# Quantitative in Situ Measurement of Ion Transport in Polypyrrole/Poly(styrenesulfonate) Films Using Rotating Ring–Disk Voltammetry

## Corey A. Salzer and C. Michael Elliott\*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

#### Susan M. Hendrickson

Department of Chemistry, Davidson College, Davidson, North Carolina 28036

An approach based on rotating ring-disk electrode (RRDE) voltammetry is described for the quantitative, in situ measurement of ion transport between solution and conducting polymer films. The specific composite film studied in this report is polypyrrole/poly(styrenesulfonate) (pPy<sup>+</sup>/pSS<sup>-</sup>). Cation flux in and out of the polymer was obtained from the mass-transport-limited reduction current for the dopant cation(s) measured at the ring during redox cycling of the polymer. Crucial to this method is the use of a supporting electrolyte that is sterically inhibited from passing into the film and the use of dopant ions that adhere to specific electrochemical constraints. With this method it was possible to quantitatively account for all changes in charge compensation in the film by the specific cation(s) involved. Three different cations were explored alone and in paired combinations. Solutions containing mixtures of dopant cations were studied to determine whether the pPy<sup>+</sup>/pSS<sup>-</sup> films exhibit preferential doping. Kinetic factors, likely due to steric differences in the dopant cations, were found to lead to significant preferential doping of the polymer.

A number of analytical techniques have been employed to study ion transport in conducting polymers, including impedance spectroscopy,<sup>1,2</sup> X-ray photoelectron spectroscopy (XPS),<sup>1,3,4</sup> luminescence techniques,<sup>5,6</sup> and scanning electrochemical microscopy (SECM),<sup>7</sup> usually combined with electrochemical methods such as cyclic voltammetry or coulometry. However, the most commonly used approach is to monitor in situ mass changes of the polymer by means of electrochemical quartz crystal microgravimetry (EQCM).<sup>4,6,9–12</sup> The change in mass of a polymer, due

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at least in part to ion influx/efflux, is then correlated to the change in polymer oxidation state obtained from its voltammetry or coulometry. The advantages of EQCM are its high sensitivity to mass changes and in situ capabilities. However, it suffers from a lack of selectivity in identifying specific dopants and in differentiating solvent molecules from ions.<sup>5,7</sup> Each of the other approaches listed above has its own advantages and limitations as well. For instance, luminescence is selective and sensitive, but is limited to ions that luminesce and, consequently, are typically rather large. On the other hand, XPS can be used to examine a wide array of ions, but lacks the ability to measure ion transport in situ. Both luminescence and SECM suffer from the fact that the polymer must be charged with the probe ion prior to voltammetric scanning. Consequently, after the first scan, probe ion transport is convoluted with supporting electrolyte cation and anion transport.

At least two prior attempts to use rotated ring-disk electrode (RRDE) voltammetry to measure ion flux across a conducting polymer/solution interface have been reported. Aizawa and coworkers<sup>13</sup> monitored the oxidation of Br<sup>-</sup> at the ring electrode while a polypyrrole film on the disk was redox-cycled in 0.10 M NaBr/water-acetonitrile (1:1). Despite efforts to quantitate these data, these results are of only qualitative value because NaBr was the sole electrolyte in solution. Migration of Br<sup>-</sup> was neglected in their data treatment. Earlier yet, Pickup and Osteryoung<sup>14</sup> used RRDE voltammetry to monitor Cl<sup>-</sup> flux from polypyrrole in a very slightly basic (i.e., a slight excess of Cl<sup>-</sup>) AlCl<sub>4</sub><sup>-</sup> molten salt. In contrast to the work of Aizawa and co-workers, these data were quantitatively useful since  $[Cl^-] \ll [AlCl_4^-]$ . Unfortunately, as these authors were also able to show, Cl<sup>-</sup> was not the only dopant ion in the polymer; consequently, it was not possible to determine exactly which ions were participating in the charge compensation process. As we will demonstrate below, the type of difficulties encountered in these earlier studies can be avoided altogether with the right combination of dopant ion(s) and background electrolyte. Moreover, it is possible with this technique to quantitatively account for all of the ions participating in polymer doping level changes in situ and in real time.

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#### BACKGROUND

Before considering how RRDE voltammetry can be applied to polymer doping studies, it is instructive to review how this technique is employed to study so-called EC reactions in solution.<sup>15</sup> Consider the following hypothetical EC reaction:

