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Effect of Dopant on Transport Properties of Polypyrrole Conducting/Electroactive Films

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This paper deals with the effect of the dopant counterion on transport of potassium cation across polypyrrole conducting/electroactive polymers used as stand alone films. Polypyrrole as free standing films or membranes doped with two different types of dopants, *p*-toluene sulfonate and *p*-dodecyl benzene sulfonate were synthesized electrochemically from aqueous solutions under optimized conditions. Controlled potential transport of K^+ ions from KCl solution was studied across the polypyrrole membranes at room temperature using an especially designed electrochemical cell. It was found that polypyrrole doped *p*-toluene surfonate conducting electroactive membranes show ion transport through membrane only with applying potential. Polypyrrole membranes doped with large size dopants such as polypyrrole doped *p*-dodecyl benzene sulfonate do not show any measurable ion transport across the membrane with or without applying potential.

Key Words: Polypyrrole, Conducting polymer, Electroactive, Membrane, Dopant, Potassium ion, Transport.

INTRODUCTION

Polypyrrole is mainly prepared electrochemically. Oxidation of pyrrole (E_{app} = 0.70 V *vs.* Ag/AgCl) yields a charged polymer film (PPy/A) with incorporated anions. The pyrrole units have positive charges, which are balanced by anions. The overall electropolymerization of polypyrrole can simply be shown in Fig. 1. where A^- is the anion of electrolyte solution in which the monomer is dissolved[1, 2].

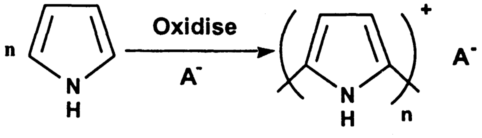

Fig. 1. Polymerization reaction of pyrrole in the presence of an electrolyte.

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. Polypyrrole conducting electroactive polymers undergo ion exchange (both anion and cation) during oxidation/reduction process for charge neutrality. Due to the unique electroactive nature of polypyrrole (PPy), it has been widely studied by investigators as a promising technological material. 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 (dopants) such as Cl^- or NO_3^- can be released, *e.g.*, by applying a negative potential and the polymer mainly exhibits anion-exchanger behaviour. Redox process of PPy conducting electroactive polymers doped with small or releasable dopants can be simply shown in Fig. 2.

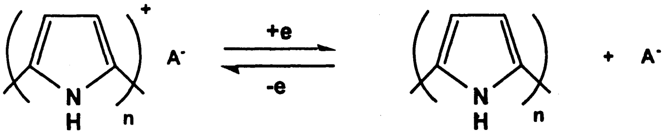

Fig. 2. Redox properties of PPy films doped with anion exchangeable dopants.

When a sufficient negative potential is applied to the polymer, the anions are expelled (undoping or discharging), thus reducing it to the neutral state. Conversely, when a positive potential is applied to oxidize the neutral film (doping or charging), the anions are mainly taken up. Consequently, the anions move during switching; the dopant anions in the PPy film can be exchanged relatively easily with electrolyte anions in aqueous solutions. In the case of immobilized polymeric dopants such as anionic polyelectrolytes or large surfactant anions, the incorporated dopant or counterion is not released during electrochemical reduction of the polymer and the electroneutrality of the polymer is conserved by the penetration of the electrolyte cation into the PPy matrix.

Polypyrrole conducting polymers suffer from over-oxidation reaction when the poential of switching or synthesis exceeds 0.80 volt or higher[3]. Over oxidation destroys the electrical properties and electroactivity of the polymers. The conjugation is interrupted and conductivity breaks down; hence the rechargeability of the polymer is lost. Higher electrochemical capacity of PPy films has been found in non-aqueous solvents under rigorous exclusion of oxygen and water. The electrical and electrochemical properties of these conjugated polymers found many applications such as drug release (delivery systems), controlled potential separation, sensors, electronic or microelectronic devices, electromagnetic shielding and nanotubes[4–10]. A new concept of separation based on electrochemical behaviour (ion exchange) has been developed for these new, electrically conductive polymer membranes (called electromembranes). The electroactive nature of PPy or incorporation/expulsion of cations and anions that is induced only by application of potential has been utilized as the basis of applications for separation devices[9, 10]. Polypyrrole conducting polymer membranes differ from the conventional ion exchange membranes used in separations, due to the nature of separation mechanism.

