

Effect of Solution Temperature on Controlled Potential Transport Properties of Polypyrrole Conducting/Electroactive Membranes

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This paper deals with the effect of the solution temperature on transport of potassium cation across polypyrrole conducting/electroactive polymer membranes doped with *p*-toluene sulfonate and dodecyl benzene sulfonate as counterions. Potassium ion was employed as a probe for investigation of the effect of electrolyte temperature. Investigation was carried out in two different solution temperatures. It was found that polypyrrole electroactive membranes or free standing films can be applied successfully at elevated electrolyte temperatures without any important loss in their mechanical properties. Little improvement in ion flux (K^+ ion) across the polypyrrole doped dodecyl benzene sulfonate membrane was observed at higher solution temperature, but in the case of polypyrrole doped *p*-toluene sulfonate some decrease influx of potassium ion was observed.

Key Words: Polypyrrole, Electroactive, Membrane, Potassium ion, Transport, Solution temperature.

INTRODUCTION

Polypyrrole (PPy) is mainly prepared electrochemically. Oxidation of pyrrole ($E_{app} \geq 0.70$ V vs. Ag/AgCl) yields a charged polymer film (PPy/A) with incorporated anions¹⁻³. The pyrrole units have positive charges, which are balanced by anions. The overall electropolymerization of polypyrrole can simply be shown in Fig. 1.

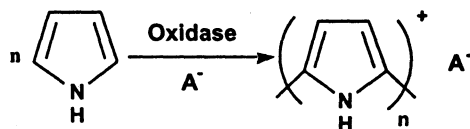


Fig. 1. Polymerization reaction of pyrrole in the presence of electrolyte M^+A^- where A^- is the anion of electrolyte solution in which the monomer is dissolved. Polypyrrole is readily synthesized both chemically or electrochemically from a range of aqueous and non-aqueous solvents. An aqueous deposition medium would offer considerably larger selection of supporting electrolyte anions. Chemical methods compared to the electrochemical method produce less conduc-

tive product, but it has the advantages of easier mass preparation, need for simple equipment, fast synthesis and preparing conducting composites or blends with inert conventional or commercial polymers. Polypyrrole conducting electroactive polymers undergo ion exchange (both anion and cation) during oxidation/reduction process for charge neutrality. During the redox process, electroneutrality can be maintained either by expulsion of these anions or by incorporation of cations, depending on the nature of dopant anion, polymerization conditions and electrolyte solution in which the polymer is switched.

A new concept of separation based on electrochemical behaviour (ion exchange) has been developed for these new electrically conductive polymer membranes⁴⁻⁸. The reduction/oxidation processes in PPy conducting polymers are accompanied by incorporation/expulsion of cations and anions in supporting electrolyte in which the polymer is switched. The unique nature of electroactivity in these polymers results in ion movement in and out of the polymer during redox reactions. It has been found that the nature of dopant (size or MW) has very important effect on the redox behaviour or mass transport properties of PPy conducting/electroactive membranes^{9,10}.

EXPERIMENTAL

The reagents and chemicals used for polymerization were all AR grade. Pyrrole (obtained from Sigma) was used after distillation. Electropolymerization and transport experiments were carried out in aqueous solution⁴. A single compartment electrochemical cell (Fig. 2) employing a three electrode system was used for preparation of PPy membranes. Stainless steel plate (5 × 6 cm) was used as the working electrode and a silver/silver chloride reference electrode was used as reference electrode and reticulated vitreous carbon was used as the auxiliary