E: 
$$O + e^{-} \leftrightarrow R$$
  
C:  $R \stackrel{k}{\rightarrow} Z$ 

Typically, the electrochemical reaction, E, is initiated at the disk. The ring potential is adjusted to give a mass-transport-limited reoxidation of R back to O. Because of the electrode rotation, the R formed at the disk is hydrodynamically transported across the insulating gap toward the ring where it can be reoxidized. Were it not for the chemical step, which irreversibly consumes some of the fraction of the R before it reaches the ring, the ring and disk currents would be related by eq 1. The quantity N is a

$$-(i_{\rm r})/(i_{\rm d}) = N$$
 (1)

constant called the collection efficiency, and its value is determined solely by the physical construction of the RRDE electrode (i.e., the disk area and the dimensions of the insulating gap and the ring).<sup>15</sup> When there is follow-up chemistry, as reaction C above, some of the R is irreversibly consumed before reaching the ring; therefore, the current ratio on the left side of eq 1 becomes less than N. The disk-to-ring transit time, and thus the chemical reaction time, is determined in a mathematically well-defined way by the rotation rate of the electrode.<sup>15</sup> Without going to unnecessary detail, the numerical value of the chemical rate constant, k, can be obtained by considering how the ratio of the ring limiting current to the disk limiting current,  $i_r/i_d$ , changes as a function of rotation rate. Of relevance here is the fact that the voltammetry of an electroactive polymer film on the disk of an RRDE is related to the mass-transport-limited voltammetry of the dopant ion(s) at the ring. This relationship is closely analogous to how the disk and ring voltammetry of O and R, respectively, are related in this hypothetical EC reaction in solution.

Prior to discussing how the currents are related, the unique constraints imposed on the experiment by the polymer/dopant system need to be addressed. Two requirements are made of the dopant redox chemistry by the fact that the voltammetry of the dopant ion (or ions) is to be used to quantitate the polymer/ solution interfacial ion flux. First, the dopant ion must be electrochemically inactive over the entire potential range applied to the polymer, and second, it must give mass-transport-limited voltammetry at the ring within the solvent window. Moreover, if multiple types of dopant ions are to be considered, their voltammetry must also be sufficiently separated in potential to avoid simultaneous reduction (vide infra). In general, either cationic or anionic dopants (or both) could be probed as long as the above criteria are satisfied.

In addition to the dopant ions, the solution must contain an inert supporting electrolyte to eliminate migration effects. However, that supporting electrolyte cannot participate in polymer





**Figure 1.** Cyclic voltammograms of pPy<sup>+</sup>/pSS<sup>-</sup> films (grown under identical conditions) cycled in acetonitrile solutions of 2 mM dopant cation and 50 mM PPNTos: cobalticinium (Cc<sup>+</sup>, solid line); 1-methyl-3-cyanopyridinium (CMP<sup>+</sup>, dash-dot); 1,3-dimethylpyridinium (DMP<sup>+</sup>, dash only).

doping; otherwise, any effort to quantitatively correlate the disk current with total ion transport would be pointless. Fortunately, differences in ion size can be used effectively to discriminate against doping by the supporting electrolyte ions. For example, the supporting electrolyte cation employed in this study, bis-(triphenylphosphoranylidene)ammonium (PPN<sup>+</sup>), is sufficiently large such that it is completely excluded from entering the polymer (vide infra). *It is the use of this sterically excluded electrolyte that circumvents the problems encountered in earlier attempts to quantitate dopant ion flux by RRDE*.<sup>13,14</sup>

As stated above, RRDE voltammetry can, in principle, be used to monitor flux of cations, anions, or both. The present work focuses only on cationic doping in polypyrrole/poly(styrenesulfonate) ( $pPy^+/pSS^-$ ) composites. When pyrrole is polymerized in the presence of  $pSS^-$ , the  $pSS^-$  polyanion is irreversibly incorporated into the polymer structure.<sup>8–10</sup> Since  $pSS^-$  cannot leave the polymer upon subsequent redox cycling, charge neutrality is maintained predominantly by cation influx and efflux:

$$pPy^+/pSS^- + e^- + C^+ \cong pPy/pSS^-C^+$$

In these experiments, the potential of a pPy<sup>+</sup>/pSS<sup>-</sup>-coated disk is typically scanned between 0.00 and -1.1 V. The range is sufficient to convert the polymer successively from fully reduced (-1.1 V) to significantly oxidized (0.00 V). Voltammograms of pPy<sup>+</sup>/pSS<sup>-</sup> obtained in electrolyte solutions of typical composition for a RRDE study are shown in Figure 1. The features of these voltammograms are similar to those of voltammograms obtained in more standard electrolyte solutions such as tetraalkylammonium hexafluorophosphate. In the RRDE experiment, the ring electrode potential is chosen to be well onto the mass-transportlimited current plateau of the dopant cation, C<sup>+</sup>, reduction.<sup>16</sup> Consequently, in the ideal case, a constant, time-independent current, *i*<sub>r,0</sub>, should pass at the ring in the absence of any polymer voltammetry at the disk.

<sup>(16)</sup> It is important to emphasize that the ring potential be chosen such that it is well onto the limiting current plateau of the cation reduction so that small variations in potential from *iR* drop do not effect the ring current.

