# Transport of copper(II) across stand-alone conducting polypyrrole membranes: the effect of applied potential waveforms

**Huijun Zhao, William E. Price and Gordon G. Wallace***
*Intelligent Polymer Research Laboratory, Department of Chemistry,
University of Wollongong, PO Box 1144, Wollongong, NSW 2500, Australia*
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High-quality polypyrrole membranes have been made by an electrochemical method. These membranes were robust and had a high conductivity (typically 60 S $cm^{-1}$). Investigations into the transport properties of these membranes using copper(II) as the transporting species demonstrated the use of applied potential to control the rate of transport. Differences of two orders of magnitude in the permeability of copper across the membrane were found.

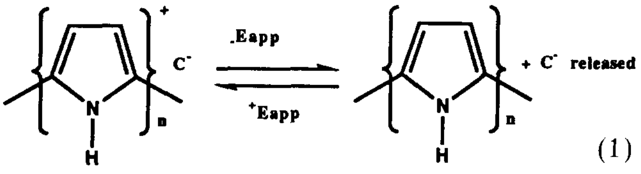
**(Keywords: polypyrrole; membranes; ion transport)**

## INTRODUCTION

The idea of polymeric materials that can respond to changing environmental conditions and external stimuli, so-called intelligent materials, is one that will be increasingly influential in many fields in the future. These materials should be able to be made such that they recognize specific species through surface or other interactions and then respond to that stimulus. Given the inherent dynamic properties of many polymers[1], they are well suited to perform such tasks. For example, polymers that respond to heat[2], light[3], or electrical stimuli[4,5] by chainging their physical or chemical properties have been described previously.

One area where intelligent materials will potentially make a significant impact is that of membrane technology. Membranes are utilized to perform separations in a wide range of applications. Well known examples of this technology include kidney dialysis, ultrafiltration of dairy products and separation of oxygen from gas mixtures. The proliferation of membrane technology is likely to continue as more sophisticated systems are designed tailored to specific applications.

One of the limitations of conventional membranes is that, however sophisticated they are, their structure and morphology are generally fixed at the time of synthesis and are not dynamic. Conducting, electroactive polymers such as polypyrrole (PPy) offer the possibility of membranes with dynamic controllable properties through the different redox states in which they can exist. Application of a cathodic potential to polypyrrole results in reduction of the positively charged polymer backbone and usually the expulsion of the negative counterion according to:



(1)

A number of groups[6–9] have utilized the redox properties of polypyrrole in membranes and have demonstrated some differences in the transport behaviour of the membrane in the oxidized and the reduced states.

In this paper we demonstrate the feasibility of using applied potential waveforms to a conducting polymer membrane to produce controllable release time profiles of a species from a reservoir. Here we investigate the transport of copper(II). Copper was chosen not only because there is much interest in the separation of copper from solution mixtures but also because the system adds another dimension to the transport mechanism: copper is electrochemically active and readily undergoes oxidation/reduction from Cu(0) to Cu(II).

## EXPERIMENTAL

### *Membrane preparation*

The pyrrole (Py) used in the manufacture of the membranes was obtained from Sigma and was distilled freshly prior to use. The anion used in the polymerization was *p*-toluenesulphonic acid (PTS). It was used in the sodium salt form, and was analytical reagent grade (Aldrich), used as received. Other anions were also investigated as to their suitability for membranes. All solutions were made up using distilled, deionized water

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*To whom correspondence should be addressed

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dispensed from a MilliQ water purification system, which had a resistance of 18 MW.

The PPy–PTS membranes were prepared from an aqueous solution containing 0.2 M pyrrole and 0.05 M $PTS^-Na^+$. The polymerization was carried out electrochemically in a three-electrode cell using controlled current conditions with a current density of 2 mA $cm^{-2}$ for 10 min. This was provided by a PAR-173 system. The working electrode was a stainless-steel plate (42 × 100 $mm^2$). After polymerization the membrane was washed thoroughly with distilled water to remove any surface liquid. The PPy–PTS membrane was then peeled off the electrode and allowed to dry in air. The valid area of the membrane was about 35 × 23 $mm^2$.

