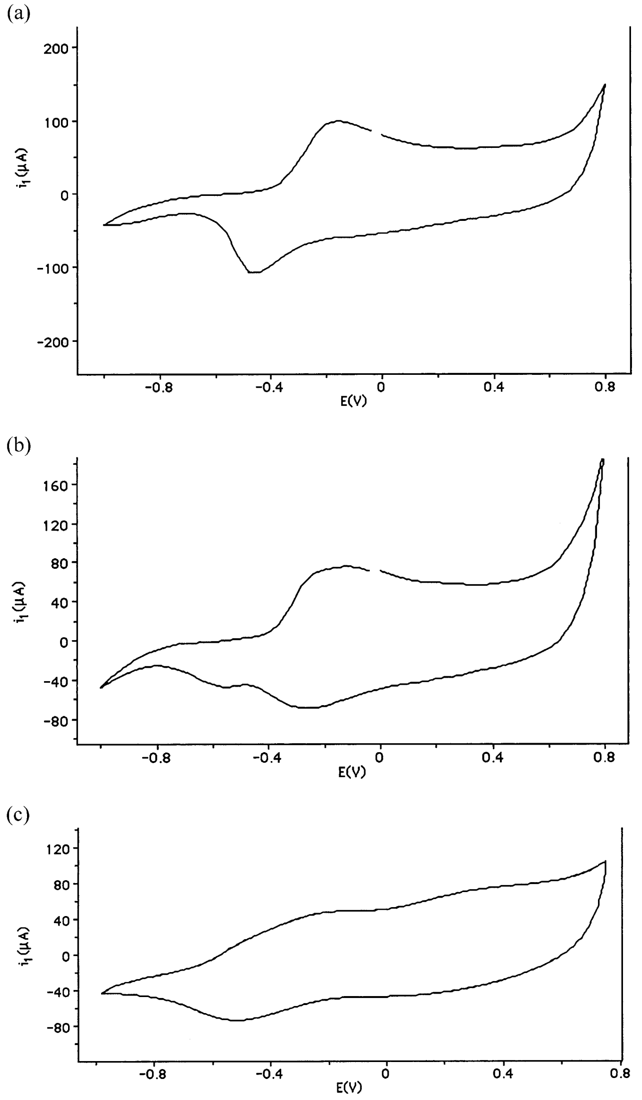

Fig. 3. Cyclic voltammograms of: (a) a PPy/BCS coated platinum electrode immersed in 0.10 M $Ni(NO_3)_2$, (b) a PPy/BCS coated platinum electrode immersed in 0.10 M $Mg(NO_3)_2$, (c) a PPy/HQS coated platinum electrode immersed in 0.10 M KNO_3. All scan rates = 100 mV s^{-1}.

Table 1
Sensitivity of platinum electrodes coated with either PPy/BCS or PPy/HQS to different ions: anodic peak potentials $E_{p(a)}$ and cathodic peak potentials $E_{p(c)}$ obtained from cyclic voltammograms of electrodes immersed in solutions containing different supporting electrolytes

Supporting electrolyte	$E_{p(c)}$ (V)		$E_{p(a)}$ (V)	
	PPy/BCS	Ppy/HQS	PPy/BCS	PPy/HQS
$NaNO_3$	−0.40	−0.70	−0.25	0.00
KNO_3	−0.35	−0.50 0.10	−0.30	−0.20 0.30
$Mg(NO_3)_2$	−0.25 −0.55	−0.15	−0.20	0.45
$Ca(NO_3)_2$	−0.20 −0.55	−0.15	−0.20	0.45
$Mn(NO_3)_2$	−0.50	0.05	−0.15	0.15
$Co(NO_3)_2$	−0.25	0.00	−0.05	0.05
$Ni(NO_3)_2$	−0.45	−0.10	−0.15	0.05
$Zn(NO_3)_2$	−0.70	−0.15	−0.15	0.05

illustrates some representative cyclic voltammograms, while Table 1 summarises the results of all cyclic voltammetry experiments. In nearly all cases at least one set of oxidation and reduction peaks were observed. The only exception to this was when either $Fe(NO_3)_3$ or $Cu(NO_3)_2$ was used as the supporting electrolyte. In these instances peaks due to oxidation and reduction of the free metal ion obscured those attributable to redox chemistry of the polymer.