Here the doping experiment deviates from the classical EC study. In the EC case, R is not present in bulk solution so there is no current at the ring unless R is being produced at the disk. By contrast, in the absence of any redox process at the disk, C<sup>+</sup> is present in bulk solution and produces a constant current  $(i_{r,0})$ at the ring. When the polymer doping level changes, the concentration of C<sup>+</sup> reaching the ring changes, causing the ring current to deviate from  $i_{r,0}$ . It is the difference between  $i_{r,0}$  and the total ring current,  $i_r(t)$ , which is quantitatively related to the total disk current,  $i_d(t)$ . Consider a positive potential scan of the disk starting at a value where the pPy+/pSS- film is fully reduced (e.g., -1.0 V). As the polymer becomes progressively more oxidized, electrons are being removed from the polymer and enter the electrode. For charge neutrality to be maintained, either cations must be ejected into solution or anions from solution must enter the polymer. If it is assumed for the present that only cation doping occurs in pPy<sup>+</sup>/pSS<sup>-</sup>, every electron removed from the polymer releases a cation into solution. From the point of view of the ring electrode, the act of releasing C<sup>+</sup> from the polymer is indistinguishable from creating C<sup>+</sup> electrochemically at the disk (as was the origin of the R being formed at the disk in the EC experiment). The difference in the two experiments is, again, that in the EC studies the only source of R is electrochemistry at the disk; in the doping experiment, C<sup>+</sup> released from the polymer adds to the constant flux of C<sup>+</sup> from the bulk solution, thus increasing  $i_r(t)$  over  $i_{r,0}$ . An identical argument can be made for the reductive potential scan of the disk except that in that case C<sup>+</sup> enters the polymer, reducing its concentration at the ring and causing  $i_r(t)$  to drop below  $i_{r,0}$ . If the corrected ring current,  $i'_r(t)$ , is defined as

$$i'_{\rm r}(t) = i_{\rm r}(t) - i_{\rm r,0}$$
 (2)

a relation analogous to eq 1 exists which takes the form

$$-i_{\rm r}'({\rm t})/i_{\rm d}({\rm t}) = N \tag{3}$$

When the doping change is accomplished exclusively by C<sup>+</sup>, the collection efficiency in eq 3, *N*, is the same as in eq 1. Just as deviations of the current ratio from *N* signal a nonzero rate of follow-up chemistry for an EC process, deviations in the current ratio in eq 3 from N signal that C<sup>+</sup> is not the sole ion participating in changing the polymer doping level.<sup>17</sup> The fraction of the doping change that *is* due to C<sup>+</sup>,  $f_{C}^+$ , can be determined by dividing the left side of eq 3 by the right and setting this equal to  $f_{C}^+$ , namely

$$f_{\rm C}^{\ +} = -i_{\rm r}({\rm t})/(N(i_{\rm d}({\rm t})))$$
 (4)

#### EXPERIMENTAL SECTION

**Chemicals and Equipment.** All chemicals except as noted below were purchased from Aldrich and used as received. Pyrrole was purified by distillation under nitrogen. Bis(triphenylphosphoranylidene)ammonium *p*-toluenesulfonate (PPNTos) was prepared by combining aqueous solutions of PPNCl and sodium *p*-toluene-sulfonate from which it precipitated. The PPNTos was filtered, rinsed with distilled water, and dried under vacuum. The dried product was subsequently recrystallized from methanol/water and from dichloromethane/ethyl acetate. In each case, small white crystals formed which were filtered from the solution and washed, respectively, with either distilled water or ethyl acetate. The rinsed solid was dried under vacuum overnight.

Tetraethylammonium poly(4-styrenesulfonate) (TEApSS) was prepared via dialysis (Spectra/Por membrane MWCO 6-8000 Spectrum Medical Industries, Inc., Los Angeles, CA) from tetraethylammonium bromide (TEABr) and poly(sodium 4-styrenesulfonate) (NapSS) in distilled water. Aqueous solutions of TEABr and NapSS were combined. The TEABr was in excess of the NapSS ( $\sim$ 2.5 g) by 2-fold. The mixture was sealed in a dialysis tube, which was then submerged in distilled water for 48 h. After this time, the tube had swollen and become taut. External water in the container was changed and to it several grams of TEABr was added. The dialysis tube remained in the stirred solution for 48 h. This external solution was then replaced with pure distilled water, which was replenished several times over a span of 48 h. The tube was removed from the container and rinsed with distilled water, and the contents were poured into a flask. The presence of bromide in the solution was tested with aqueous silver nitrate. The absence of a precipitate indicated the dialysis was complete. The aqueous solution was taken to dryness on a rotary evaporator leaving a tan film on the flask walls. This film was hard and difficult to remove from the side of the flask. By dissolving the product in a minimum of absolute ethanol and slowly re-evaporating the ethanol on the rotary evaporator, a tan, bubbly solid coated the flask walls, which could readily be removed. Once removed, the material was further dried under vacuum. Finally, this procedure is general for preparing acetonitrile-soluble R<sub>4</sub>N<sup>+</sup>pSS<sup>-</sup> salts when R is hexyl or smaller (for R larger than hexyl, see ref 18).

