tapping mode. Optical micrographs were recorded with polarized light microscopy (Zeiss LM Axioplan) equipped with digital camera. The cell thickness was determined by UV-visible spectroscopy (Shimadzu UV-3102 PC).

**Electro-Optical Characterization:** The electro-optical characteristics were investigated using DMS 703 display measuring system (Autronic-Melchers GmbH). A square wave was used in order to drive the cells for the dynamic response measurements.

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**Visualizing Ion Currents in Conjugated Polymers**

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In numerous technologically important materials, electrochemical reactions are accompanied by the mass transport of charged particles. For example, ion ingress and egress during...

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electrochemical oxidation and reduction of conjugated polymers is the basis of a broad range of devices from electrochromic displays to batteries, chemical sensors, and actuators.[1] The direct measurement and visualization of ion transport would therefore be instrumental in formulating and validating physics-based models of such electrochemical reactions.

In this paper we report a new technique for the study of ion transport in materials that are electrochromic, and show initial results obtained by applying the method to polypyrrole doped with dodecylbenzenesulphonate, PPy(DBS), a conjugated polymer that is starting to find commercial applications in biomedical microactuators.[2] We introduce an experiment that makes electron transport fast compared with ion transport, allowing the ionic current to be characterized independently of the electronic current, and we present a first-cut model. These experimental and modeling results are the first from an ongoing research effort; the aim of this particular study was to elucidate the roles played by ion drift and diffusion in the reduction reaction.

Previous studies have shed light on the oxidation and reduction (redox) processes and the associated volume change in conjugated polymers that we understand the basic mechanisms.[3-6] Yet despite the numerous laboratory demonstration actuators that have been reported,[7,8] we do not yet have predictive models for actuator behavior. Without determining the constitutive equations governing the volume change, it will be impossible to design materials with non-incrementally increased speed, strain, and other performance metrics as required for particular applications.

When a reducing potential is applied to oxidized PPy(DBS), electrons are transferred to the polymer backbone and cations, which are typically solvated, enter the material in response to the electric field.[9] This mass insertion is responsible for the volume increase that is exploited in actuators. Space between the polymer chains must be created in order for the ions to enter, so the ion current depends on chain movements,[10] as well as on the degree of polymer solvation, the ion size, ion–polymer interactions, etc. Diffusion in conjugated polymers is therefore not Fickian.[11,12]

The discussion in the literature has focused on whether a diffusion model or a migration (drift) model is more appropriate to describe charge transport in conjugated polymers, and different authors have seen evidence for each. This is because in actual fact, electron and ion currents have both diffusion and migration terms. Which one is dominant depends on the magnitude of the applied potential.

Results from a first-cut model that includes both diffusion and drift are presented below. The first equation in the model is standard and describes the conservation of species:

\[ \frac{\partial C_i}{\partial t} = - \nabla \cdot J_i \]  

where \( C_i \) is the concentration of \( i \) (mol cm\(^{-3}\)) and \( J_i \) is the flux of species \( i \) (mol s\(^{-1}\) cm\(^{-2}\)). This equation is exact: it simply counts molecules. The flux \( J_i \) must next be quantified in terms of the physical conditions. Accepted models are given by

\[ J_i^{\text{diff}} = -D_i \nabla C_i \]  

for the diffusion component, where \( D_i \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), and

\[ J_i^{\text{drift}} = z_i \mu_i E \]  

for the drift component, where \( z_i \) is the charge, \( \mu_i \) is the mobility (cm\(^2\) V\(^{-1}\) s\(^{-1}\)), and \( E \) is the electric field. It is important to note that these two equations contain a number of assumptions, as described in the literature.[13,14] We ignore convection since this is not present in the polymer and is negligible in an unstirred solution. This results in:

\[ \frac{\partial C_i}{\partial t} = - \nabla \cdot J_i = - \nabla \cdot \left( -D_i \nabla C_i - z_i \mu_i C_i \nabla \phi \right) \]  

where we have expressed the electric field as the gradient of the electric potential, \( \phi \): \( E = -\nabla \phi \). If the Einstein relation,[14] \( D_i/\mu_i = kT/q = RT/F \), is employed, which may or may not be true for conjugated polymers, then Equation 4 reduces to the familiar Nernst–Planck equation.[13] Equation 4 can be used for both ions and electrons. Finally, Maxwell’s equations give the potential in terms of the net charge density \( Q \):

\[ \varepsilon_0 \nabla \left( \varepsilon \nabla \phi \right) = Q = C_i - n \]  

