

Measuring the Ionic Flux of an Electrochemically Actuated Conducting Polymer Using Modified Scanning Ion Conductance Microscopy

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S Supporting Information

ABSTRACT: We propose a modification of a scanning ion conductance microscope suitable for probing an electrode in an operating electrochemical cell. We demonstrate its use by measuring salt concentration variations near a conducting polymer electrode as the polymer is electrochemically oxidized and reduced. The electrochemical control circuit is opened to isolate the working electrode, at a frequency sufficiently high that the electrode capacitance maintains the electrode potential. The local solution conductivity variations are detected through the probe current during the open-circuit time. We demonstrate two-stage ion exchange during oxidation and reduction of poly(3,4-ethylenedioxythiophene) films that develops strongly with repeated cycling and is correlated with actuation changes. Spatial composition variations of the film, caused by redox current distribution over the surface, and electromigration to the probe tip, causing local solution composition changes, have clear and characteristic effects on the measured transients.

In this communication we address two questions: in general, how to use scanning ion conductance microscopy (SICM)^{1,2} to probe local dynamics of an electrode in an operating electrochemical cell, and specifically, how to characterize the local ion flux of actuating conducting polymers (CPs). Interest in CPs arises from the potential combination of plastic properties with metal conductivity.^{3,4} Electrochemical reduction or oxidation of the polymer requires an associated exchange with the solution of ions and hence solvent to maintain electroneutrality, resulting in volume changes. Whether anions, cations, or both exchange, the resultant ion fluxes and the response of the polymer microstructure to the changes of solvation associated with the fluxes are dependent on the nature of the polymer and of the ionic dopants introduced during fabrication.^{5–11} Direct measurement of the ion flux, its correlation with actuation, and its variation with sample history are thus of importance, since this flux directly impacts the design and feasibility of CP applications.^{9,11–14} The idea underpinning our study is that, as ions move from the solution into the polymer and vice versa, the local solution conductance will change, which should in principle be measurable by SICM.

Considerable research effort has concentrated on CP ion flux, using tools such as electrochemical quartz crystal microbalance (EQCM),¹⁵ electrochemo-mechanical deformation (ECMD),¹⁶

atomic force microscopy (AFM),⁵ transport-limiting barriers,¹⁷ and bulk chronoamperometry.¹¹ These complementary techniques approach the ion flux problem from the macroscale. In this study we look to address this problem by introducing the SICM as a technique to carry out microscale chronoamperometric studies on poly(3,4-ethylenedioxythiophene) (PEDOT) films. The technological advance is that this is the first SICM-type work carried out in an active electrochemical cell, that is, where the substrate being investigated is connected as a working electrode. The strategic significance can be understood by contrasting the information given by AFM and EQCM: AFM has excellent spatial resolution but cannot detect ion flux; EQCM can detect ion flux but has no spatial resolution.

Our instrument differs from conventional SICMs in some key aspects, as outlined below and detailed in the Supporting Information (SI). All SICMs measure the conductivity between an electrode in the solution and one inside a pipet close to the surface to be probed (the working surface). The main purpose is to image topography. However, ionic fluxes to or from the working surface will change the conductivity of the solution in the immediate vicinity, as in our CP system. These changes should be detectable using SICM. The method has indeed been used to image local ionic fluxes through membranes.^{1,18} Significantly, though, if the working surface is to be controlled in an electrochemical cell, then an important measurement problem is posed by the coupling between the two measurement circuits: the electrochemical control circuit and the SICM measurement circuit, as illustrated in Figure 1. Since CP electrodes have a large capacitance, the problem can be overcome by momentarily disconnecting the working surface from the control circuit. The working electrode capacitance sustains the working electrode potential during this period. The local solution conductivity around the pipet tip can then be probed when the only current path is from the reference electrode in the bulk solution to the reference electrode inside the pipet. This interruption technique bears some similarities to classic approaches developed for IR drop corrections.²⁴ Our application differs in its focus on spatially resolved measurements of conductance change close to a surface.