1-Methyl-3-cyanopyridinium hexafluorophosphate (CMPPF<sub>6</sub>) was prepared by dissolving 3-cyanopyridine in acetonitrile and adding dropwise a stoichiometric amount of iodomethane. The reaction mixture was refluxed for 4 h and then allowed to cool to room temperature. The iodide salt (CMPI) formed as a yellow solid upon cooling. It was filtered and recrystallized from acetonitrile to yield yellow, needlelike crystals. The CMPI was then dissolved in water and excess of ammonium hexafluorophosphate added. The solution was cooled in a refrigerator until white needlelike crystals formed. This mixture was filtered and the solid, CMPPF<sub>6</sub>, was washed with cold water and then dried for 12 h under vacuum. 1,3-Dimethylpyridinium hexafluorophosphate (DMP-PF<sub>6</sub>) was synthesized in a similar manner starting with 3-picoline in place of 3-cyanopyridine. The half-wave potentials for the

<sup>(17)</sup> The magnitude of *i*<sub>r,0</sub> in eq 2 is proportional to ω<sup>1/2</sup>, where ω is the electrode rotation rate; the quantities *i*<sub>d</sub>(t) and *i*<sub>r</sub>'(t) are, on the other hand, independent of ω. Consequently, the signal-to-background ratio in these experiments increases as ω decreases. In all experiments reported here, ω was maintained at 400 rpm, which is the lowest rotation rate available with the PIR rotator. While they are independent of ω, the values of *i*<sub>d</sub>(t) and *i*<sub>r</sub>' do depend on the polymer thickness and the potential scan rate, ν. At fast scan rates, a collection of problems can arise from *iR* drop, from ion/electron transport rates within the polymer film, and from maintaining insufficient flux of dopant ions from solution to the polymer interface (see text). A scan rate of 50 mV/s was determined to be an optimum compromise and was used in all of the studies reported here unless otherwise noted.

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reduction of CMP<sup>+</sup> and DMP<sup>+</sup> were determined from steady-state voltammetry at the Pt ring of the RRDE. The values for CMP<sup>+</sup> and DMP<sup>+</sup> were calculated to be -1.13 and -1.70 V, respectively vs a Ag/Ag<sup>+</sup> (0.10 M AgNO<sub>3</sub>, DMSO) reference electrode. The measurements were made in acetonitrile solutions containing 2 mM electroactive cation and 50 mM PPNTos.

The bis(cyclopentadienyl)cobalt(II) hexafluorophosphate (CcPF<sub>6</sub>) was purchased from Aldrich and was used as received. The half-wave potential was determined as above and calculated to be -1.21 V vs a Ag/Ag<sup>+</sup> (0.10 M AgNO<sub>3</sub>, DMSO) reference electrode.

An EG&G Princeton Applied Research model 173 potentiostat/ galvanostat with a model 175 digital coulometer was used for film growth (vide infra). A Pine Instruments RDE4 bipotentiostat, modified to provide a potential range of  $\pm 5$  V, was utilized for the ring-disk electrochemistry. Electrode rotation was accomplished using a Pine Instruments PIR electrode rotator. Data acquisition was accomplished using a program, written in ASYST, provided by Professor Daniel Buttry of the Department of Chemistry, University of Wyoming. The program was modified locally. A BAS 100B Electrochemical Workstation was used for the chronocoulometry experiments.

**Cells and Electrodes.** The electrochemical cells used in film growth and in ring-disk experiments were each single-compartment cells and were employed in three- and four-electrode configurations. The working electrode was a platinum ring-platinum disk electrode purchased from Pine Instruments. The disk electrode had a 2.6-mm radius. The radius to the inside of the ring was 4.0 mm, and the radius to the outside of the ring was 4.3 mm. This gave a large ring-disk gap width of 1.4 mm. The counter electrode was a platinum wire coil. A Ag/Ag<sup>+</sup> (0.10 M AgNO<sub>3</sub>, DMSO) reference electrode was employed for film growth and for some of the ring-disk experiments; however, more typically, a Ag pseudoreference electrode was utilized in the RRDE experiments. All potentials are reported relative to the Ag/Ag<sup>+</sup> (0.10 M AgNO<sub>3</sub>, DMSO) electrode.

**Film Growth.** Composite polypyrrole/poly(styrenesulfonate) films were grown potentiostatically at +0.8 V. The acetonitrile growth solution was 1.0 M in pyrrole and 0.10 M in TEApSS and was stored at 0 °C under argon between uses. The extent of film growth was determined from the coulombs passed during polymerization. All films were grown with the passage of 15 mC. Following film polymerization, the working electrode was removed from the growth solution and rinsed with copious amounts of acetonitrile. The electrode and film were then placed into the rotator and positioned in the RRDE cell. Shape and peak magnitudes of the polymer's cyclic voltammetry were used to qualitatively verify film quality.

**Solutions.** All solutions used for analysis of cation transport in the composite films were prepared in the same manner. The total concentration of electroactive cation(s) in solution was maintained at 2.0 mM. The concentration of the PPNTos supporting electrolyte was 50 mM. Acetonitrile was used as the solvent in all electrochemical experiments.

