Proton Transport Accompanies Redox Switching of Polypyrrole: A Spectroelectrochemical Study

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Spectroelectrochemical detection of local pH changes has shown that proton expulsion accompanies redox switching of polypyrrole perchlorate thin films from the insulating to the conductive state.

It is generally believed that electrochemical reduction of anodically synthesized polypyrrole (PP) thin films leads to the expulsion of the dopant anions to preserve electrical neutrality in the resulting uncharged polymer.[1] However, recent reports have shown instances where electrolyte cations can instead be incorporated into PP during this process.[2—5] Subsequent oxidation of the polymer should then lead to expulsion of these charge-compensating cations from the film. In view of the importance of proton transport in a diverse variety of materials, and the facile diffusion of this species, the possibil-

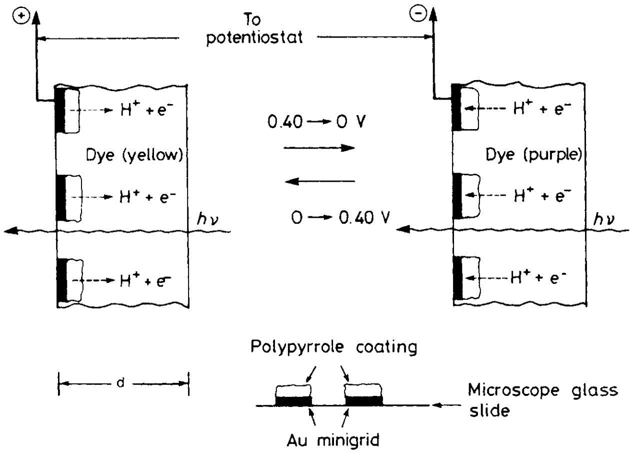

Figure 1. Spectroelectrochemical strategy for detecting proton transport during redox switching of polypyrrole (PP). The dye colour change due to the local pH modulation is shown for the specific example of Bromocresol Purple. The cross-section of the spectroelectrochemical cell is grossly expanded for clarity's sake; *d* is the thin-layer path length traversed by the light beam.

ity of proton transport accompanying the redox switching of PP was intriguing to us. Using a spectroelectrochemical technique recently developed in our laboratory,[6] we demonstrate that protons are indeed incorporated into PP perchlorate thin films during electrochemical reduction, and are subsequently expelled on redox switching back to the conductive state. In a broader perspective, our preliminary results also indicate the complexity of the chemistry which accompanies the redox switching of PP. The transport of at least three different species, *viz.*, the dopant anions, the electrolyte cations, and protons, must be taken into account in the development of a complete model for this process. Furthermore, in the light of the results described below, PP joins other important members of the conducting polymer family (*e.g.*, polyaniline, polythiophene) in which proton transfer is already known, as an integral component of the redox switching mechanism.

Figure 1 outlines the spectroelectrochemical procedure that was employed in this study. As detailed elsewhere,[6] the distinction between our methodology, and spectroelectrochemistry as done in the usual manner, is to be emphasized: in our methodology, the chromophores are not directly electrogenerated in the thin-layer cell, rather the electrogenerated protons interact with the 'electrochemically-silent' probe dye molecules to generate the optical signal. Polypyrrole was anodically electrodeposited at +0.65 V (*vs.* nonaqueous $\mathrm{Ag/Ag^+}$) on an Au minigrid (Buckbee-Mears/Interconics, 100 wires/in) from $\mathrm{MeCN{-}H_2O}$ (2% v/v) 0.1 M-$\mathrm{LiClO_4}$ solution containing the monomer (0.2 M). The PP thus formed on the Au minigrid was electrochemically reduced at −0.5 V (*vs.* Ag/AgCl reference electrode) in aqueous 0.1 M-$\mathrm{LiClO_4}$. The spectroelectrochemical measurements were performed on this reduced film in a 0.40 mM solution of Bromocresol Purple in 0.1 M-$\mathrm{LiClO_4}$ which was adjusted to pH 6.2 (the dye $\mathrm{p}K_\mathrm{a}$) by titration with 0.1 M-$\mathrm{HClO_4}$.

Figure 2a illustrates the spectral changes undergone by the probe dye as the PP electrode potential was stepped from 0 to +0.4 V in 50 mV increments. The colour change of the dye from purple to yellow can be repeated over many cycles and the direction of the optical change unambiguously establishes that proton expulsion occurs on redox switching of PP to the conductive (oxidized) state. The absorbance change at 590 nm with PP potential is mapped in Figure 2b. Also displayed in this graph is the variation of electrolyte pH with PP film potential. The absorbance–pH calibration required knowledge of the thin-layer cell volume which was afforded by constant potential coulometry on the $\mathrm{Fe(CN)_6}^{4-/3-}$ redox system.[7] For the cell considered in Figure 2, a volume of 40 µl was thus measured.