A second measurement issue is to decide the common terminal for the two circuits. Conventionally, this would be the working electrode. However, that choice is not compatible with the requirement to isolate the working electrode. Thus, we chose the common point to be the counter electrode for the

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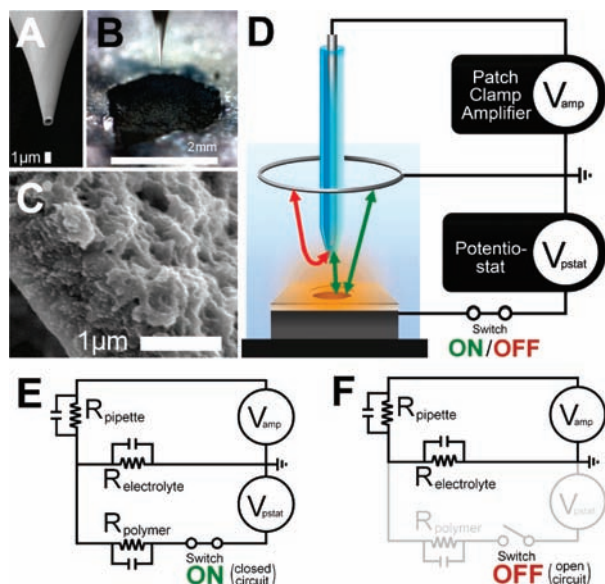


Figure 1. SICM micropipet tip (A) imaged by SEM and (B) hovering above PEDOT film. (C) SEM image of PEDOT film. (D) Schematic of the experimental setup, in closed-circuit mode, showing possible current paths. Circuit diagrams for (E) closed-circuit, (F) open-circuit modes. In (F), the light gray lines represent the parts of the circuit that the switch disconnects when it is in the OFF position.

electrochemical cell. This choice dictates a two-terminal configuration for the electrochemical cell, in which the counter electrode also functions as reference electrode, both for control of the working electrode and for the SICM measurement. Options are a dynamic hydrogen reference electrode²⁰ or a sufficiently large Ag/AgX electrode. We chose the latter option to study systems with a chloride electrolyte.

Figure 1 illustrates the system. A battery-powered potentiostat was run in two-electrode mode, with the counter electrode and reference electrode terminals connected to the PEDOT/glassy carbon (GC) substrate, while the working electrode terminal was connected to a Ag/AgCl ring electrode. This is the reverse of a typical electrochemical setup, purposefully chosen as a means of sharing a common point between the two circuits present in the setup: the V_{potat} circuit which actuates the CP, and the V_{amp} circuit which reads currents through the micropipet (Figure 1D). In this communication, however, potentials of the CP electrode are expressed relative to the Ag/AgCl ring electrode, the inverse of the potential applied in the control circuit. A computer program controlled both the applied electrode potential and a MOSFET switching relay in series with the PEDOT/GC electrode. For this proof of principle, a dilute electrolyte, 0.01 M aqueous NaCl, and a relatively thick ($\sim 1 \mu\text{m}$, see Figure 1C) CP film were used to develop an easily detectable conductivity contrast as a consequence of the ion flux to or from the polymer. We studied PEDOT formed on a GC substrate (3 mm^2 area) by potentiostatic electropolymerization in the presence of a TBACF₃SO₃ electrolyte in propylene carbonate (PC) solvent. The synthesis procedure^{16,21} is detailed in the SI. These samples were positioned below a suspended piezoactuator-driven micropipet assembly (Figure 1).

CP ion fluxes were measured using micropipets with $1 \mu\text{m}$ i.d. tips (Figure 1A), which contained embedded Ag/AgCl wire electrodes and the same 0.01 M NaCl solution as in the

electrochemical cell. The pipet was lowered (with the electrochemical control circuit disconnected) until the pipet current began to decrease due to physical blockage of the micropipet tip opening by the sample. The separation can be deduced from that current decrease:^{1,2} we chose a micropipet–film separation of $2 \mu\text{m}$. Following this approach, the pipet was kept in the same position throughout the remainder of the experiment.

Conventional electrochemical characterization of the redox cycling of the film in the dilute aqueous electrolyte is presented in Figure S7 and was consistent with the literature.¹⁶ The SICM current was in agreement, showing a response specifically correlated with oxidation and reduction of the polymer (Figure S7). Cyclic voltammetry with the isolation relay running at 10 Hz showed that the general electrochemical behavior was unperturbed. For more detailed investigation, the SICM experiments shown in Figure 2 implemented a repeating actuation cycle: 60 s at +0.8 V, which was sufficiently positive to fully oxidize the film, followed by 60 s at −0.8 V, which was sufficiently negative to fully reduce the film. The isolation relay operated at 10 Hz throughout. Figure 2 shows one cycle. Figure 2A shows the change in open-circuit electrode potential in response to the change in polymer oxidation state. The change in open-circuit cell potential is smooth and gradual, taking ~ 60 s to reach the voltage being applied (e.g., +0.8 V). In a control experiment that used a bare GC substrate instead of PEDOT/GC, the open-circuit cell potentials reached the applied values in a fraction of a second. The change of oxidation state is quantified by the current flow into and out of the PEDOT (Figure 2B: the outermost defining edges of the gray curves).