**Current Decay Correction.** In the discussion leading up to eqs 2–4, the results from the RRDE experiment were treated as ideal. In practice, the peak-to-peak excursion of the  $(i_r(t) - i_{r,0})$  is typically only ~10% of the value of  $i_{r,0}$ . Therefore, if  $i_{r,0}$  were not

rigorously constant, significant errors would be introduced into the data treatment. In actual experiments, ring current data are collected over many cycles of the disk potential requiring between 5 and 10 min. Over such extended periods, changes to the ring electrode surface often resulted, which were sufficient to cause the value of  $i_{r,0}$  to slowly, and monotonically, decrease. This decrease is typically small in absolute terms, but is large enough to make eqs 3 and 4 unusable as previously defined. To deal with this problem, the time dependence of the background current at the ring was determined and the constant value of  $i_{r,0}$  in eq 2 replaced with the time-dependent function,  $i_{r,0}(t)$  thus, redefining  $i'_r(t)$  in eqs 3 and 4:

$$i'_{\rm r}(t) = i_{\rm r}(t) - i_{\rm r,0}(t)$$
 (2')

To approximate the function  $i_{r,0}(t)$ , the points where  $i_d(t)$  crossed the zero current axis were determined over the course of multiple cycles of the disk potential. When  $i_d(t) = 0.00$  mA, no net change in polymer doping can be occurring; thus, the concentration of  $C^+$  at the ring should be exactly its bulk concentration. It follows then that  $i_r(t)$  at these points equal values of  $i_{r,0}(t)$ . The ring current data for the points where  $i_d(t) = 0.00$  mA (as a function of potential or time) were quite adequately fit to a simple quadratic function. This function was then used to generate values of  $i_{r,0}(t)$ at the intervening potentials (times).

### **RESULTS AND DISCUSSION**

**Cyclic Voltammetry.** Films of  $pPy^+/pSS^-$  give stable, reproducible voltammetry with each of the three electroactive cation dopants examined. The general shape of the voltammograms are as expected; however, the total charge passed for a given film during redox cycling is different for the different dopant cations. Comparison of the voltammograms in Figure 1 shows that the amount of charge passed follows the order  $DMP^+ > CMP^+ > Cc^+$ . The peak potentials of the voltammograms are also dopant dependent; the less charge passed, the more positive the peak potentials for a given film.

Single-Dopant Ion Transport Measurements. Figure 2 shows both the  $i_r(t)$  and  $i_d(t)$  data for a pPy<sup>+</sup>/pSS<sup>-</sup> film cycled repeatedly between 0.0 and -1.1 V in a solution containing DMP<sup>+</sup>. The ring potential is held at -1.9 V giving a mass-transport-limited reduction of DMP<sup>+</sup>. The qualitative response for pPy<sup>+</sup>/pSS<sup>-</sup> films is similar to that shown in Figure 2 regardless of which electroactive dopant is being studied. The current response of the polymer is stable and centered about the zero current axis. The value of  $i_{r,0}$  at the beginning of the experiment is represented in the upper part of Figure 2 by a solid line. Over the course of this experiment ( $\sim$ 4 min.), the background current at the ring decays by roughly 10%. The dashed line labeled  $i_{r,0}(t)$  is the timedependent background current obtained as described in the Experimental Section. The corrected ring current response calculated from eq 2',  $i_r'(t)$ , is less than, and has the opposite sign from, the disk current,  $i_d(t)$ . From consideration of eq 4, if  $f_{\rm C}^+ = 1$ , then  $i_{\rm r}'(t)$  should be smaller than  $i_{\rm d}(t)$  by exactly the collection efficiency, N (i.e., 0.12 in the present case).

Typically, for each dopant ion studied, the value of  $f_{\rm C}^+$  obtained from eq 4, within experimental error, is equal to unity. A visually informative way of displaying the current data is in the form of a



**Figure 2.** Current vs time plot for a pPy<sup>+</sup>/pSS<sup>-</sup> film on the disk electrode ( $i_d(t)$ , dash-dot line) in an acetonitrile solution of 2 mM DMPPF<sub>6</sub> and 50 mM PPNTos cycled between 0.00 and -1.10 V and the simultaneously recorded mass-transport-limited ring current for the reduction of the DMP<sup>+</sup> ( $i_r(t)$ , solid line). Electrode rotation rate was 400 rpm.



**Figure 3.** Plot of  $i_d$  (dashed line) and  $-Ni_r$ '(solid line) vs  $E_{disk}$  for a pPy<sup>+</sup>/pSS<sup>-</sup> film (disk) cycled in an acetonitrile solution of 2 mM DMPPF<sub>6</sub> and 50 mM PPNTos.  $E_{ring}$  was held at -1.9 V in the mass-transport-limited reduction of DMP<sup>+</sup>. Electrode rotation rate was 400 rpm.

conventional cyclic voltammogram. When  $f_{\rm C}^+ = 1$ , a plot of  $-N(i_{\rm r}')$ should exactly overlay the disk voltammetry; when  $f_{\rm C}^+ < 1$ , the plot of  $-N(i_r)$  will be smaller than  $i_d$  by  $f_c^+$ . Figure 3 contains an overlay plot of  $i_d$  and  $-N(i_r)$  for three multiple scans of the disk potential. Once steady state is obtained, the two currents correlate, within experimental error, over all but the most positive part of the three scans. Only when the potential goes positive of  $\sim$ +0.8 V do the two plots deviate. Positive of +0.8 V on both the positiveand negative-going scans  $i_d > -Ni_r'$  indicating  $f_c^+ < 1$ . Recall that the  $pPy^+/pSS^-$  films were grown potentiostatically at +0.8 V. Cycling the potential positive of +0.8 V therefore oxidizes the polymer beyond the state in which it was grown. Consequently, there is insufficient negative charge from the pSS<sup>-</sup> to compensate the additional positive charge injected into the film; thus, additional anions from solution must enter the film to maintain charge balance.