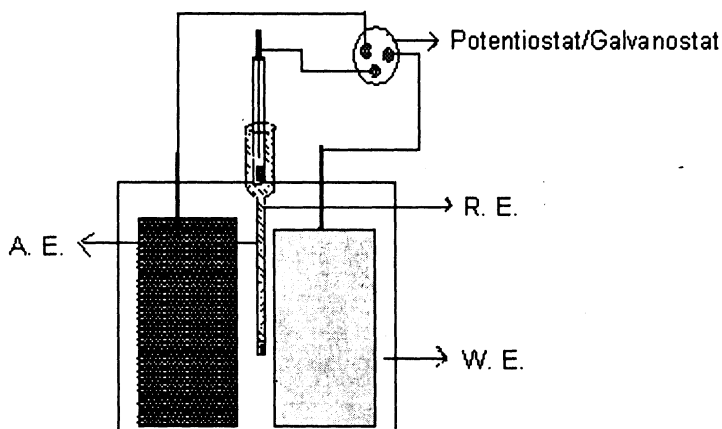


Fig. 2. Electrochemical cell used for electrosynthesis of PPy/PTS membranes. Electropolymerization was carried out galvanostatically using a current density of 2 mA/cm^2 , from a solution containing 0.2 M pyrrole as monomer and 0.05 M of counterion (NaPTS) in distilled water

electrode (AE). The time of polymerization was selected 12 min in order to synthesize polymer films with a thickness of 5 μm . The membranes were checked for pin-holes using a suitable light source before being used for transport experiments.

Instrumentation: Electrical stimuli were applied to one side of the membrane in a special electrochemical cell design for transport studies (Fig. 3) using a potentiostat (PAR), controlled by a pulse generator, the other side being in contact with deionized water⁴. The temperature of the cell solution was controlled using a temperature controller instrument (Julambo 20) and a peristaltic pump.

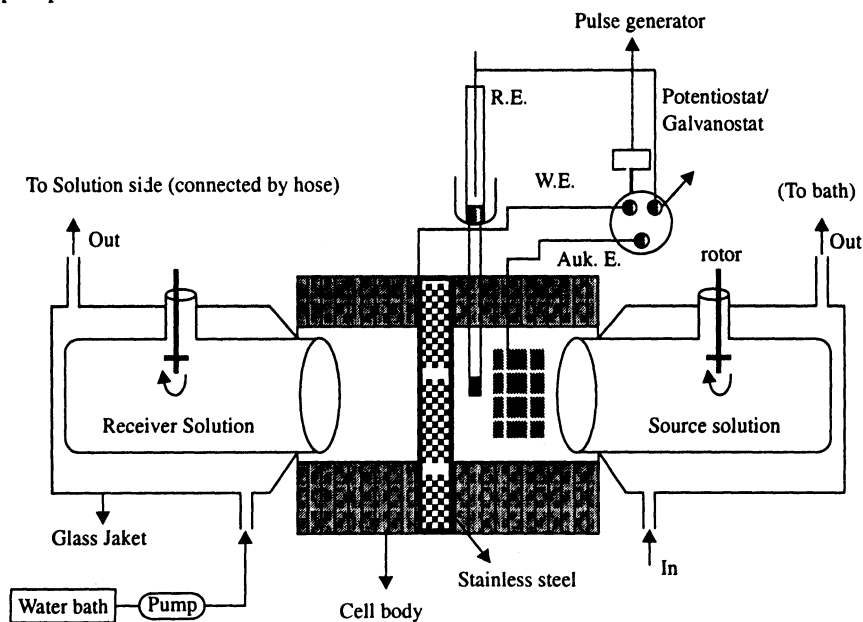


Fig. 3. Electrochemical cell set up used for controlled potential transport studies under controlled solution temperatures. The exposed area of the polymer for transport of ions was 8 cm^2 . Electrical stimuli was applied only in the source side of the cell. A platinum gauze electrode was used as the auxiliary electrode during transport experiments

RESULTS AND DISCUSSION

Polypyrrole conducting electroactive polymers undergo ion exchange (both anion and cation) during oxidation/reduction process for maintaining of charge neutrality in polymer. During the redox process, electroneutrality can be maintained either by expulsion of these anions or by incorporation of cations, depending on the nature of dopant anion, polymerization conditions and electrolyte solution in which the polymer is switched. The small size counterions or dopants (*e.g.*, Cl^-) can be released by applying a negative potential and the polymer mainly exhibits anion-exchanger behaviour. PPy films doped with medium size dopants (*e.g.*, PTS anions) show both anion and cation exchange properties and PPy films doped with large or unreleasable dopants (*e.g.*, polymeric dopants) show mainly cation ex-

change properties during the redox process. The redox behaviour and the appropriate switching potentials of PPy electrodes can be easily found out using simultaneous cyclic voltammetry, cyclic resistometry and quartz crystal microbalance techniques⁹.