EXPERIMENTAL

A Princton Applied Research (PAR) potentiostat/galvanostat model 363 was employed for electropolymerization. Electrical stimuli were applied to one side of the membrane in a special electrochemical cell designed for transport studies using a potentiostat (PAR), controlled by a pulse generator, the other side being in contact with deionized water. The solutions in both sides of the transport cell were gently stirred during transport experiment using a DC rotor. Electrical stimuli were applied to the polymer *via* ring shaped metal contacts (stainless steel). A solution of 0.2 M KCl was used in the source side. In the receiver side pure water was used. Then, the measurement of the concentration of potassium (K^+) ions in the receiver solution was used as a probe for determining the effect of solution temperature on the transport properties of PPy membranes. Electrical stimuli were applied to the conducting polymer membrane using a potentiostat controlled by a home made pulse generator. Sampling from the receiver side was carried out every 20 min. Atomic absorption spectrometer (AAS, Varian Spect. AA20) was used for analysis of K^+ ions in receiver side.

The reagents and chemicals used for polymerization were all of AR grade. Pyrrole (Sigma, USA) was used after distillation. Electropolymerization was carried out galvanostatically using a current density of 2 mA/cm^2), from a aqueous solution containing 0.2 M pyrrole as monomer and 0.05 M of selected counterion in distilled water. The anions used for preparation of PPy membranes were sodium salts of *p*-toluene sulfonate (PTS) and *p*-dodecylbenzene sulfonate (DBS). The time of polymerization was 12 min. A single compartment electrochemical cell employing a three electrode system was used for the preparation of PPy membranes. Reticulated vitreous carbon (RVC), was used as the auxiliary electrode. Mirror finished stainless steel plate was used as the working electrode and a silver/silver chloride reference electrode was used as reference electrode in order to monitor the potential of the working electrode. The electrolyte and monomer solutions were prepared freshly and the cell solution was deoxygenated using high purity nitrogen gas before electropolymerization. The electrodes coated by polymer were peeled from the electrode after soaking in distilled water for 15–20 min using a sharp blade. The membranes were washed thoroughly with Milli-Q water in order to remove any remaining monomer, electrolyte and any impurities such as oligomers and finally dried at room temperature. Pinhole free membranes were checked using a suitable light source before being used for transport experiments. The thickness of the films was 5 ± 1 μm and was controlled by controlling the total charge passed during polymerization. The prepared membranes had surface area of 30 cm^2.

RESULTS AND DISCUSSION

Polypyrrole conducting polymer membranes do not afford any measureable transport of ions across them in the absence of an external pulsed potential. The separation in these new membranes is based on the use of redox processes while the separation in conventional ion exchange relies on the relative ionic affinity of the compounds being separated.

The unique dynamic nature of conducting polymers where electrically induced redox changes in the polymer results in ion movement in and out of the material by using the membrane as a working electrode in a transport cell and hence separation of ions is readily achieveable. The results obtained from the transport experiments using polypyrrole doped *p*-toluene sulfonate (PPy/PTS) membranes are shown in Fig. 3.

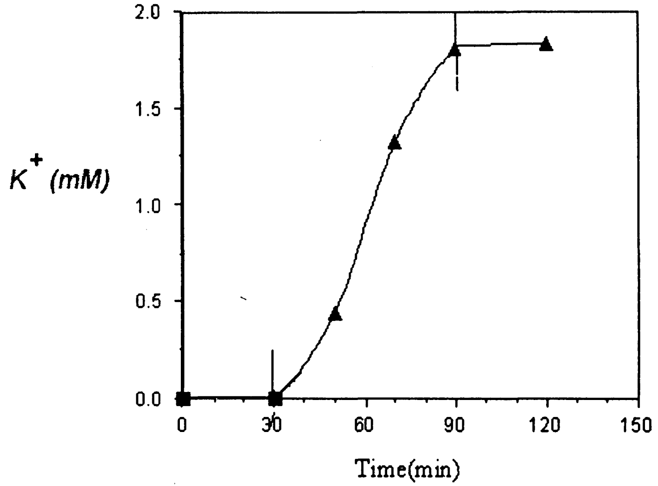

Fig. 3. Electrochemically controlled transport of KCl across PPy/PTS membranes. Electrochemical set-up: Each compartment 80 cm^3 separated by membrane; three electrode system in source compartment (membrane working electrode); pulsed potential applied +0.6 V to −1.0 V; pulse width of 25 s applied for 60 min (between bars on the graphs); source compartment 0.2 M KCl; receiver compartment deionised water.