### *Membrane characterization*

Prepared membranes were characterized in a number of ways in order not only to gain an understanding of their structure but also to assess their suitability for use as a membrane. The simplest characterization tests performed were film thickness, scanning electron microscopy, mechanical stability and the conductivity of the membrane. The latter test was carried out using a four-point probe, enabling the resistance of the film to be determined as a function of area.

### *Transport experiments using copper(II)*

The cell utilized in the transport experiments is depicted in *Figure 1*. It consisted of two compartments of 75 ml separated by a PPy membrane. The solutions in the compartment were stirred by small polytetrafluoroethylene (PTFE) paddles run off d.c. motors. These stirrers had some holes in order to facilitate the passage of liquid. For experiments investigating the effect of applied potential to the membrane upon the flux of copper(II), a three-electrode system was used. The membrane acted as the working electrode. An Ag/AgCl reference electrode was in contact with both solutions by means of a salt bridge. In addition, two parallel-connected electrodes were set up in each side of the cell to act as auxiliary electrodes. In this manner a known potential could be applied to the membrane without introducing a significant potential across the solutions or the membrane.

Aqueous solutions of copper(II) nitrate in 0.1 M sodium nitrate were prepared by volume from analytical reagents. The concentrations of copper(II) were 0.01 and 0.1 M. One side of the cell was filled with the copper(II)-containing solution (75 ml) containing 1% $HNO_3$ (v/v) (subsequently referred to as the *source* compartment or solution) and the other side with an equal volume of solution containing only the background electrolyte (*receiver* solution). Samples were then taken from the low-copper(II)-concentration side as a function of time. Samples were withdrawn every 20–30 min and analysed electrochemically for $Cu^{2+}$ using differential pulse stripping voltammetry. The set-up used employed a mercury–glassy carbon working electrode with Ag/AgCl electrode as reference. A deposition time of 60 s was employed. The system was calibrated using a series of copper(II) standards with concentration range 0–500 ppb $Cu^{2+}$. The samples were diluted if required.

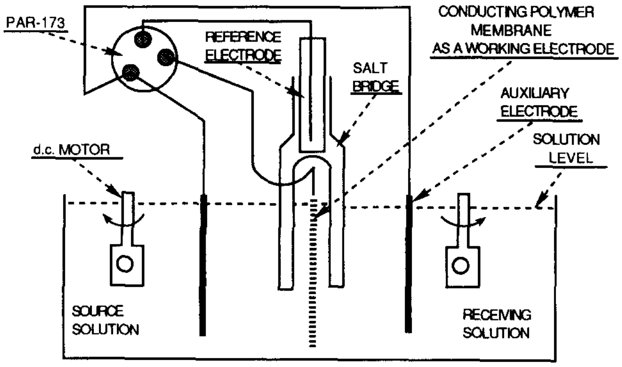

**Figure 1** Diffusion cell diagram

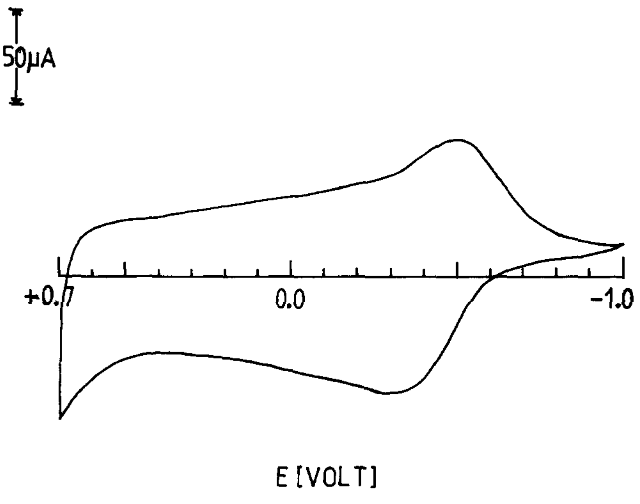

**Figure 2** Cyclic voltammogram of PPy–PTS electrode in 0.1 M $NaNO_3$: scan rate, 10 mV $s^{-1}$

## RESULTS AND DISCUSSION

The PPy–PTS membranes prepared were found to be mechanically robust, pinhole-free and suitable for use as a membrane separating two solutions. The conductivity of the film, the other important property requirement for our purposes, was found to be about 40–80 S $cm^{-1}$ as measured by four-point probe resistometry. This is highly conducting and compares favourably to films of PPy made by other groups[6–9].