In situ cyclic voltammetry (CV) and cyclic resistometry (CR) were first used to characterize the redox properties of the polymer membrane and the measurement of the resistance changes of the polymer as it is switched between the oxidized and reduced states (Fig. 4). Using these techniques the appropriate switching potentials of PPy can also be ascertained.

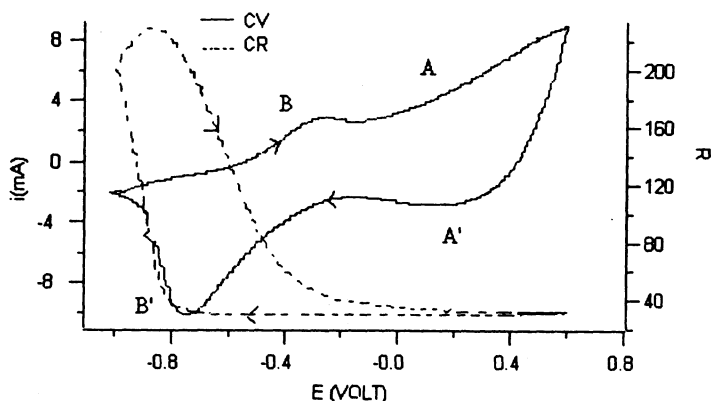


Fig. 4. Simultaneous CV and CR analyses of PPy/PTS membrane. The CV and CR experiments were carried out in transport cell (shown in Fig. 3) in a solution of 0.2 M KCl (Scan rate = 5 mV/sec)

PPy films are prepared in oxidized state. During reduction of the polymer, surface releaseable anions are expelled (A'). As the polymer is reduced further then cation incorporation is observed (B') in order to maintain charge balance in polymer since deeply dopant anions in the polymer matrix are not released. During subsequent oxidation, cations are expelled (B) or anion incorporation occurs (A). Therefore, polypyrrole doped *p*-toluene sulfonate (PPy/PTS) has both cation (couple B/B') and anion exchange (couple A/A') properties. The redox peaks in CV obtained for PPy/PTS membrane corresponding to anion and cation expulsion/incorporation have been labelled by (A/A') and (B/B') respectively (Fig. 4). The redox reaction of the film becomes more difficult as the thickness increases (see A/A'). Peak separation and broadening increases with increasing the thickness. In spite of the great differences in the surface morphology of the growth (porous) and plate (very smooth) side in PPy films, the CV or CR data obtained from both sides of the polymer did not show significant differences. The increase in resistance is attributed to the changing of PPy from oxidized (PPy⁺) form to reduced (PPy⁰) which is accompanied by anion expulsion and/or cation incorporation. Increases in the resistance of the polymer during reduction have been indicated to be associated with a cation insertion process.

In resistometry technique, the resistance changes of polymers may be measured as the potential of the electrode is varied. This new technique allows resistance changes during doping/undoping to be measured *in-situ*¹¹. It is based on the

principle of measuring the resistance with square galvanostatic pulses (less than $200 \mu\text{s}$ applied every $50 \mu\text{s}$), which are so fast that Faradaic reactions and double-layer charging do not respond to them. As the CR shows (Fig. 4), the resistance of the polymer increases during reduction (applying negative potential) and decreases during the oxidation of polymer. Polypyrrole films change into a non-conductive state when a potential more negative than $-0.80 \text{ V vs. Ag/AgCl}$ is applied. It should be noted that applying high positive anodic potentials ($0.80 \text{ V vs. Ag/AgCl}$) should be avoided because these lead to an irreversible loss of electroactivity and conductivity of the polymer due to the overoxidation process¹². The results obtained from our transport experiments using PPy/PTS and polypyrrole doped dodecyl benzene sulfonate membranes at two different solution temperatures are shown in Figs. 5 and 6 respectively.