In the case of PPy membranes doped with an immobile counter ion such as DBS^-, the results obtained for transport of K^+ ions were completely different from PPy/PTS membrane (Fig. 4). When polypyrrole doped *p*-dodecyl benzene sulfonate (PPy/DBS) membranes were used, no measureable potassium ion transport across the membrane was observed.

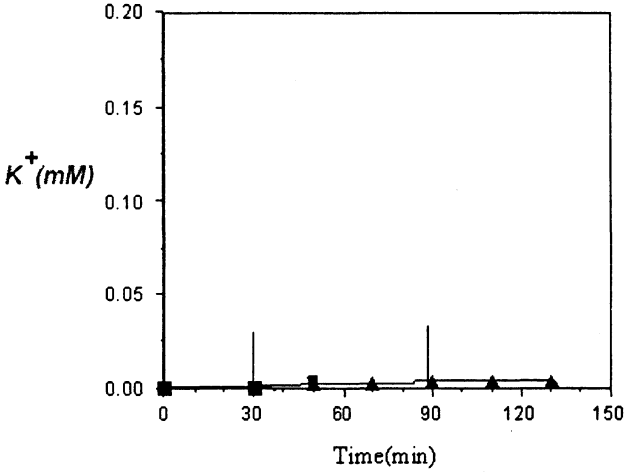

Fig. 4. Electrochemically controlled transport of KCl across PPy/DBS membranes. All experimental conditions were the same as employed for PPy/PTS in Fig. 3.

The poor transport properties of PPy/DBS membrane compared to PPy/PTS membranes can be due to the differences in the mobility of their counterions. With PPy/DBS membrane during reduction/oxidation processes, the DBS^- anions remain mostly immobilized in the polymer matrix and only the cations are moved in and out during redox reactions. In the case of PPy/PTS both anion and cation exchanges occur during redox reactions. On the other hand, the mobility of dopant anion of PPy is of prime importance for this new class of polymeric materials in order to be used as separation devices. It is interesting to note that the same transport behaviour as PPy/DBS membrane was observed for polypyrrole films doped with other large size or immobile counter ions (*e.g.*, polymeric), such as polyvinyl sulfonate (not shown). Therefore, it may be concluded that the mobility of the counter ion 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. Transport of cations is subject to having 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.

Using cyclic voltammetric and electrical conductivity measurements, the dry state thermal treatment of polypyrrole conducting polymer membranes doped with some benzene sulfonates up to 150°C (under nitrogen) improves both conductivity (by as much as 30–40%) and electroactivity considerably have been already reported[11]. The improvement in conductivity after mild thermal treatment could be due to the annealing effect and removing of volatile insulating impurities which are trapped in the polymer matrix during synthesis. Then in another experiment, PPy/PTS membranes were thermally treated under nitrogen for 1 h at 150°C under inert atmosphere and then cooled slowly at same atmosphere before its use for transport experiments. The results obtained using thermally treated polymer (PPy/PTS) membrane for transport experiments are shown in Fig. 5.

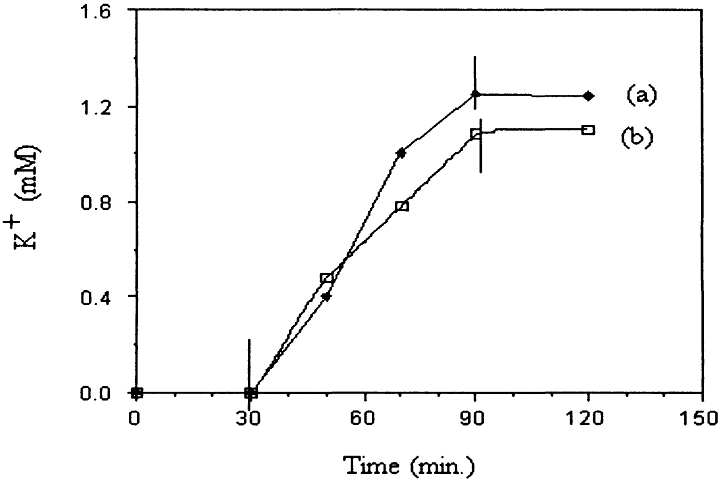

Fig. 5. (a) Without thermal treatment, (b) above 150°C for 1 h under N_2. Pulse potentials applied were between +0.70 and –1.0 volts. The experiment was carried out at room temperature. Volumes of cell solutions were 60 mL. The other conditions were as given in Fig. 3.