### *Characterization of prepared membranes*

*Cyclic voltammetry. Figure 2* shows a cyclic voltammogram (c.v.) of a PPy–PTS film, prepared as described above, supported on a glassy carbon electrode. The electrolyte solution used was 0.1 M $NaNO_3$. The figure clearly shows redox changes taking place in the film according to the usual scheme. The release of PTS during these experiments was tested by measuring the u.v. absorbance of the solution during these c.v. runs. Spectroscopy after reduction of the film revealed the presence of PTS in the supporting electrolyte. Clearly some expulsion of counterion had taken place.

*Figure 3* shows another c.v. of the film. The conditions are the same as above except that the supporting electrolyte solution now contains 40 ppm Cu(II). The current peaks clearly show the oxidation and reduction process for the Cu(II)/Cu(0) redox couple taking place on the film surface.

*Scanning electron microscopy.* Electron micrographs and other simpler direct techniques indicated a

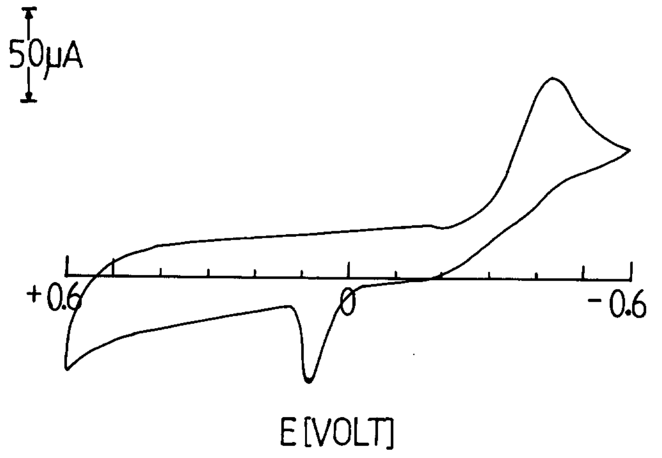

**Figure 3** Cyclic voltammogram of PPy–PTS electrode in 0.1 M $NaNO_3$ with 40 ppm $Cu^{2+}$: scan rate, 10 mV $s^{-1}$

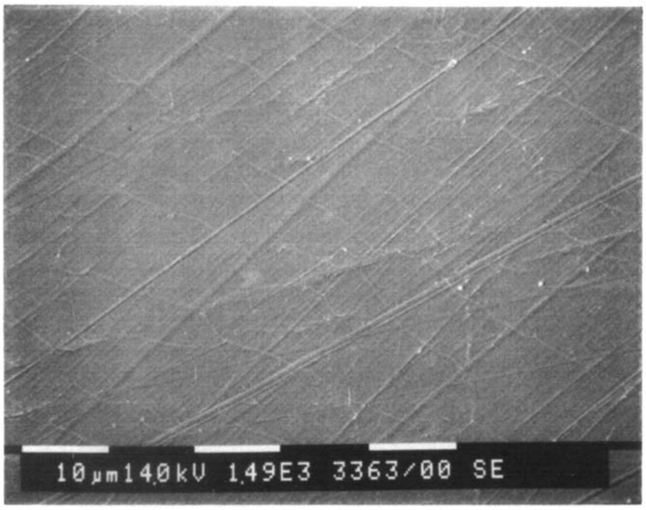

**Figure 4** SEM of PPy–PTS membrane: plate side

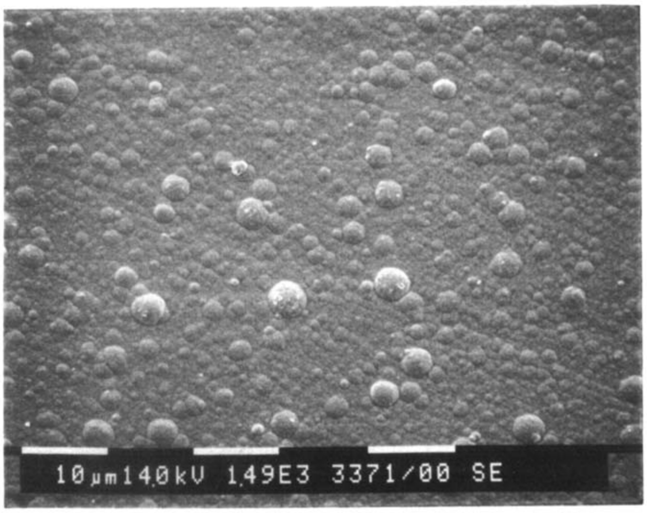

**Figure 5** SEM of PPy–PTS membrane: solution side

membrane thickness of approximately 5–6 μm. SEM photographs of the two sides of the film are shown in *Figures 4* (plate side) and *5* (solution side). It is striking that the two different sides have quite dissimilar appearances. The plate side has a much more compact surface whereas the solution side surface appears more porous. This effect has been noticed previously by other workers[7]. This may be ascribed to the fact that the inner (plate) side of the film has its initial layer deposited on a metal substrate and subsequent layers are grown on top of polypyrrole[10].

*Transport of copper(II) using constant potential waveforms*