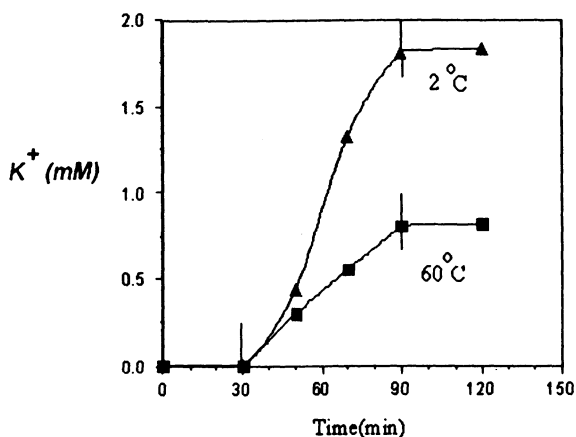


Fig. 5. Electrochemically controlled transport of KCl across PPy/PTS membranes at two different electrolyte temperatures. Pulsed potential applied $+0.6 \text{ V}$ to -1.0 V ; pulse width of 25 s applied for 60 min (between bars on the graphs). Source compartment 0.2 M KCl ; receiver compartment deionized water

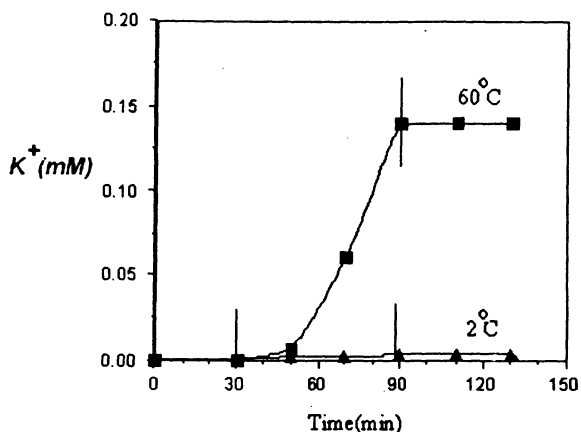


Fig. 6. Electrochemically controlled transport of KCl across PPy/DBS membranes. All experimental conditions were the same as employed for PPy/PTS in Fig. 5

As the results show (Fig. 5) the rate of transport of K^+ ions decreases with increasing solution temperature. This may be due to deterioration of conductivity and electroactivity of the polymer when switched at elevated temperatures. On the other hand, the performance of PPy membrane for controlled potential transport of ions decreases at elevated solution temperatures. The decrease in conductivity and electroactivity of PPy/PTS might be the possible reason for decreased transport properties of PPy/PTS membrane at elevated solution temperature.

In the case of PPy membranes doped with an immobile counterion such as dodecyl benzenesulfonate (DBS^-), the results obtained for transport of K^+ ions was completely different from PPy/PTS membrane (Fig. 5). When PPy/DBS membranes were used, no transport was observed at room temperature or lower⁴. Increasing the temperature most likely increases the mobility of the counterions, so some anion movement probably is induced and some improvement in transport is observed at 60°C. So, both anion/cation movements seem to be of prime importance for PPy conducting polymer membranes as free standing films in order to be used as ion gates for controlled potential ion transport⁴. *In-situ* measurement of the resistance changes of PPy/PTS and PPy/DBS during transport experiments at two different temperatures were then considered (Figs. 7 and 8).

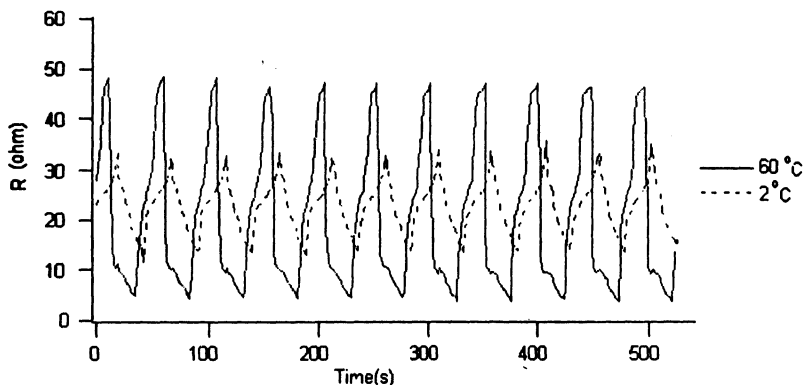


Fig. 7. The resistance changes (ohm) observed for PPy/PTS membranes at different solution temperatures recorded during application of pulse potentials (pw = 25 s) as used for transport experiment.