The most commonly observed cyclic voltammogram is typified by that obtained using a PPy/BCS coated platinum electrode and $Ni(NO_3)_2$ as the supporting electrolyte (Fig. 3a). A single peak at −0.45 V is present which may be attributed to polymer reduction, most probably accompanied primarily by the movement of Ni^{2+} ions into the polymer. The corresponding oxidative peak at −0.15 V is therefore indicative of movement of some of these Ni^{2+} ions out of the polymer. In some instances cyclic voltammograms contained additional features which indicate that anion movement into and out of the polymer also occurred to a significant extent during redox cycling. For example, Fig. 3b shows the cyclic voltammogram obtained using a PPy/BCS coated platinum electrode and $Mg(NO_3)_2$ as the supporting electrolyte. Two features attributable to polymer reduction were present, with the peak at a more positive potential attributable to anion expulsion. A single broad peak due to polymer oxidation was present, which most likely consists of overlapping peaks attributable to anion incorporation and cation expulsion. A cyclic voltammogram with a very similar appearance was obtained when the same type of electrode was immersed in a $Ca(NO_3)_2$ solution. However, the cyclic voltammograms obtained when PPy/HQS coated platinum electrodes were immersed in either of these solutions showed only a single peak attributable to polymer oxidation and reduction. In contrast, when solutions containing KNO_3 (Fig. 3c) were used, cyclic voltammograms obtained using PPy/HQS coated platinum electrodes showed two sets of peaks attributable to polymer oxidation and reduction.

Inspection of Table 1 reveals that in general relatively small variations in the positions of cathodic and anodic peak potentials for a given polymer occurred when the supporting electrolyte was varied. One exception to this, however, was in the magnitude of first peak cathodic potentials observed using PPy/HQS coated electrodes, which varies by 0.75 V. For all systems relatively small variations in the magnitudes of the currents flowing during polymer oxidation and reduction were noted. Overall these observations suggest that the two polymers do not interact significantly differently with the wide variety of metal ions surveyed over the time scale (scan rate) investigated.

3.4. Transport studies

Transport experiments were performed using PPy/HQS and PPy/BCS coated membranes deposited onto Pt/PVDF using galvanostatic control (current density = 2 mA cm^{-2}) for 4.5 min. This time was chosen as it was demonstrated that this was the minimum amount of time that membranes must be grown to be impermeable to water. The fluxes of metal ions across both types of membranes are presented in Table 2. In all cases transport only occurred when the membrane was stimulated with a repetitive pulsed potential (e.g. Fig. 4). For PPy/BCS membranes all metal ions could be transported, however, this was not true for PPy/HQS membranes. Sodium, potassium, copper and cobalt were all found to be transported across the latter membrane, while calcium, magnesium, iron, nickel, manganese and zinc did not. In most cases when transport was observed with either membrane, removing the applied pulsed potential stopped ion transport. The only exceptions to

Table 2
Metal ion fluxes obtained from transport experiments involving PPy/HQS/Pt/PVDF and PPy/BCS/Pt/PVDF membranes (ND = not detected in receiving solution)

Ion	Flux accross Pt/ PVDF/PPy/HQS composite membrane (10^9 mol s^{-1} cm^{-2})	Flux across Pt/ PVDF/PPy/BCS composite membrane (10^9 mol s^{-1} cm^{-2})	Effective ionic radius (Å)
Na^+	0.27	9.29	4
K^+	0.11	7.12	3
Mg^{2+}	ND	0.48	8
Ca^{2+}	ND	0.68	6
Mn^{2+}	ND	0.81	6
Fe^{3+}	ND	3.39[a]	9
Co^{2+}	0.39	0.72	6
Ni^{2+}	ND	0.66	6
Cu^{2+}	0.51[a,b]	4.58[a,b]	6
Zn^{2+}	ND	1.28	6

[a] Values obtained after measuring the concentration of metal ion in the permeate solution after it had been allowed to stand for 24 h.