**Figure 4.** Cyclic voltammograms showing the change in the current response of a  $PPy^+/pSS^-$  film as the solution is progressively changed from pure CMP<sup>+</sup> (inside solid curve) to pure DMP<sup>+</sup> (outside solid curve). Each solution was 50 mM in PPNTos and the total dopant ion concentration ([CMP<sup>+</sup>] + [DMP<sup>+</sup>]) was kept at 2 mM. Electrode rotation rate was 400 rpm.

**Doping Competition Studies.** Studies with each of the individual electroactive dopants demonstrate that, at potentials negative of +0.8 V, these pPy<sup>+</sup>/pSS<sup>-</sup> composite films undergo doping changes exclusively via cation transport. Having established this fact, we were interested in how the various cations compete in the doping process. Such competition studies would be virtually impossible via techniques such as EQCM, but they are straightforward employing the RRDE experiment.

We chose to consider two pairs of cations:  $DMP^+$  vs  $Cc^+$  and  $DMP^+$  vs  $CMP^+$ . The other possible combination,  $CMP^+$  vs  $Cc^+$ , was not considered because the reduction potentials of the cations are too close to allow detection of each cation independently.

In the competition studies, the potential of the disk electrode was cycled in a series of solutions in which the relative concentrations of the two dopant cations was varied but their sum was held constant. Figure 4 shows a progression of voltammograms in solution containing 2.0 mM total electroactive cation ( $[CMP^+] +$ [DMP<sup>+</sup>]) as the relative fractional concentration of CMP<sup>+</sup> is varied from 1.0 to 0.0. Consistent with the voltammograms shown in Figure 1, the amount of charge passed increases, the voltammogram becomes more peak-shaped, and the peak shifts to more negative potentials. Somewhat suprisingly, the shape of the disk voltammogram proved to be mildly dependent upon the order in which the polymer was exposed to the two dopant cations. If the solution was changed progressively from one of pure DMP+ to one of pure CMP<sup>+</sup>, the shape of the final voltammogram differed moderately from that obtained from a film exposed only to CMP+. Apparently, cycling the oxidation state of the polymer in a solution containing DMP<sup>+</sup> causes irreversible changes in the film. When the reverse order of cation exposure is used, as depicted in Figure 4, the voltammograms at each extreme (i.e., DMP<sup>+</sup> only and CMP<sup>+</sup> only) are the same as if the film had been exposed only to the respective electrolyte. Similar results were observed in Cc<sup>+</sup> and DMP<sup>+</sup> competition studies. Consequently, for the majority of the data reported here, the film was exposed to DMP<sup>+</sup> last. Irrespective of the film's history and the order of electrolyte exposure, the relative fraction of the doping level change due to

each dopant cation in a given mixture appears to depend only on the ratio of the dopant cation concentrations in solution (vide infra).

When the potential of the disk is cycled, the rate of change of polymer doping (as reflected by the disk current) changes over the course of the experiment. From eq 4, the fractional doping change rate due to a given cation (or combination of cations) can be calculated at every point in the voltammogram. When multiple dopant cations are present in solution, there is no a priori reason that  $f_{\rm C}^+$  for each cation remains constant at all doping rates (currents). Nonetheless, under most circumstances,  $f_{\rm C}^+$  remains constant within experimental error over the entire potential scan. There are two situations where  $f_{\rm C}^+$  was observed to change during a potential sweep: (1) when the potential is taken positive of where the film was grown (as discussed previously) and (2) when the flux of the lower concentration cation during the anodic sweep is insufficient to provide the required degree of doping. To determine whether sufficient cation flux exists, one need only compare the ratio  $i_{r,0}/i_d$  to the electrode parameter  $\beta^{2/3}$ . The value  $\beta$ , like the collection efficiency, N, is specific for each RRDE and is determined by electrode geometry.<sup>13,19</sup>

For the reduction of the polymer at the disk not to be cationflux-limited, the following must be true:

$$i_{\rm r,0}/i_{\rm d} > \beta^{2/3}$$
 (5)

In experiments where the solution contained a single dopant cation at 2 mM,  $i_{r,0}/i_d$  was always at least a factor of ~2.5 greater than  $\beta^{2/3}$ . In the mixed electrolyte experiments, the doping rate can become flux-limited for the less concentrated component. In this situation,  $f_C^+$  for both cations was observed to vary during the anodic scan. Fortunately, this situation only arises when one component is present in a very small relative concentration.<sup>20</sup>