Here, \( n \) is the electronic charge, \( \varepsilon_0 \) is the permittivity of a vacuum, and \( \varepsilon \) is the dielectric constant of the conjugated polymer. When charge neutrality does not hold \((C_i \neq n)\), the resulting electric field in the polymer is the driving force for ion transport.

There has also been a discussion in the literature about whether the speed of the redox reaction is limited by electron transport or ion transport. However, the rate-limiting step depends on the experiment. Unfortunately, the electronic and ionic components of the current are difficult to disentangle in most experiments. As a result, the literature reports values for an “apparent diffusion coefficient” whose meaning is not clearly defined, but that seems to include both diffusion and drift components of both electron and ion transport. Reported apparent diffusion coefficients vary over thirteen orders of magnitude.[11]

Below, we describe an experiment that allows ion transport parallel to the surface of the film to be characterized independently of the electronic current during redox. This work was inspired by that of Tezuka et al.[16,17]. These authors established electrical contact to a polypyrrole film along only one of its edges, and when an oxidizing potential was applied, they observed a phase front that traveled outward from the electrode. The phase front was detected by changes in the optical absorption of the PPy, which is electrochromic. (Oxidation introduces new electronic states into the bandgap, causing the color of the polymer to change.) In that experiment, however, electron and ion transport rate limitations could not be definitively separated.
Lacroix et al.\textsuperscript{[18]} presented a theoretical analysis of mass transport during redox that assumed ion transport could be described as a migration phenomenon, rather than a diffusion phenomenon. This resulted in a moving front that separated the conducting and insulating states during switching. These authors also found that a moving front could result from an oxidation-level-dependent electron diffusion constant.

Our experimental configuration is illustrated in Figure 1. (The figure is not to scale: the vertical axis is exaggerated for clarity.) A thin conjugated polymer film 0.3 \( \mu \)m thick, 300 \( \mu \)m wide, and 8 mm long is covered by a transparent ion-blocking layer that prevents ions from entering or exiting the film through the top surface, allowing ion transport only from the sides. This makes the path for ions to and from the center of this stripe (150 \( \mu \)m) 500 times longer than the path for electrons (0.3 \( \mu \)m), since electrons are able to enter and leave along the entire bottom surface. This configuration ensures that ion transport is the rate-limiting step in the reaction. (In addition, the mobility of electrons is believed to be orders of magnitude higher than that of ions.) Since the ion-blocking layer is transparent, the color change of the electrochromic film during redox can be visualized.

In this paper, we focus only on the reduction reaction in PPy(DBS), which is a cation-transporting material since DBS is immobile in the polymer.\textsuperscript{[19-21]} (To describe the behavior during oxidation, we must take into account conformational relaxation of the polymer chains,\textsuperscript{[19]} which is beyond the scope of our first-cut model.) During reduction of PPy(DBS), the polymer starts in the fully oxidized, conducting state in which one DBS’ anion compensates each positive charge on the backbone.

The PPy was electrochemically cycled in deoxygenated aqueous 0.1 M NaDBS by stepping the voltage between 0 and various negative potentials. For potentials more negative than \( -0.8 \) V versus Ag/AgCl, we observed phase fronts that traveled from the outer edges of the stripe to the center. Figure 2a shows an overhead image of a film part-way through the reduction process under an applied potential of \( -1 \) V versus Ag/AgCl. The center of the stripe is oxidized (dark red), and the outer edges are reduced (transparent yellow). Between them is a broad phase boundary. Red, blue, and green channel intensities were measured along a cross-section of the stripe, schematically indicated by the dashed line in Figure 2a; all three channels gave essentially the same signal, with red having the largest intensity variation, so the red channel was used for tracking the color change (Fig. 2b). Thresholds were set, with intensities below the lower threshold marking the “inner boundary,” inside which all the material was deemed to be still fully oxidized, and intensities above the upper threshold marking the “outer boundary,” outside of which all of the material was taken to be completely reduced. The positions of the boundaries were traced over time (Fig. 2d) to give the phase front velocities.