[b] From Ref. [32].

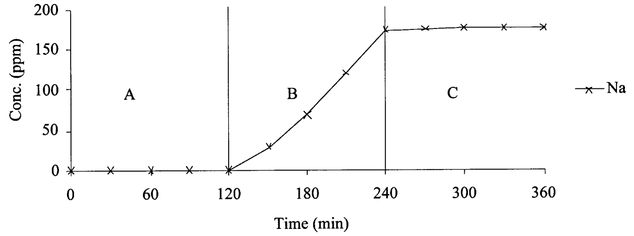

Fig. 4. Electrochemically controlled transport of Na^+ across a PPy/BCS/Pt/PVDF composite membrane. Feed solution: 0.10 M $NaNO_3$. Permeate solution: Milli-Q water. Region A: no applied potential. Region B: applied potential pulsed between +0.75 and −0.40 V; pulse width 50 s. Region C: no applied potential.

this occurred when experiments were performed with either copper or iron, and these are discussed below.

Previous studies have shown that the flux of alkali metal ions and alkaline earth metal ions across conducting polymer membranes decreases in the following order: flux $K^+ >$ flux $Na^+ >$ flux $Ca^{2+} >$ flux Mg^{2+} [13,14]. This trend was explained as being a result of decreasing ability to pass through the pores in the membrane as the size of the hydrated metal ion increased. Using either PPy/BCS or PPy/HQS membranes the measured fluxes followed a slightly different trend: flux $Na^+ >$ flux $K^+ >$ flux $Ca^{2+} >$ flux Mg^{2+}. The reversal of the positions for Na^+ and K^+ is not surprising given the similarity in the size of the hydrated ions of these metals (4 and 3 Å, respectively) [29]. This would also explain why the fluxes of these two metals across PPy/PVP membranes were almost identical [14].

The fluxes for sodium, potassium, calcium and magnesium across PPy/BCS (9.29×10^{-9}, 7.12×10^{-9}, 6.82×10^{-10} and 4.80×10^{-10} mol s^{-1} cm^{-2}, respectively) are comparable to or slightly larger than most other values previously determined for these metal ions under similar conditions. For example, the corresponding values reported using PPy/PVP membranes are 5.63×10^{-9}, 5.74×10^{-9}, 4.36×10^{-10} and 1.03×10^{-11} mol s^{-1} cm^{-2} [14]. Alkali metal ions and alkaline earth metal ions are known to form relatively weak complexes with 'phenanthroline-like' ligands. For example, log K_1 for the Mg^{2+} and Ca^{2+} complexes of phenanthroline itself are 1.5 and 0.7, respectively, while those for the transition metal ions Ni^{2+} and Cu^{2+} are 8.6 and 9.1, respectively [30]. Therefore, it is difficult to ascribe the slightly higher than usual fluxes for Na^+, K^+, Mg^{2+} and Ca^{2+} to favourable interactions with the dopant, rather than changes in membrane structure. In contrast to what was observed with PPy/BCS, the fluxes of alkali metal ions and alkaline earths through PPy/HQS membranes were, in general, smaller than what has been observed previously for these metal ions. This is best exemplified by magnesium and calcium, for which no metal ion transport was detected through PPy/HQS. Furthermore, the flux of K^+ through the PPy/HQS membrane was approximately 60 times smaller than that found with PPy/BCS.