The open-circuit currents measured using the SICM micropipet are shown in Figure 2C. These transients clearly delineate several distinct phases during the oxidation and reduction of the CP film. For correlation, in separate experiments using the same electrochemical cell setup, we performed *in situ* height measurements of the PEDOT film using an atomic force microscope, with the height of a single spot being sampled in tapping mode. We observed actuation on the order of 10%, with the film swelling upon oxidation and shrinking upon reduction.

Effects of film swelling and effects of local solution conductivity change can, in principle, be distinguished on the basis of their different dependence on the ratio d/r_i , where r_i is the internal radius of the pipet and d the perpendicular distance from the bottom of the pipet to the top of the substrate. In the present work ($r_i \approx 0.5 \mu\text{m}$, $d \approx 2 \mu\text{m}$) the effect of the 100 nm film expansion would be a change in pipet current of $< 1\%$.²² Resolution of topography changes on the scale of 100 nm would require $d \approx 250$ nm and simulations to fit the signals at different spacings in order to deconvolute the effects of solution composition change, which we have not attempted here.

The measurements of ion flux and height change are correlated in Figure 2C,D. Several regions of interest are labeled as R_1 – R_5 . Immediately upon application to the reduced-state film of a potential sufficiently high to fully oxidize it, there was a small contraction (R_1) followed by a relatively rapid expansion (R_2) which then markedly slowed (R_3). Immediately upon re-reduction, there was a rapid contraction (R_4) which then also markedly slowed (R_5). In R_1 , the SICM current magnitude immediately increased above the value in the unperturbed state. In R_2 , it decreased and passed through a minimum. In R_3 , it went through a shallow maximum before decreasing. In R_4 , the pipet current immediately after the potential step went through a sharp minimum, less than the value in the unperturbed

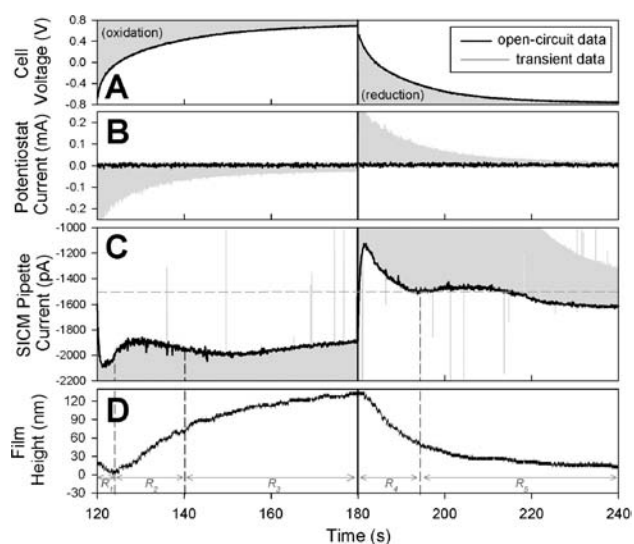


Figure 2. Redox cycling of a new PEDOT film, between +0.8 and −0.8 V, alternating at 10 Hz between closed- and open-circuit configurations: (A) electrode potential, (B) potentiostat current, (C) SICM micropipet current, (D) PEDOT film height changes. Five fairly distinct rates of height change (R_1 to R_5) were identified. Note that dark lines correspond to open-circuit periods and the gray areas to transient data. The pipet bias current in the absence of effects due to the CP electrode was −1500 pA, marked by the horizontal dotted line.

state, and then increased until R_5 , going through a shallow maximum and then minimum before increasing toward the unperturbed state.

The SICM transients changed over time as the CP film was cycled repeatedly (Figure 3). The minima and maxima on both oxidation and reduction became much more prominent, and on oxidation, particularly, a significant and stable offset of the SICM current developed. If, however, the electrode potential was maintained constant and the SICM tip was retracted and then re-approached, this offset disappeared. Finally, as shown in Figure 4, the form of the transient depended on the sign of the bias applied to the SICM tip, the various oscillations being much less pronounced if the pipet was biased positive with respect to the solution. A significant transient current was also observed if there was no bias between the interior of the pipet and the external solution. The zero-bias transients diminished with greater pipet–CP separation (Figure S9). No such effects appeared with an uncoated GC electrode (Figure S11).