The increase in resistance of the polymer at 60°C might be a possible reason for decreased transport properties of PPy/PTS membrane at elevated solution temperature. The resistance of the PPy/DBS polymer at negative potentials decreased when the electrolyte solution temperature was increased from 2 to 60°C (Fig. 8). The mobility of the counterion and unique ion exchange properties of PPy during redox process seem to be the dominant factors in determining transport properties of the PPy conducting polymer membranes using electrical stimuli.

The mobility of DBS^- ions in polymer seems to increase with increasing temperature. Previously reported electrochemical quartz crystal microbalance (EQCM) studies⁹ have shown that increasing solution temperature leads to an

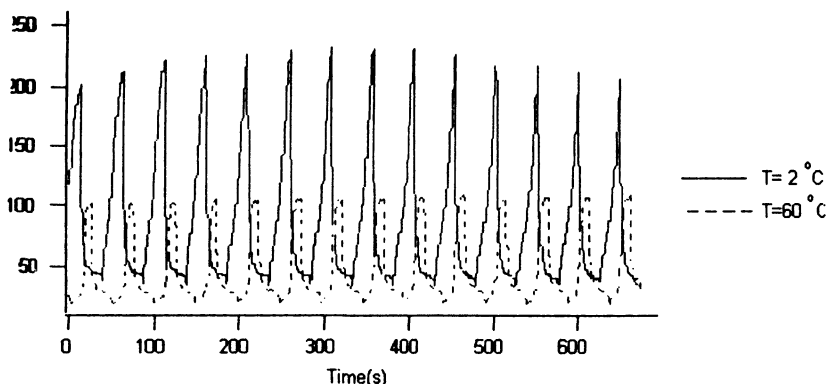


Fig. 8. The resistance changes (ohm) observed for PPY/DBS membranes at different solution temperatures recorded during application of pulse potentials ($p_w = 25$ s) as used for transport experiment

increase in DBS mobility. Inducing anion exchange behaviour, as well as decreasing the resistance of the polymer, are the most likely reasons for increasing the flux in PPY/DBS at high solution temperature. Then it may be concluded that in order to induce the transport of ions across the polymer, the polymer should have anion exchange properties as well as cation movements. Transport of cations is subject to have anion exchange properties in addition to cation exchange properties in the polymer since the transport of cations occurs with anions in order to maintain charge balance in receiver solution. Increasing the temperature increases the mobility of counterions in the case of PPY/DBS; so some improvement in the flux of potassium ion is observed at 60°C.

In our preliminary investigations, it is found that electropolymerization of PPY in the presence of some arylsulfonates can be prepared as free standing films with adequate mechanical and electrical properties in order to be used as a membrane in separation technology¹³. Thermal stability of PPY conducting polymers in both dry state and solution is greatly dependent on the nature of dopant¹³⁻¹⁵. Maximum conductivity obtained for PPY/PTS and PPY/DBS films used in present study were 100 and 25 S/cm respectively, using standard four point probe¹⁴.

Conclusions

Electroactive conducting polypyrrole membranes with high conductivity, electroactivity and mechanical stabilities can be prepared using arylsulfonates such as *p*-toluene sulfonate for controlled potential transport of ions. Increasing solution temperature results in considerable decrease of electrochemically controlled transport properties of PPY/PTS membranes. However; in the case of immobile dopants (*e.g.*, PPY/DBS), increasing solution temperature induces some anion movements, hence increasing the transport properties of the polymer.

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