Optical Probes of Ion Transport in Electrochemical Processes based on *In situ* Derivatization; Application to Polypyrrole and Polythiophene Thin Films

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Dopant ion fluxes during the electrochemical reduction of polypyrrole perchlorate and polythiophene tetrafluoroborate thin films were measured at parts per billion sensitivity, and the polymer doping levels assayed *via* derivatization with 2,6-di-*p*-tolyl-4-phenylpyrylium reagent followed by extraction of the ion pair complex into chlorobenzene, and its detection by spectrofluorimetry.

The electrochemistry of many electrode/membrane/electrolyte systems involves ion transport as an integral component.[1] There is now ample evidence that the rate at which such systems could be switched between characteristic redox states will be ultimately controlled by the facility with which ions can be transported across the membrane/electrolyte interphase. Important thus to the understanding and, perhaps, subsequent optimization of ion transport dynamics is the development of versatile (preferably *in situ*) and non-invasive analytical probes.

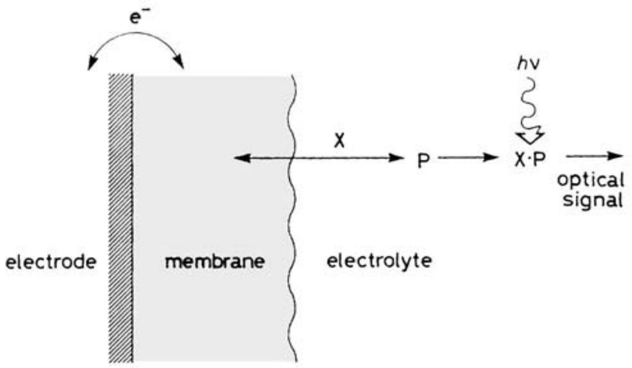

Figure 1. A generic scheme for the detection and quantitation of ion fluxes at a membrane (or thin film)/electrolyte interphase. These ion fluxes are triggered by electrochemical oxidation or reduction of the membrane (thin film). Refer to text for symbols X, P, and X·P.

We now describe a new analytical scheme which affords several variants for the study of ion transport in electrochemical situations (Figure 1). In this scheme, X denotes the ion under consideration (for the sake of generality, the charge borne by the ion is not specified). At a critical electrochemical potential, X exits from the membrane or thin film phase into the electrolyte wherein it interacts with an optical probe, P. The X·P complex is then detected and quantitated *via* either its chromophoric properties or its luminescence behaviour. This scheme was utilized in our previous work for the detection of proton transport at the RuO_x/electrolyte[2] and polypyrrole/electrolyte[3] interphases respectively. In these studies and within the framework of Figure 1, Bromocresol Purple served as the probe molecule, P; changes in the optical absorption profiles of the protonated dye (the X·P complex) were monitored as a function of electrode potential. In another variant of this scheme, we have employed luminescent anions and cations to monitor ion transport during redox switching of polypyrrole membranes.[4]

We now describe experiments based on yet another variant to measure dopant ion fluxes during electrochemical reduction of polypyrrole perchlorate and polythiophene tetrafluoroborate thin films. We electrochemically trigger the release of ClO_4^- (or BF_4^-) from the polymer, followed by derivatization with 2,6-di-*p*-tolyl-4-phenylpyrylium ($DTPP^+$) reagent. The resultant ion pair complex is partitioned into chlorobenzene and detected *via* fluorimetry.[5] We will show that the total ion content of the polymer (*i.e.*, the doping level) is also conveniently obtained in this manner *via* fluorometric assays.

It is important to emphasize within the context of our scheme (Figure 1) that the ionic species being probed and X·P complexes themselves are electrochemically 'silent.' Figure 2 contains data from both *in situ* and *ex situ* experiments with a Pt-button electrode coated with polypyrrole perchlorate.† For the *in situ* measurements, the electrode surface was in contact with a 3.00×10^{-4} M solution of $DTPP^+Cl^-$ in H_2SO_4 of pH 1.0.‡ This formed the top aqueous layer within the cuvette in the fluorescence spectrometer sample compartment. Electrochemical reduction of the polypyrrole thin film at −0.70 V (*vs.* a Ag quasi-reference) results in the release of ClO_4^-, subsequent formation of $DTPP^+ClO_4^-$, and partitioning of the $DTPP^+ClO_4^-$ complex into the lower chlorobenzene layer,§ wherein the fluorescence excitation beam (λ_{ex} 376 nm) is focused. Calibration of the fluorescence data results in ClO_4^- concentration–time profiles such as that in Figure 2a.