As the results show, dry state thermal treatment of PPy membranes, in spite of increasing the conductivity and electroactivity of the polymer (PPy/PTS), did not increase the flux of potassium ions across the polymer membrane at all. Therefore, it may be concluded that electrical conductivity, electroactivity accompanied by mass transport properties, morphology, thickness and porosity of a PPy membrane should be important parameters, but the mobility of dopant and possessing both anion and cation exchange properties, seem to be of prime importance for this new class of synthetic membranes in order to be used in switchable (electrochemically controlled) separation devices. Poor transport properties of PPy/DBS across the polymer can also be partially dependent on the porosity of the membrane. As SEM analyses show (Fig. 7), PPy/DBS membranes look more dense than PPy/PTS films.

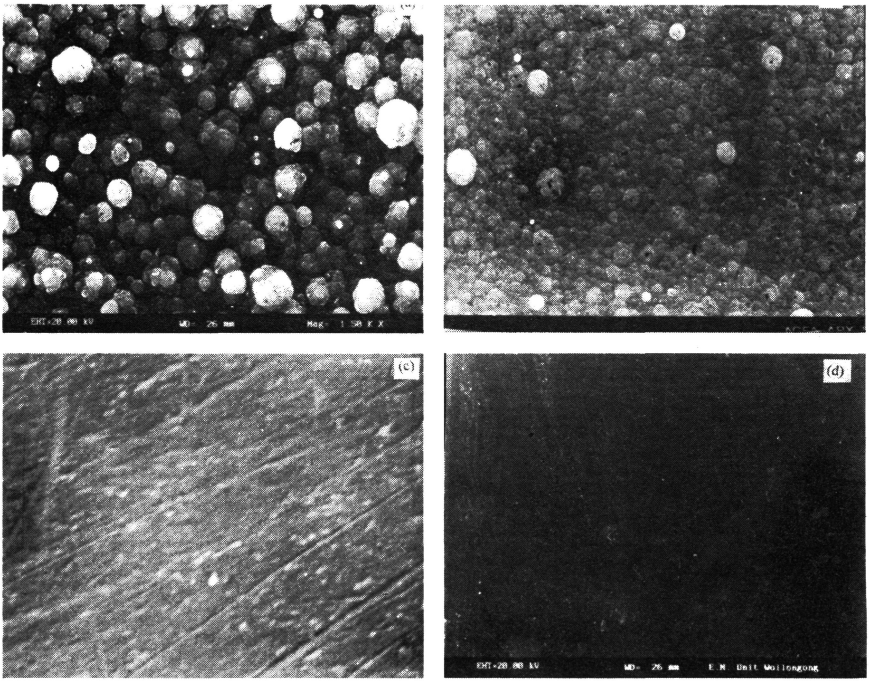

Fig. 6. SEM photographs of (a) PPy/PTS (solution side) and (b) PPy/DBS (solution side) membranes; (c) PPy/PTS, plate or electrode side and (d) PPy/DBS, plate or electrode side.

Increasing the density or compactness of a membrane normally make permeability or transport of the ions across the membrane more difficult. Although, the mechanism of ion transport through PPy conducting polymer membranes occurs *via* redox reaction and not a sole diffusion based phenomenon (in contrast to conventional synthetic ion exchange membranes), but the importance of the electrical and electrochemical properties, polymer thickness, porosity and its morphology should not be completely ignored. For example, in our previous investigations[11], it has been found that PPy/PTS films are more conductive (*ca.* 100 S/cm) than PPy/DBS films (*ca.* 25 S/cm). The nature of redox properties of PPy/PTS was also different from PPy/DBS. PPy/PTS shows both anion and cation movements in and out of the film during redox process, but PPy/DBS due to its large size shows only cation movements.

Conclusions

Electroactive conducting polypyrrole membranes with sufficient mechanical properties can be prepared electrochemically from aqueous solutions in the presence of some arylsulfonates for controlled potential transport of ions. Among the various parameters that may affect transport properties of the polypyrrole membranes, the nature of counterion (*e.g.*, mobility) used during synthesis has the most important effect. Since cation transport of a salt is accompanied by its anion, so a polypyrrole membrane, in order to be used as ion gate (*e.g.*, metal ions) with controlled potential transport, should have mobile dopant or counter-ions. Polypyrrole films doped with large size or immobile dopants do not show measureable ion transport across the film, when used as working electrode.

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