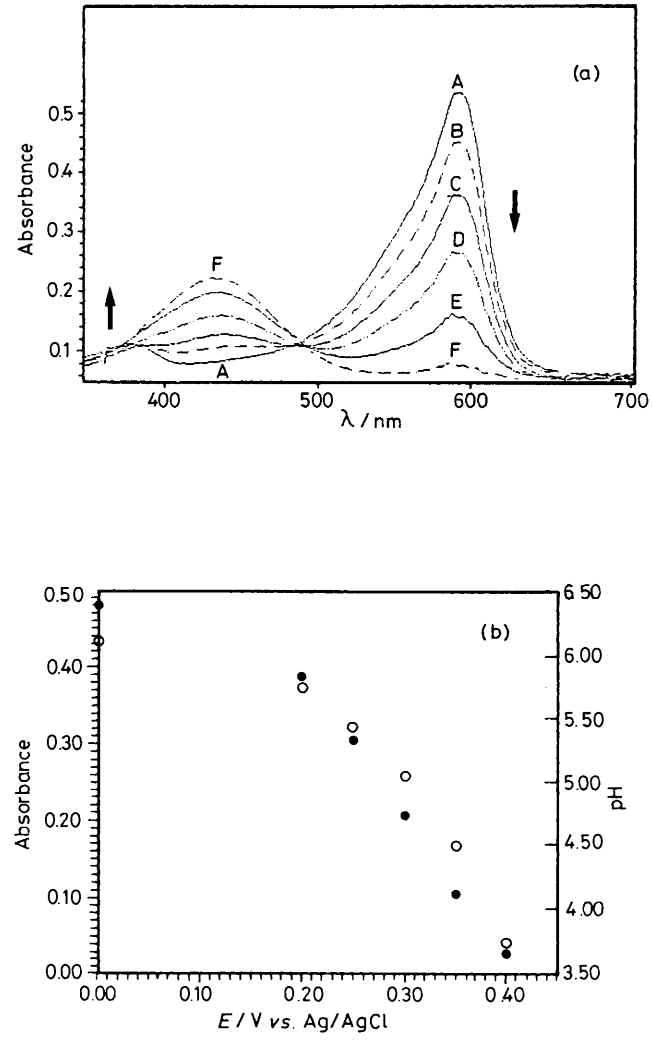

Figure 2. (a) The optical changes undergone by the probe dye, Bromocresol Purple, as the reduced PP is oxidized at specific potentials: A: 0 (*vs.* Ag/AgCl); B: 0.20; C: 0.25; D: 0.30; E: 0.35; F: 0.40 V. The electrolyte composition is described in the text. (b) Variation of the purple absorbance (590 nm) of the dye with PP potential (●). The corresponding variation in the local pH at the PP–electrolyte interface is also displayed (○).

The efficiency of proton injection into the electrolyte (expressed in terms of the coulombs passed *vs.* the number of moles of protons detected) approached *ca.* 25% for the experimental conditions corresponding to Figure 2. Obviously, cation (*e.g.* $\mathrm{Li^+}$) and dopant anion (*e.g.* $\mathrm{ClO_4^-}$) fluxes comprise the residual (competing) pathways for charge neutrality. We propose the scheme described by equations (1)—(3) to account for the above observations. In equations

(1)—(3), the parentheses denote the solid (membrane) phase and M = H or Li.

$$(\mathrm{PP^{+}ClO_4^{-}}) \xrightarrow[-0.5\,\mathrm{V}]{\text{undoping}} (\mathrm{PP^{0}}) + \mathrm{ClO_4^{-}} \qquad (1)$$

$$(\mathrm{PP^{+}ClO_4^{-}}) \xrightarrow[-0.5\,\mathrm{V}]{\text{undoping}} (\mathrm{PP^{0}M^{+}ClO_4^{-}}) \qquad (2)$$

$$(\mathrm{PP^{0}M^{+}ClO_4^{-}}) \xrightarrow[+0.4\,\mathrm{V}]{\text{redoping}} (\mathrm{PP^{+}ClO_4^{-}}) + \mathrm{M^{+}} \qquad (3)$$

An indirect route to proton transport involving adsorbed water [*e.g.* equation (4)] has literature precedent.[8] However, for the PP films grown from the predominantly nonaqueous medium considered in this work, we favour the more direct route to the undoping process as represented by equation (2).

$$(\mathrm{PP^{+}ClO_4^{-}H_2O}) \xrightarrow[-0.5\,\mathrm{V}]{\text{undoping}} (\mathrm{PP^{0}H^{+}ClO_4^{-}}) + \mathrm{OH^{-}} \qquad (4)$$

The pH modulation on redox switching of PP spanned several seconds, which would be consistent with the relatively sluggish diffusion of ions through the PP membrane. Diffusion coefficients in the range 10^{-10} to 10^{-12} cm^2 s^{-1} have been measured recently in this laboratory[9] for a variety of dopant species in PP membranes.

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