Dual Ion Transport during Electrochemical Switching of Conducting Polymer Bilayers

Myoungho Pyo and John R. Reynolds*

Department of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611, USA

Conducting polymer bilayers, prepared using polypyrrole/poly(styrene sulfonate) and poly(*N*-methylpyrrole chloride), have separate redox switching potentials and electrode potential dependent dual ion transport behaviour, exhibiting cation dominated transport at low potential and anion dominated transport at high potential.

Electrically conducting, electroactive, conjugated polymers undergo ion transport during redox switching for charge neutrality. The ionic species responsible for this ion transport mechanism can be either anions or cations, depending on polymer-ion interactions. These interactions can be controlled by judicious choice of the charge balancing dopant anion used during electrosynthesis, or by changing the electrolyte solutions used during redox cycling.[1] This allows the design of conducting polymers with controlled dominant ion flux directions during switching which are important in many of their present and potential applications.

Recently, it has been proposed that the low potential cation dominated transport of polypyrrole/poly(styrene sulfonate) (PP/PSS)[2,3] is altered to anion dominated in the high potential portion ($E > E_{p,a}$) of the scan.[4] In that work, however, anion transport at a high potential appears to be appreciably mixed with concurrent cation transport. In developing conducting polymer electrodes for various applications (*e.g.* controlled drug release along with pH control) it can be useful to have separate redox processes at which different ions are the dominant mobile species.

In this communication, we describe the electrode potential

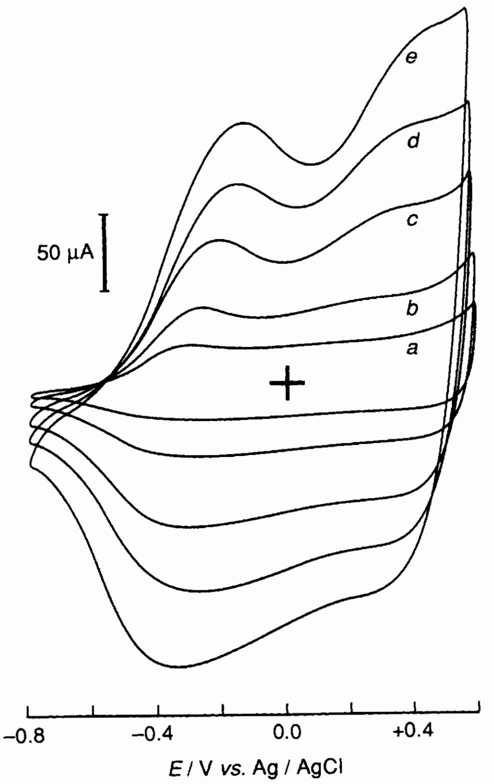

Fig. 1 Cyclic voltammograms of a PP/PSS : PMP bilayer film grown on Pt button electrode (0.02 cm^2) in a 0.1 mol dm^{-3} $NaClO_4$ aqueous solution at (*a*) 25, (*b*) 50, (*c*) 100, (*d*) 150 and (*e*) 200 mV s^{-1}. Charge passed during electropolymerization was 10 mC for PP/PSS film and 5 mC for PMP-Cl film.

controlled dual ion transport properties of a conducting polymer bilayer which consists of a PP/PSS inner film and a poly(*N*-methylpyrrole chloride) (PMP-Cl) outer film. PP/PSS has a 0.6 V lower redox potential than PMP and cation dominated transport at potentials less than or equal to 0.0 V *vs.* Ag/AgCl.[2,3] All further potentials are reported relative to this reference electrode. This is in contrast to the anion dominated transport of PMP-Cl observed during switching at potentials greater than or equal to +0.2 V. By constructing a PP/PSS : PMP-Cl bilayer, potential dependent dual ion transport with a clear switch between cation and anion dominated transport has been obtained. Bilayer and multilayer electrodes have been constructed using electroactive, non-electronically conducting, polymers.[5–8] Some of these systems show rectification behaviour. This concept was extended to conducting polymers in a study of charge-trapping behaviour, but ion transport properties were not addressed.[9]

A bilayer film was prepared in aqueous solutions by first electropolymerizing 0.1 mol dm^{-3} pyrrole in 0.1 mol dm^{-3} NaPSS (aq.) at +0.8 V and immediately electropolymerizing 0.2 mol dm^{-3} *N*-methylpyrrole in 0.1 mol dm^{-3} NaCl (aq.) on top of it at +0.9 V. The electropolymerization of the *N*-methylpyrrole was carried out as quickly as possible to avoid diffusion of the monomer into the bulk of the PP/PSS. Typical film thicknesses for these depositions were between 150–300 nm. Both the pyrrole and the *N*-methylpyrrole were vacuum distilled before use.