The simplest experiments carried out were ones where a single constant potential was applied to the membrane for a period during the transport of copper(II). Potentials of ±0.60 V were applied, since at these extremes copper is oxidized/reduced, but the polymer remains in the oxidized state (see *Figures 2* and *3*). These would typically have the following profile: no potential (2 h); followed by either +0.6 V or −0.6 V applied potential (2–3 h); followed by a period of no applied potential. Experiments of this type employing a single period of constant applied potential had little effect upon the rate of copper(II) transport across the PPy membrane. The average flux obtained in this manner for a source solution of 0.1 M $Cu(NO_3)_2$ was $4(\pm 1.5) \times 10^{-12}$ mol $cm^{-2}$ $s^{-1}$. For a 0.01 M Cu(II) source a typical flux was $6(\pm 1.5) \times 10^{-13}$ mol $cm^{-2}$ $s^{-1}$. We can use standard steady-state Fickian diffusion to model[11,12] the transport across a thin film membrane to obtain simple estimates of the permeability of the membrane to the diffusing species:

$$\text{Flux } j_1 = \frac{DK}{x}\Delta C \qquad (2)$$

where $D$ is the diffusion coefficient of the transporting species (Cu) across the membrane of thickness $x$ and $K$ is the partition coefficient for the copper between the solution phase and the membrane. $\Delta C$ is the concentration difference between the source solution and the receiver solution. The product $DK$ is an often reported quantity for membranes and is called the permeability. For the fluxes and conditions quoted above, the permeability ($DK$) of the membrane to the Cu(II) is estimated as $2(\pm 1.5) \times 10^{-11}$ mol $cm^2$ $s^{-1}$.

It was found that application of two constant potential periods to the system had a marked effect upon the transport of copper as shown in *Figure 6*. This type of experiment has a potential sequence as follows: no

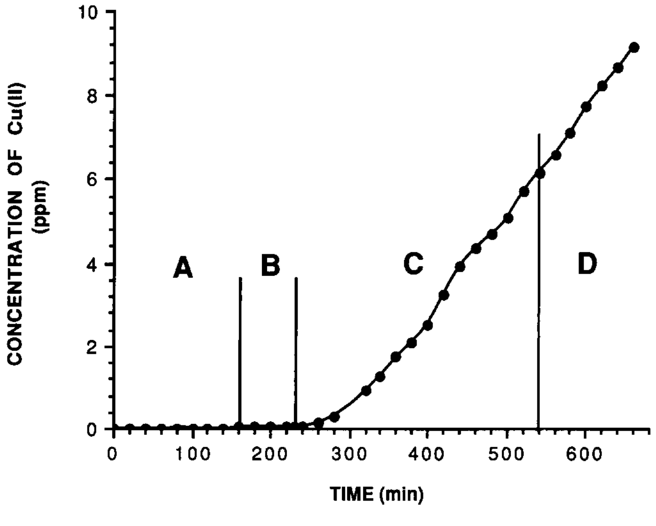

**Figure 6** Transport of 0.01 M Cu(II) across PPy–PTS membrane: A, no potential applied; B, −0.06 V vs. Ag/AgCl applied to membrane; C, +0.60 V vs. Ag/AgCl applied to membrane; D, application of potential to membrane stopped