For reduction potentials smaller than approximately \( -0.8 \) V, there were no clearly visible phase boundaries (after the first reduction scan); instead, the film gradually lightened (see Figure 2c). The concentric bands shown in Figure 2c are due to the periodic nature of the color changes. The time-dependent concentrations of red and blue are plotted in Figure 2d. The intensity around the inner boundary was obtained by using a high threshold in order to distinguish between the reduced and oxidized phases. The processing involved tracking the position of the boundary by correlating the intensity profiles during each electrolysis step.

![Figure 1](image1.png) **Figure 1.** An experimental configuration that makes ion transport the rate-limiting step (vertical dimensions exaggerated). A thin stripe of the electrochromic material is in contact with an electrode on its bottom side, and its top side is covered by an ion-blocking layer. During electrochemical reduction, cations are transported into the film, but they can only enter from the edges. Electrons therefore have a short path, ions a long one. The polymer cannot significantly change its oxidation level until charge compensating cations arrive. The change in oxidation level results in a color change.

![Figure 2](image2.png) **Figure 2.** a) Overhead view of a film in the process of being reduced. The oxidized material appears dark red, and reduced material is nearly transparent; there is a broad phase front between them. Inner and outer boundaries of the front are indicated schematically. b) The intensity of the red channel at the cross-section indicated by the dashed line in a). Thresholds for fully oxidized and reduced states are indicated schematically. The negative intensity spikes arise from the shadows at the edges of the polymer strip. c) During the first-ever reduction cycle, the phase boundary is very sharp, and the front velocity very slow. d) The position of the phase boundaries versus time, 0 \( \mu \)m being the center of the stripe and 150 \( \mu \)m the edge. The slopes used to calculate the phase front velocities of the inner and outer boundaries were taken from the linear regions.
cross-section intensity profiles shown below in Fig. 4a). This is consistent with an interpretation that the diffusion component of the ion current is larger than the drift component in this regime.

For larger reduction potentials, we always observed phase fronts. After the front had progressed some distance into the film, both inner and outer boundaries moved with constant velocity (Fig. 2d). The velocities of the boundaries are plotted as a function of applied potential in Figure 3. Between -0.8 and -1.6 V versus Ag/AgCl the velocity, \( v \), was proportional to the voltage, as would be expected for migration: \( v = \mu E \)\(^{[14]} \). In this voltage range, therefore, migration plays the dominant role in ion transport.

The transition region between oxidized and reduced states (the distance between inner and outer boundaries, or the front width) broadened over time (Fig. 2d). Our hypothesis is that the broadening is due to diffusion, but additional experiments are required to confirm this. As the fronts from either side of the stripe approached each other, they started to interact and move faster.

At potentials more negative than -1.6 V, the velocity did not increase any further, but remained constant at approximately 70 \( \mu \text{m s}^{-1} \). The speed may be limited by diffusion in the electrolyte, or possibly by electron transport; further work is necessary to determine the cause.

During the first-ever reduction of the film, the phase boundary was very sharp (Fig. 2c), and it stayed sharp from the outer edge right to the center. Moving fronts were seen for reducing potentials as small as -0.7 V, at which ion transport is primarily diffusion driven. This is a clear demonstration that the diffusion process is not Fickian, since in the film’s as-deposited state, the polymer chains are exceptionally compactly packed\(^{[9,10]} \) so the ion diffusion coefficient and mobility are very low. This is a clear validation of the finding in the Lacroix model\(^{[18]} \) that an oxidation-level dependent diffusion coefficient can give rise to a phase front. The velocity of the front was 20–30 times slower during the first scan than during subsequent reductions.

Our simulations of the ion transport were based on Equations 4.5. The equations were solved in only a single spatial dimension (left to right in Fig. 2), a small vertical distance above the equipotential electrode surface. Ion transport was assumed to be much slower than electron transport due to the design of the experiment, so Equation 4 for electrons was discarded. Instead, we assumed a fixed electron density, \( n(x,t) = n_0 \). The ion diffusion coefficient was assumed to be constant. The resulting nonlinear partial differential equations were solved using the software FEMLAB. The simulation results are compared with experimental red-channel intensity data in Figure 4.