Cyclic voltammetric measurements were carried out using an EG&G Model 273 potentiostat with a bilayer film on a Pt button (0.02 cm^2) working electrode. The film was scanned between −0.8 V to +0.6 V in 0.1 mol dm^{-3} $NaClO_4$ (aq.) solutions until the current response was stable. Fig. 1 shows the scan rate dependence of the cyclic voltammograms. The PP/PSS inner film is electroactive with an $E_{\frac{1}{2}} = -0.2$ V in the presence of the PMP outer film. The oxidation and reduction of the PMP can be seen with an $E_{\frac{1}{2}} = +0.4$ V. The linear dependence of all of the current responses with scan rate is due to the surface bound nature of the electroactive sites on both polymers. While these experiments demonstrate the coelectroactivity of the bilayer, they yield no information on ion transport and subsequent microgravimetric analyses were carried out.

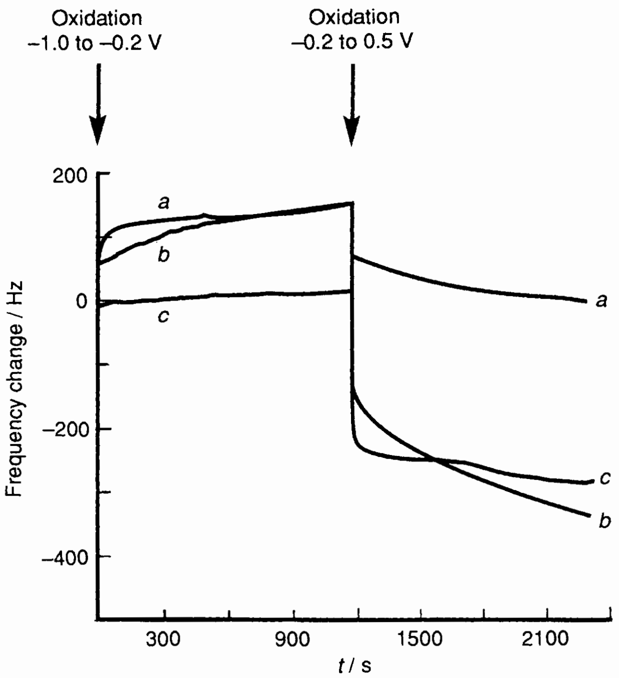

Fig. 2 Frequency responses of (*a*) PP/PSS film (*b*) bilayer film of PP/PSS (300 nm) and PMP (150 nm) and (*c*) PMP film upon the application of step potentials in 0.1 mol dm^{-3} $NaClO_4$ aqueous solutions

The direction of dominant ion flux (either into or out of the film) during oxidative doping of PP/PSS, PMP-Cl and a bilayer was investigated utilizing the electrochemical quartz crystal microbalance (EQCM). Details of the EQCM technique are well known and documented in previous literature.[1–4,10,11] A PP/PSS (*ca.* 300 nm), a PMP-Cl (*ca.* 150 nm) and a bilayer film (*ca.* 300 nm PP/PSS and 150 nm PMP-Cl) were electrosynthesized on an Au working electrode, using the conditions outlined above, and equilibrated by several potential scans between −1.0 V to +0.5 V until their frequency and current responses remained constant. Frequency changes during oxidation were monitored after applying a step potential from −1.0 V to −0.2 V in a 0.1 mol dm^{-3} $NaClO_4$ (aq.). After equilibration at this potential for 20 min, the potential was subsequently stepped to +0.5 V. Using this two step process, the first step oxidized the PP/PSS while the PMP remained reduced. The second step subsequently oxidized the PMP. The frequency results results shown in Fig. 2 illustrate the controlled dual ion transport properties of the bilayer. The PP/PSS film, both alone and as the inner film of the bilayer, shows cation dominated transport at −0.2 V as the frequency increases (mass loss due to emission of Na^+). The cation release rate of the bilayer during the initial stage of oxidation is a little slower due to the presence of the PMP outer film, but equilibrates at the same frequency difference as the PP/PSS film alone. This indicates that the electroactivity of the PP/PSS inner film does not decrease. With a step to −0.2 V the PMP is not oxidized and no mass transport (zero frequency change) is observed.