potential applied (2–3 h); −0.6 V potential (1 h); +0.6 V potential (3–4 h); no applied potential. There is an increase in the Cu(II) flux on application of the second (positive) constant potential. This transport continues even after the anodic potential was removed, presumably due to some build-up of Cu(II) ions in the polymer. A typical value for the flux is $5 \times 10^{-11}$ mol cm$^{-2}$ s$^{-1}$, which yields a membrane permeability of $2.5 \times 10^{-9}$ mol cm$^{2}$ s$^{-1}$, a ten-fold increase on the experiments above. Note that this increase only occurs after application of a negative potential followed by an anodic potential.

### *Transport studies of copper(II) using pulsed applied potentials*

The application of pulsed potential waveforms also had dramatic effects on the transport rate of copper(II). *Figures 7* and *8* present copper(II) concentration profiles with time, showing transport across the PPy–PTS membrane, with initial copper(II) concentrations in the high-concentration side of 0.01 and 0.1 M respectively. In both cases a pulsed applied potential waveform was used on the membrane during the experiment. This consisted of a ±0.6 V potential square waveform with a 10 s pulse width. The important feature of these two curves is that the rate of transport through the membrane rapidly increased when the period of applied potential finished. We will call the average flux of Cu(II) (in units of mol cm$^{-2}$ s$^{-1}$) before and during the applied potential $\Phi_1$, and use $\Phi_2$ for the flux of copper(II) after the applied potential phase. These are shown in *Table 1*. Clearly the effect of the pulsed potential is to enhance the transport of Cu(II) in the 'after potential' phase. In the 0.01 M experiments the enhancement of the flux is about 600% and in the 0.1 M experiments it is some 4000%. The fact that the permeability of the membrane from these two results appears to be concentration-dependent reflects that the simple Fickian model[11] is not realistic. The two experiments described were carried out using different membranes, and, although made using identical conditions, differences in morphology and bulk properties may have occurred.

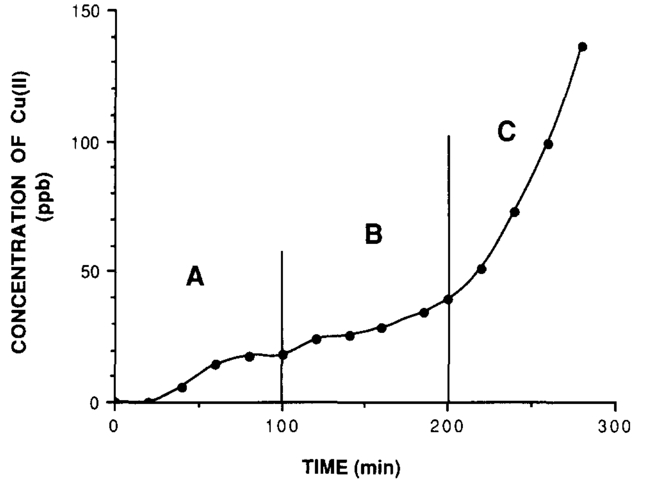

**Figure 7** Transport of 0.01 M Cu(II) across PPy–PTS membrane: A, no potential applied; B, ±0.60 V pulsed potential applied to membrane (pulse width = 10 s); C, no potential applied to membrane