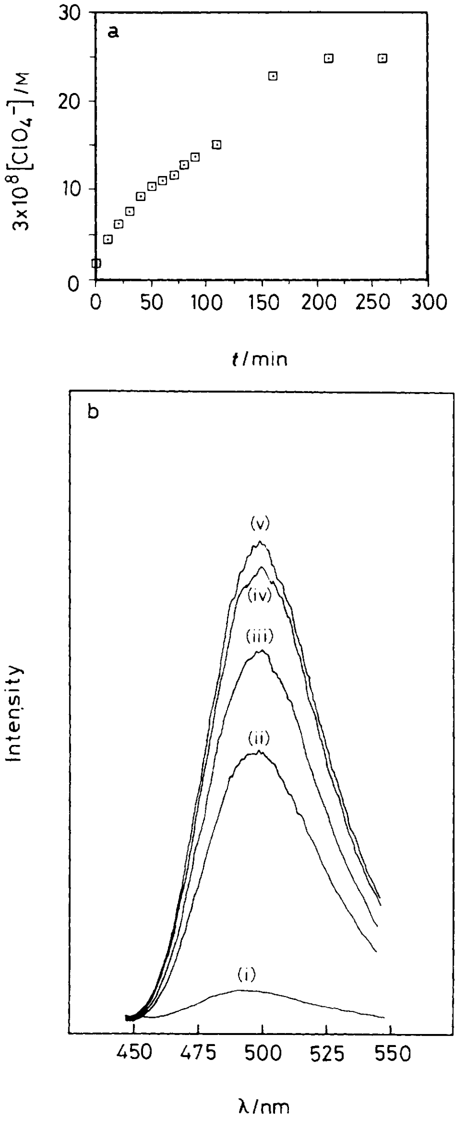

Figure 2. Time evolution of the ClO_4^- dopant ion from a Pt-supported polypyrrole thin film (~0.017 cm^2 geometrical area). (a) ClO_4^- concentration–time profile obtained from *in situ* derivatization of ClO_4^- with $DTPP^+Cl^-$ and subsequent partitioning into the chlorobenzene layer which was fluorimetrically sampled (see text). (b) Fluorescence emission spectra of the $DTPP^+$ ClO_4^- complex obtained *ex situ*: (i) 0, (ii) 15, (iii) 60, (iv) 90, (v) ≥120 s. The excitation wavelength was 376 nm and the excitation and emission bandwidths were both 4 nm. The polymer electrode was switched from open circuit to −0.70 V (*vs.* Ag quasi-reference) to trigger the ClO_4^- release in both the cases.

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† Polypyrrole was anodically electrodeposited at +0.65 V (*vs.* nonaqueous Ag/Ag$^+$ reference) on the Pt electrode from MeCN–H_2O (2% v/v), 0.1 M $LiClO_4$, containing 0.2 M pyrrole. The thin films in this study were ~1 μm thick as estimated from the charge consumed during the electrosynthesis. The thin films were thoroughly washed free of any adsorbed perchlorate.

‡ The chloride complex was synthesized by a literature procedure (*cf.* ref. 6).

§ The partition coefficient of the $DTPP^+ClO_4^-$ complex in the chlorobenzene layer was determined in separate experiments using authentic samples to be ~5. This partition coefficient is ~80 times that of the chloride complex. The equilibrium constant for the reaction: $DTPP^+Cl^- + ClO_4^- \rightleftharpoons DTPP^+\ ClO_4^- + Cl^-$ is estimated to be ~10 from the data in ref. 5.

The solution in contact with the polymer in the experiments in Figure 2a was quiescent. To deconvolute the influence of solution kinetic effects (*e.g.* diffusion, partitioning time) from polymer effects, *ex situ* experiments were also done with the polypyrrole perchlorate thin films. Figure 2b contains representative fluorescence emission spectra for solution aliquots withdrawn at increasing time intervals from the electrochemical cell. The polymer was reduced at −0.70 V in 0.1 M K_2SO_4 in this experiment. The temporal evolution of the fluorescent emission intensity of the green $DTPP^+ClO_4^-$ complex (λ_{max} 495 nm) now reflects mainly the kinetics of ion transport through the polymer thin film. The 'background' intensity at time zero reflects the contribution of $DTTP^+$ Cl^- in the chlorobenzene layer. Further kinetics experiments with polymer thickness as a variable are currently in progress.

Another set of experiments with a Pt-supported poly(3-methylthiophene) thin film containing BF_4^- as the dopant anion¶ resulted in similar spectral profiles to those in Figure 2. Thus, the $DTPP^+$ reagent binds with BF_4^-, and partitions into the organic layer, equally readily.

The above procedure also affords the total ion content (*i.e.* doping level) of the polymer thin films. Thus, a Pt-supported polypyrrole perchlorate thin film (~1 mg) was rinsed with MeOH in a Soxhlet apparatus for ~6 h to remove trapped perchlorate. The washed thin film was electrochemically reduced in a 0.1 M K_2SO_4 solution** of $DTPP^+Cl^-$. The ClO_4^- release was monitored as above till no further change in fluorescent activity was noted. Calibration was performed with 0.1—1.0 p.p.m. solutions of $LiClO_4$ worked up under the same conditions.

Doping levels in the 24—26% range (mole basis) were computed for the polypyrrole thin films in this study. These are in good accord with doping levels determined by more conventional (*e.g.* elemental analysis) techniques. The chief advantages with the optical procedure are its high (p.p.m. → p.p.b.) sensitivity and its non-destructive nature.

The derivatization strategy, as demonstrated in this study, is completely general; it should be applicable for the detection of cations and the study of ion transport in other types of thin films (*e.g.* redox polymers) as well. Indeed, the ability to detect and quantitate ions based on the scheme in Figure 1 should be limited only by the availability of appropriate reagents for the derivatization.

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¶ The poly(3-methylthiophene) thin films (~1 μm thick) were electrodeposited on Pt from a 0.1 M solution of 3-methylthiophene in MeCN containing 0.1 M tetrabutylammonium tetrafluoroborate. A nominal deposition potential of +1.8 V (*vs.* nonaqueous Ag/Ag^+ reference) was employed.

** In these experiments as well as those in Figure 2b the solution was subsequently adjusted to pH 1.0 with 0.1 M H_2SO_4 prior to extraction into chlorobenzene. This was done to ensure that proton fluxes into the polymer upon electrochemical reduction (*cf.* ref. 3), which would introduce an error in the ClO_4^- quantitation, were minimal.

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