Since  $f_{\rm C}^+$  was determined to be effectively constant over the entire polymer voltammogram, except as considered above, it has a value characteristic of each set of concentrations in the binary mixtures. Figure 5 is a plot of  $f_{\rm C}^+$  vs percent solution concentration of the most easily reduced cation of each pair in (i.e., the solid triangles for  $f_{CMP}^+$  in the CMP<sup>+</sup>/DMP<sup>+</sup> pair and the solid circles for the  $f_{Cc}^+$  in the Cc<sup>+</sup>/DMP<sup>+</sup> pair). The open triangles and circles along the horizontal line at  $f_{\rm C}^+ = 1.0$  represent the combined doping by both cations obtained from eq 4 by potentiostating the ring in the mass-transport-limited reduction of both dopant cations of the pair. Within experimental error, the total doping change of the polymer can be accounted for by the electroactive cations. The different sizes of the data symbols delineate data obtained from different, yet identically grown, pPy<sup>+</sup>/pSS<sup>-</sup> films. Finally, for none of the data presented in Figure 5 was the doping rate limited by flux of either ion to the polymer surface.



**Figure 5.** Results of doping competition studies for CMP<sup>+</sup> vs DMP<sup>+</sup> (triangles) and Cc<sup>+</sup> vs DMP<sup>+</sup> (circles). The diagonal line represents the case of no doping preference between the cations. The ordinate is percent  $f_{C}^+$  for the more easily reduced ion (i.e., either CMP<sup>+</sup> or Cc<sup>+</sup>). The abscissa is the relative fraction of the same ion in solution. The horizontal line at the top of the plot indicates values having a total  $f_{C}^+ = 1$  (i.e., accounting for all doping occurring in film). Departure of the data from the diagonal line indicates a preferential doping in the film by DMP<sup>+</sup>.

When there is no preference for one cation over the other, the fractional contribution to the doping,  $f_{c}^+$ , of each cation should exactly correspond to its fractional solution concentration. All data would then lie on the diagonal line in Figure 5. For both pairs of cations represented in the Figure 5, all data points lie below the diagonal line indicating a preference for DMP<sup>+</sup>.

Based on molecular models,<sup>21</sup> the Cc<sup>+</sup> is roughly cylindrical in shape with a long-axis dimension (measured from a corner of one cyclopentadiene through the cobalt to the far corner of the other ring) of ~5.6 Å. The length from center to center of the two cyclopentadiene rings is 4.6 Å, and the diameter of each ring is 4.2 Å. DMP<sup>+</sup> is more nearly the shape of an oblong disk with a long-axis dimension of ~6.6 Å (measured from carbon to carbon of the two methyl groups) and a short-axis dimension of ~4.9 Å. Given their physical dimensions, one might anticipate a preference for DMP<sup>+</sup> based simply on size. In fact, the data in Figure 5 demonstrate a strong preference for the smaller DMP<sup>+</sup> cation over Cc<sup>+</sup>. For example, when the relative solution concentration of Cc<sup>+</sup> is 70%, it is responsible for less than 20% of the polymer doping change!

While the Cc<sup>+</sup>/DMP<sup>+</sup> pair was studied because of difference in size, the CMP<sup>+</sup>/DMP<sup>+</sup> pair was selected because of differences in reduction potential (CMP<sup>+</sup> is ~700 mV easier to reduce than DMP<sup>+</sup>). Assuming initially both ions to be the same size, we presumed any doping preference in this pair would reflect electronic differences in the ions (e.g., charge-transfer interactions between the cation and the pyrrole sites). Consideration of the

<sup>(19)</sup> The quantity β<sup>2/3</sup> is experimentally the ratio of the independently determined ring and disk currents measured from the mass-transport-limited oxidation or reduction of some arbitrary solution species. Since the limiting currents at either electrode are proportional to the flux of species to the respective surface, knowing the limiting flux at one electrode and β, the flux at the other electrode can be calculated.

<sup>(20)</sup> While it would be interesting to quantitate the potential dependence of  $f_c^+$  under flux-limited conditions, the small absolute and relative concentrations of the minor component make such studies virtually impossible because of the poor overall signal-to-noise ratio. Nonetheless, the dependence is qualitatively obvious.

<sup>(21)</sup> The Cc<sup>+</sup> was modeled using CAChe Editor, Release 3.9. The CMP<sup>+</sup> and DMP<sup>+</sup> measurements were done with Biograf by BioDesign, Inc., Version 2.2.



**Figure 6.** Chronocoulometry for a  $pPy^+/pSS^-$  film (charge passed by reduction of the polymer) on the disk of the RRDE with rotation at 400 rpm. The potential step is from 0.0 to -1.1 V. Each solution was 2 mM in electroactive cation and 50 mM in PPNTos.

data shown in Figure 5 (triangles) shows that there is indeed an obvious preferential doping, but it is for the more electron rich DMP<sup>+</sup>. Consideration of charge-transfer interaction predicts the opposite. While the physical size of the bare cations does not suggest a steric preference, allowing for differences in solvation might. CMP<sup>+</sup> incorporates a nitrile function (like the solvent) while DMP<sup>+</sup> is distinctly hydrophobic around its entire periphery. Therefore, postulating differences in the "effective volume" of these two cations is reasonable and may explain the preferential partitioning of DMP<sup>+</sup>.