![Figure 3. Upper: the cyclic voltammogram of an uncovered PPy(DBS) film shows, approximately, the applied potentials relative to the redox peaks. Lower: velocity versus applied potential. Different symbol shapes correspond to different samples, and repeated symbols indicate duplicate runs on the same sample. Above -0.8 V, no phase boundaries were observed, and below -1.6 V, the velocity saturated at ~70 \( \mu \text{m s}^{-1} \).](image-url)

![Figure 4. Experimental data (points) versus modeling results for ion concentration (line). The edges of the film are positions 0 and 1. The intensity minimum is for the fully oxidized state, and the maximum is for the fully reduced state. a) Applied potential = -0.7 V (versus Ag/AgCl); data at 30, 60, and 90 seconds. Modeling curves are not equally spaced in time. b) Applied potential = -1.5 V; data at 0.6, 1.5, and 2.4 seconds (0.9 seconds apart). The modeling curves are again not equally spaced in time.](image-url)
ersion-like behavior behind the leading edge of the phase front was not captured. The assumption of a fixed electron density did not take into account the important fact that additional electrons are transferred to the polymer once charge neutrality is re-established locally by the arrival of the cation front. Also, the assumption that the diffusion constant is fixed, rather than a function of the oxidation level, is not valid, as shown by the striking differences in shape and velocity during the first-ever reduction. The next stage in our modeling will take these effects into account.

While the experimental and modeling curves in Figure 4 are strikingly similar, it is important to keep in mind that the experimental curves are color intensity profiles. In order to convert the intensities in the images into ion concentrations (the quantity in our model), the Faradaic charge consumed by the PPy needs to be determined, and these measurements are under way. Once we know \( \dot{E} \) in the film, we will extract the mobility from the data in Figure 3. Future studies will also more closely examine the diffusion terms in the model.

In conclusion, we have introduced a simple experimental tool that directly measures ion transport in electrochromic materials and have presented preliminary results on the reduction process in PPy(DBS). We have shown that there are different rate-limiting processes at different potentials, that migration plays a critical role in ion transport, and that a simple model can account for much of the behavior. Initial physics-based modeling has correctly predicted the existence of the phase fronts and captured much of their shapes. Future experimental work will include quantification of the coefficients in the equations as well as studies of the oxidation process and correlations between ion transport and volume change. The next stages in modeling will take additional physics into account.

**Experimental**

The fabrication process for the devices was as follows. Over an oxidized silicon wafer, an adhesion layer of Cr (100 Å thick) was deposited by either electron-beam evaporation or sputtering, followed immediately by a layer of Au (3000 Å thick) that served as the working electrode. A layer of PPy(DBS) was electrochemically deposited from an aqueous solution of 0.1 M NaDBS and 0.1 M pyrrole (pH 7) at a constant potential of 0.47 V (versus Ag/AgCl) with an EcoChemie pgstat30 to a thickness of 0.3 μm, at which the color changes are very apparent. All thicknesses were measured by profilometry (Tencor Alphastep 500). A 2 μm thick layer of a photosensitive polymer (SU8-2000, MicroChem Corp.) was photolithographically patterned over the PPy into the shape of a rectangular stripe following the manufacturer’s directions. The PPy that was not covered by SU8 was removed by dry etching in an oxygen plasma [22], leaving a stripe of PPy covered by SU8 on the electrode surface. All cycling experiments were performed under a nitrogen atmosphere to prevent oxygen doping. The electrochemical response was recorded with a digital camera (Nikon Coolpix 4500) connected to a camcorder (Sony DCR-TRV 330) from directly overhead through a microscope (Leica MZ12c) onto digital tape. The images were later processed using Studio DV to reduce the number of frames and Matlab to analyze the images.

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**Observation of Field-Effect Transistor Behavior at Self-Organized Interfaces**

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Self-organization is a fascinating subject with important applications ranging from surface passivation to assembly of

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