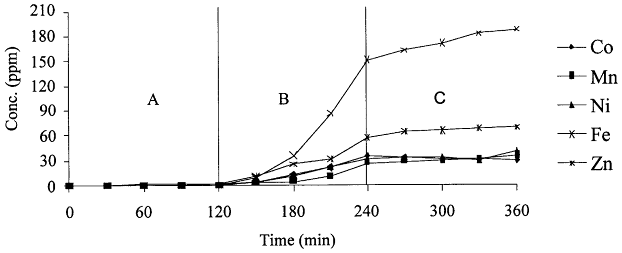

Fig. 5. Electrochemically controlled transport of separate solutions containing Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} or Zn^{2+} across PPy/BCS/Pt/PVDF composite membranes. Feed solutions: 0.10 M metal ion in 0.01 M H_2SO_4. Permeate solution: 0.01 M H_2SO_4. Region A: no applied potential. Region B: applied potential pulsed between +0.75 and −0.40 V; pulse width 50 s. Region C: no applied potential.

Prior to the present study transport experiments involving membranes and transition metals had focussed primarily on copper and, to a lesser extent, iron and manganese [10,12,31,32]. Fig. 5 illustrates the results of experiments performed using PPy/BCS membranes and iron, manganese, nickel, cobalt and zinc. Significant amounts of each of these metal ions were transported on application of an applied potential waveform. Importantly this system is the first for which electrochemically facilitated transport of cobalt, nickel and zinc across a conducting polymer membrane has been demonstrated. When the applied potential was removed metal ion transport stopped in the case of zinc, nickel, manganese and cobalt. However, the concentration of iron continued to increase during the next 2 h owing primarily to slow dissolution of iron metal that had deposited on the auxiliary electrode in the permeate solution, as well as either on or within the membrane itself. Since this iron had been transported during the applied potential phase of the experiment, the solution was allowed to stand for a further 24 h until the iron concentration in the permeate solution had stabilised, and this final concentration used to calculate the true iron flux.

A similar procedure was used to calculate the true flux of

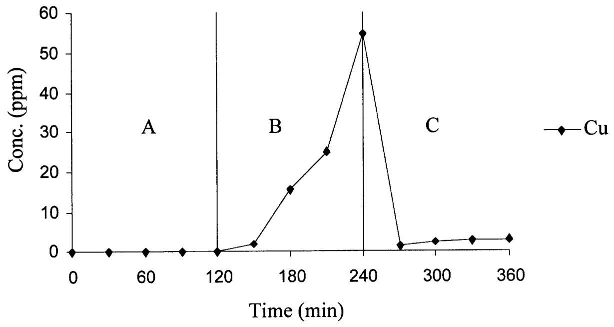

Fig. 6. Electrochemically controlled transport of Cu^{2+} across a PPy/BCS/Pt/PVDF composite membrane. Feed solution: 0.10 M metal ion in 0.01 M H_2SO_4. Permeate solution: 0.01 M H_2SO_4. Region A: no applied potential. Region B: applied potential pulsed between +0.75 and −0.40 V; pulse width 50 s. Region C: permeate solution replaced with fresh 0.01 M H_2SO_4. Auxiliary electrode in permeate solution removed. No applied potential.

copper through a composite membrane containing PPy/BCS in the transport experiment illustrated in Fig. 6. During the applied potential phase of the experiment the concentration of copper in the permeate solution increased dramatically. After stopping the applied potential, the permeate solution was transferred to a beaker, and then the auxiliary electrode that had been present in the permeate solution was removed and placed in the beaker. A fresh solution of 0.01 M sulfuric acid was then placed in the permeate compartment of the transport cell and the concentration of copper in the permeate solution was again monitored. Despite no potential being applied to the membrane a small amount of additional copper transport was observed. This had essentially finished after 2 h, and may be attributed to further transport of copper metal and ions trapped within the membrane, as well as dissolution of copper present on the membrane itself. By far the greatest amount of copper, however, had deposited on the auxiliary electrode in the original permeate solution. After 24 h complete dissolution of this copper metal had occurred, raising the concentration of copper in the original permeate solution to 240 ppm, considerably higher than the 55 ppm determined at the end of the applied potential phase. The former value was then used to calculate the flux reported for copper in Table 2.