The RRDE experiments, which generated the data in Figure 5, confirm preferential doping of  $pPy^+/pSS^-$  by DMP<sup>+</sup>. What these experiments do not address is whether the origin of the preference is kinetic, thermodynamic, or some combination of both. Examination of the voltammograms taken in Cc<sup>+</sup> and CMP<sup>+</sup> electrolyte included in Figure 1 show that the polymer continues to reduce after the -1.1 V switching potential is reached. Even at a sweep rate as low as 50 mV/s, the polymer is not entirely at equilibrium in these electrolytes, at least at the most reducing potentials. To develop a more quantitative picture of the doping kinetics, potential step chronocoulometry experiments were conducted for a pPy+/ pSS- film in solutions that were each 50 mM in PPNTos and 2 mM in one of the electroactive cations. In these experiments, the potential of the polymer was stepped between 0.0 V, where the film is partially oxidized, and -1.1 V, where, in the DMP<sup>+</sup> case at least, the polymer appears to be fully reduced. During each experiment, the disk was rotated at 400 rpm to ensure that the rate of reduction was not limited by cation flux to the polymer/ solution interface. The charge-time responses for the first 32 s of a reductive potential step are shown in Figure 6 for each cation. In none of the electrolytes has the polymer reached its equilibrium doping level. In fact, it was found that the DMP<sup>+</sup> charge response attains a steady state at  ${\sim}53$  s while the CMP<sup>+</sup> takes  ${\sim}122$  s and  $Cc^+$  takes ~137 s. The final value for the charge passed, however, is the same for each of the cations. It is obvious from these data that there is a significant difference in the rate of doping by the three cations, this being fully consistent with the different shapes of the cyclic voltammograms in Figure 1. Slowing the scan rate to 5 mV/s yields voltammograms that are more nearly the same shape and size. Unfortunately, as scan rate decreases, the signalto-noise ratio (S/N) of the ring current also decreases. At scan rates much below 50 mV/s, the S/N becomes so poor that measurements of changes in doping level are unreliable.

While the chronocoulometry and slow-scan CV results demonstrate that there is a major kinetic component to the preferential doping at 50 mV/s scan rates, these experiments do not rule out the possibility of concomitant thermodynamic preferences. In an effort to obtain some qualitative information on the equilibrium doping state, a pPy<sup>+</sup>/pSS<sup>-</sup> film was potentiostated at -1.10 V in 1:1 solutions of each doping ion pair (1 mM concentration of each of the two ions) for 10 min. The potential of the disk was then scanned in the positive direction. On this first anodic scan, the values for  $f_{\rm CMP}^+$  and  $f_{\rm Cc}^+$  were slightly greater than predicted by the data in Figure 5. While there is no way to determine whether, even after 10 min, the film has reached a true partition equilibrium, these results do suggest that if there is a thermodynamic preference for DMP<sup>+</sup>, it is smaller than the kinetic preference.

Given the absence of any other compelling explanations, it seems reasonable to conclude that steric factors are responsible for the kinetic preference of  $pPy^+/pSS^-$  films to dope with  $DMP^+$  in both pairs of ions. The Cc<sup>+</sup> unarguably occupies a larger volume than does the  $DMP^+$  and it is slower to pass through the film. For the CMP<sup>+</sup>/DMP<sup>+</sup> case, there is only a slight preference for the later dopant, which is consistent with steric differences in the two cations based on differential solvation.

#### CONCLUSION

We have demonstrated the utility of rotating ring-disk voltammetry in quantitating studies of ion transport in conducting polymer films. In the past,  $pPy^+/pSS^-$  has been assumed, without real direct proof, to undergo only cation doping. With judicious selection of the supporting electrolyte and the dopant cation(s), we have been able to show by RRDE voltammetry that this assumption is entirely correct under conditions similar to those used in previous studies. Moreover, we have shown that RRDE voltammetry can provide quantitative, in situ information on competitive ion-doping processes. Finally, there is, in principle, no reason why the technique is limited to cation dopants and composite films. For example, we presently have preliminary data on  $Cl^-$  doping in conventional polypyrrole.

The major limitation of this approach lies in the fact that, for the dopant ions to be directly monitored, they must be electrochemically active within the solvent window but inactive over the potential range of the polymer. This is admittedly a nontrivial constraint because it significantly reduces the number of dopant ion candidates for study. That caveat notwithstanding, we have found in preliminary work that, by using mixtures of electroactive and nonelectroactive ions, it is often possible to gain considerable in situ information on doping by electroinactive ions. This can be accomplished by considering the difference between the total doping requirement of the polymer and the part due to the electroactive dopant.

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