Subsequent stepping of the potential to +0.5 V was then used to oxidize the PMP. In all cases a frequency loss (mass gain due to inclusion of ClO_4^-) is observed. The smallest response was observed for PP/PSS and this potential dependent reversal of the dominant ion flux has been previously observed.[4] In contrast to the PP/PSS film, the frequency

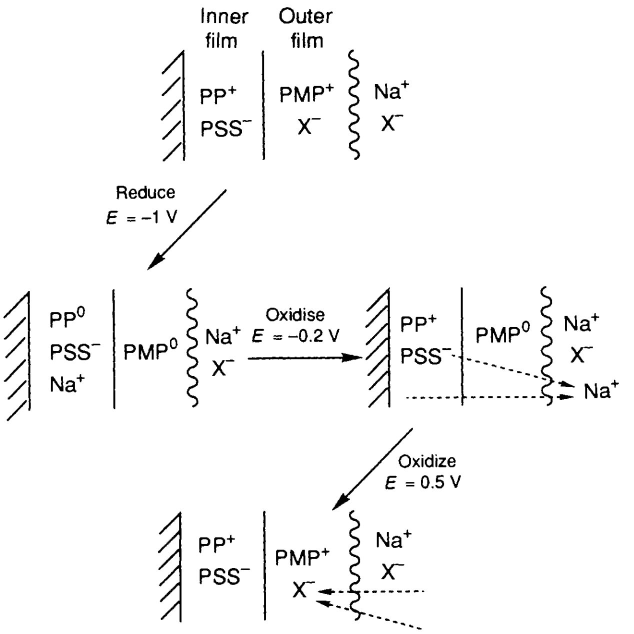

Fig. 3 Schematic diagram showing potential dependent dual ion transport of a conducting polymer bilayer

response of the PMP and the bilayer films are large as anions are mobile and neutralize the positive charge of the PMP. The magnitudes of these frequency responses are similar indicating that the bulk of the ion transport is occurring in the PMP outer layer of the bilayer. Most of the anion incorporation occurs immediately after application of the potential, which demonstrates relatively fast kinetics of the PMP outer film oxidation. On the other hand, anion penetration through the PMP outer film towards the PP/PSS inner film in the bilayer is hampered leading to a tail in the frequency drop.

We term the combination of these two directions of dominant ion flux on a single electrode dual ion transport as outlined in Fig. 3. By constructing a bilayer (or possibly multilayers) of electroactive and ion transporting polymers, where the redox states of the polymers are sufficiently separated in potential, a single electrode can be made to absorb and emit specific ions over controllable potential ranges. This has been demonstrated here with the conducting polymer bilayer of PP/PSS and PMP, but can be easily extended to many other conducting polymer systems. We believe it is possible to design the conducting polymer bilayers, and multi-film laminates, as modified electrodes which are selective to the moving species, depending on the potentials.

Financial support through grants from the Defense Advanced Research Projects Agency, monitored by the Office of Naval Research, and the University of Florida, Division of Sponsored Research, are gratefully acknowledged.

Received, 22nd September 1992; Com. 2/05072B

References

1 Y.-J. Qiu and J. R. Reynolds, *Polym. Eng. Sci.*, 1991, **31**, 417.
2 K. Naoi, M. Lien and W. H. Smyrl, *J. Electrochem. Soc.*, 1991, **138**, 440.
3 C. K. Baker, Y.-J. Qiu and J. R. Reynolds, *J. Phys. Chem.*, 1991, **95**, 4446.
4 M. Lien and W. H. Smyrl, *J. Electroanal. Chem.*, 1991, **309**, 333.
5 H. D. Abruna, P. Denisevich, M. Umana, T. J. Meyer and R. W. Murray, *J. Am. Chem. Soc.*, 1981, **103**, 1.
6 P. Denisevich, K. W. Willman and R. W. Murray, *J. Am. Chem. Soc.*, 1981, **103**, 4727.
7 K. W. Willman and R. W. Murray, *J. Electroanal. Chem.*, 1982, **133**, 211.
8 A. J. Downard, N. A. Surridge, T. J. Meyer, S. Cosnier, A. Deronzier and J.-C. Moutet, *J. Electroanal. Chem.*, 1988, **246**, 321.
9 A. R. Hillman and E. F. Mallen, *J. Electroanal. Chem.*, 1990, **281**, 109.
10 M. R. Deakin and D. A. Buttry, *Anal. Chem.*, 1989, **61**, 1147A.
11 C. K. Baker and J. R. Reynolds, *J. Electroanal. Chem.*, 1988, **251**, 307.