The fluxes for each of the six transition metal ions examined with PPy/BCS follow the sequence: $Cu^{2+} > Fe^{3+} \gg Zn^{2+} > Ni^{2+} \sim Mn^{2+} \sim Co^{2+}$. Of these metal ions the tripositive Fe^{3+} has the largest hydrated ion radius, with those of the remaining metal ions all being comparable to one another, and significantly less than that of Fe^{3+}. If the membrane discriminates on the basis of the size of the metal ions hydration sphere, then iron should have had the lowest flux, and the fluxes of the remaining metal ions should have been similar to one another and significantly higher than that of Fe^{3+}. Since this is not what was observed it suggests that for transition metals several factors can play a significant role in determining metal ion flux across the membrane. One factor is the existence of more than one mechanism of transport for some metal ions. For electroinactive metal ions such as the alkali metal ions and alkaline earths, transport is believed to involve incorporation of the positively charged metal ion into the membrane during the reductive phase of the pulsed potential waveform, and subsequent expulsion into the receiving solution during the oxidative phase. Movement through the membrane itself is believed to occur by a variety of processes including ion diffusion and ion shunting. For the transition metal ions manganese, cobalt, nickel and zinc, membrane transport also probably occurs predominantly via this mechanism. However, for iron and most importantly for copper, significant transport also apparently occurs by a second mechanism involving reduction of the metal ion to the elemental metal onto the membrane, followed by shunting through the membrane and oxidation at the receiving solution surface.

Another important factor to consider when rationalising differences in transition metal ion fluxes is the variation in interactions between the different transition metal ions and the dopant present in the polymer membrane. Direct evidence for the formation of metal/dopant complexes during the course of transport experiments is difficult to obtain, primarily owing to the very low quantities of such complexes present. Compounding this problem are difficulties associated with making definitive assignments based on spectroscopic data. We attempted to characterise by visible absorption spectroscopy metal/BCS and metal/HQS complexes formed within PPy/BCS and PPy/HQS thin films. Both types of films were soaked in solutions containing different metal ions, and spectra of the resulting films compared with those of the initial film. In all cases no significant differences were noted. In contrast, square wave voltammetry has been used to provide direct evidence for the formation of copper/BCS and copper/BPS complexes (BPS = bathophenanthroline) within PPy/BCS and PPy/BPS thin films, after soaking in solutions containing either Cu(I) or Cu(II) [17]. The square wave voltammograms obtained after soaking the films in either copper solution were reported to be very similar to that of aqueous solutions containing either copper/BCS or copper/BPS complexes.

There have been very few reports previously describing transport of transition metal ion across conducting polymer membranes. However, a value of 1×10^{-10} mol cm^{-2} s^{-1} was reported for the flux of copper across PPy membranes doped with pTS [10]. This experiment was performed using an identical source ion concentration (0.10 M) to that used here, but a different transport cell design was used. Nevertheless the flux of Cu^{2+} reported here across a PPy/BCS membrane is almost 50 times larger. This suggests that BCS may be playing a significant role in assisting copper transport through the membrane, possibly through favourable metal/ligand complexation/decomplexation equilibria, and/or minimising the amount of copper depositing as the metal within the membrane.