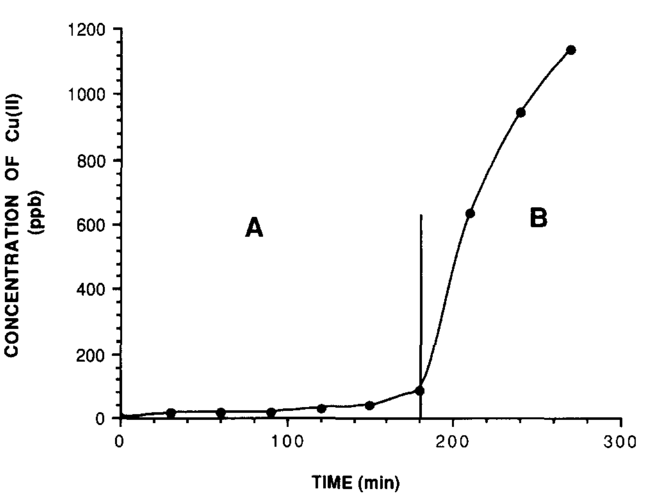

**Figure 8** Transport of 0.10 M Cu(II) across PPy–PTS membrane: A, ±0.60 V pulsed potential applied to membrane (pulse width = 10 s); B, no potential applied

**Table 1** Cu(II) fluxes through PPy membrane and membrane permeabilities during and after pulsed applied potential with varying Cu(II) source concentrations

| [Copper(II)] (M) | Flux ($10^{-12}$ mol cm$^{-2}$ s$^{-1}$) | | Permeability ($10^{-11}$ mol cm$^{2}$ s$^{-1}$) | |
|---|---|---|---|---|
| | $\Phi_1$ | $\Phi_2$ | $(DK)_1$ | $(DK)_2$ |
| 0.01 | 0.92 | 6.00 | 4.6 | 30 |
| 0.10 | 2.50 | 100.00 | 1.3 | 50 |

Work by Burgmayer and Murray[6,7] first highlighted the potential of so-called switch-ion effects in transport studies looking at KCl fluxes through polypyrrole membranes. In these experiments either an oxidizing or a reducing constant potential was applied to the membrane. Quoted KCl fluxes for the oxidized and reduced form of the membrane (estimated as 10 μm thick) were $23 \times 10^{-11}$ and $3.6 \times 10^{-11}$ mol cm$^{-2}$ s$^{-1}$ respectively. These were higher than the non-enhanced fluxes found for copper here, but the concentration gradient employed by Burgmayer and Murray was 1.0 M. They did not find it necessary to apply both a negative and then a positive potential to increase the flux. This would indicate that, as expected, the mechanism controlling the copper(II) transport was different in nature.

These facts together with the observation of the greatly enhanced copper(II) flux using pulsed potential sequences (which are merely repeated sequences of the experiment in *Figure 5*) suggest that the electrochemical reaction of copper at the membrane surface is the important factor.

The effect of applying a negative −0.6 V potential to the film is to reduce copper ions to copper metal on the membrane. This was in fact observed, with the black coloured membrane becoming golden brown as more copper was deposited. Consequently a plausible explanation of the enhancement of the transport of copper(II) in experiments using a period of negative potential and then one of +0.6 V is as follows. The negative potential provides a period of deposition upon the membrane surface. During this time the flux of copper(II) is approximately the same as that during a 'no potential' period. On application of a positive (+0.6 V) potential a large concentration of copper(II) is produced at the membrane surface and within the pores of the membrane. This represents an enhanced concentration gradient, which according to equation (2) would increase the flux. If this was the case then a concentration gradient of about 1 M would be enough to explain the flux increase.

It might be possible to explain the large flux increase in the pulsed potential experiments (*Figures 7* and *8*) in a similar manner. In this case after 10 s of depositing copper the positive potential removes it, creating an enhanced concentration gradient. This is then a repeated sequence resulting in an 'electrochemical pumping' effect of the copper through the membrane. The fact that the effect of the pulsed potential is much greater than for the constant potential sequence suggests that the large layer of deposited copper on the surface of the membrane in the latter case acts as an inhibitor to transport of copper, thus negating the effect of a very large localized concentration.

Although these is some evidence[8,9] suggesting that transport of divalent cations is not greatly enhanced by changing the redox states of the PPy membrane, further work is needed to elucidate the phenomena described for copper(II) transport. This is currently being undertaken.

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