The only other metal ion for which comparative transport data is available is manganese. When experiments were performed examining transport of Mn^{2+} across membranes composed of PPy polymers or copolymers doped with pTS, fluxes of 1.72×10^{-10} and 3.36×10^{-10} mol cm^{-2} s^{-1} were obtained [12]. These values are slightly smaller than that reported here (8.1×10^{-10} mol cm^{-2} s^{-1}) for transport of Mn^{2+} across a composite membrane containing PPy/BCS. However, the former values were obtained from experiments performed using source solutions containing both Mn^{2+} and K^+, which would most likely have led to smaller fluxes than if Mn^{2+} had been the sole ion in the source solution. Based on the above data concerning transport of Cu^{2+} and Mn^{2+}, it appears that BCS can, in some instances, significantly enhance metal ion transport. A possible explanation for the differing influence of BCS on the fluxes of Mn^{2+} and Cu^{2+} can be proposed based on the likely differences in thermodynamic stability of the complexes formed by these metals with BCS. While formation constant data for many transition metal complexes of BCS are not available, they have been reported for the closely related 1,10-phenanthroline ligand [29]. For the transition metals examined here, the log K_3 values for the tris(phenanthroline) complexes follow the sequence $Mn^{2+} \ll Zn^{2+} < Co^{2+} < Cu^{2+} < Fe^{3+} \sim Ni^{2+}$. Clearly Cu^{2+} is therefore more likely to form a more stable complex with BCS than Mn^{2+}, which may be an important factor in facilitating movement of the former ion through the membrane relative to PPys doped with ligands not capable of chelation. According to this theory Fe^{3+} and Ni^{2+}, which form the most stable complexes with phenanthroline, should also exhibit relatively high fluxes across composite membranes containing PPy/BCS. While the flux for Fe^{3+} was the highest amongst the transition metals apart from Cu^{2+}, that for Ni^{2+} was less than that for Mn^{2+}.

Of the transition metal ions examined only copper and cobalt were able to pass through composite membranes containing PPy/HQS at a detectable rate. The complete lack of transport for any of the remaining four transition metal ions examined is surprising, but in keeping with the absence of transport observed earlier in experiments with calcium and magnesium carried out using the same membrane. Overall it is clear that composite membranes containing PPy/HQS do not allow the passage of metal ions as readily as composite membranes containing PPy/BCS. Further evidence in support of this is provided by a comparison of the fluxes observed for copper and cobalt with both types of membranes. For cobalt the flux is almost two times smaller with the PPy/HQS membrane, while with copper the reduction is close to a factor of 10.

Three of the metal ions examined, copper, manganese and zinc, are known to form four-coordinate complexes with HQS in aqueous solution, while the remaining three transition metal ions all bind 3 HQS molecules to give six-coordinate species [29]. Examination of the stability constants for these complexes provides no explanation for why only two of the six transition metal ions are transported across composite membranes containing PPy/HQS. By far the most stable complex is that with Fe^{3+}, for which a log K_3 value of 35.65 has been reported [29]. This equilibrium constant is more than 10 orders of magnitude greater than that for the next most stable complex, and may point to the formation of thermodynamically inert complexes that are trapped within the membrane. Log K_3 for cobalt and HQS is 20.41, which is comparable to that for log K_3 for nickel (22.90) and log K_2 for copper (21.87) [29], suggesting that all three metal ions should form complexes of comparable thermodynamic stability with HQS in the polymer membrane. However, the observation that composite membranes containing PPy/HQS are permeable to cobalt and copper, but not nickel, suggests that the thermodynamic stability of any metal ligand complexes present in the membrane is not singularly important in determining the metal ion flux.

4. Conclusions

Incorporation of the chelating agents 8-hydroxyquinoline-5-sulfonic acid and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid into PPy resulted in new materials which displayed contrasting metal ion transport properties. Composite membranes containing PPy/BCS were permeable to alkali metal ions, alkaline earth metal ions and transition metal ions under the influence of an applied electrical potential. In contrast composite membranes containing PPy/HQS were permeable to a much smaller range of metal ions. Furthermore, the fluxes observed for this small range of metal ions were lower than for transport across composite PPy/BCS membranes. This strongly suggests that metal/dopant interactions within the membrane are an important factor in determining metal ion permeability. However, further work will be required to delineate the relative contributions of variations in membrane thickness, conductivity and morphology, as well as metal/ligand interactions, to differences in metal ion fluxes between different membranes. The transport results presented in Table 2 suggest that composite membranes containing PPy/HQS may be useful materials for separating mixtures of metal ions, e.g. Cu^{2+}/Fe^{3+} and K^{+}/Ca^{2+} mixtures. It will be important to determine whether it is possible to further fine tune PPy/HQS membranes to increase the flux of metal ions, while maintaining this selectivity.

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