We interpret these results with three ideas: (i) anion and cation exchange with the CP occur on different time scales and change with continued cycling of the film, in agreement with previous experimental findings and modeling;²³ (ii) composition variations of the CP develop in the plane of the electrode, caused by the current distribution in the cell and by screening effects of the pipet, and also change with continued cycling; and (iii) solution composition changes immediately underneath the pipet tip are caused by electromigration associated with the pipet current. The latter two effects are artifacts, though also informative. We note that film expansion is expected to be associated with a net ion ingress and film contraction with a net ion egress. Now, for the “new” film whose behavior is detailed in Figure 2, in the region R_1 , the first 2 s of oxidation, there is a small contraction of the film associated with an increase in pipet current magnitude, consistent with ion expulsion from the film. We interpret the net

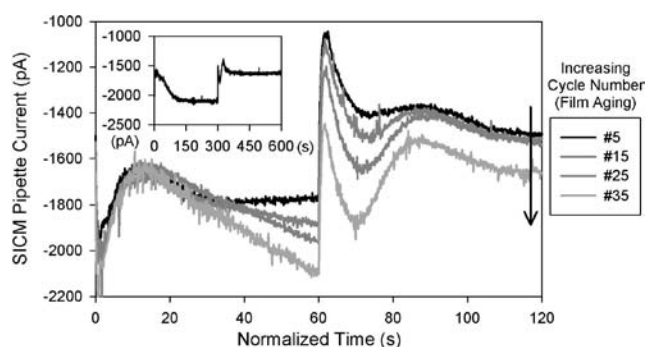


Figure 3. Aging effects as a function of redox cycle number, measured using the SICM, with only open-circuit data plotted. Cycles are oxidation and reduction, each 60 s, alternating at 10 Hz between closed- and open-circuit configurations. Inset: Long-term behavior, with 5× cycle time length.

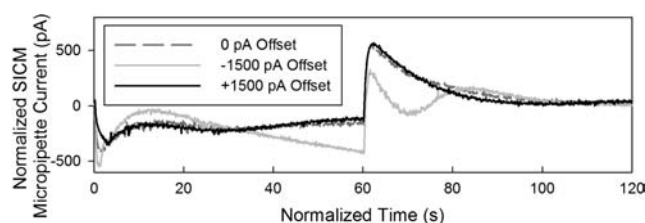
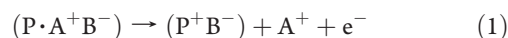
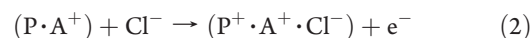


Figure 4. SICM micropipet currents for a 50-cycle aged film as a function of offset V_{amp} , with open-circuit regions of the data plotted.

reaction in this phase as



where P denotes the polymer and A^+ and B^- are the ions associated with it. R_1 is likely due to an initial expulsion of surface cations from the immediately accessible top layers of the PEDOT, namely TBA^+ cations in the first few cycles and Na^+ in the later ones ($TBACF_3SO_3$ was the electrolyte used during electropolymerization, while 0.01 M NaCl was used as the cycling solution). This initial oxidation region was followed, in R_2 , by a change in behavior, with the film expanding and the pipet current magnitude decreasing before a relaxation to the final state when the oxidation approached completion. The interpretation is that the film is growing because of Cl^- anion intake into the polymer beneath the immediate solution interface. The net reaction can be written



Upon reduction, there was an immediate decrease of pipet current magnitude, corresponding to the reverse of eq 1, followed by an increase on a longer time scale, corresponding to the reverse of eq 2, before the relaxation corresponding to completion of reduction. The strong variation of these effects with continued cycling of the film is shown in Figure 3. The “surface” (eq 1) and “bulk” (eq 2) processes become much more strongly distinguished and the effects of cation exchange (eq 1) perhaps more dominant. The aging may be related to microstructure changes caused by the cycling in water²⁴ and changes in polymer ionic composition from TBA^+ to Na^+ cations and from CF_3COO^- to Cl^- anions. However, the effects are also significantly influenced by artifacts of the measurement which

themselves partly arise as specific consequences of the changes induced in the polymer by the cycling.

The zero-bias pipet current observed (Figure 4) can be interpreted as a current due to short-circuit discharge of a capacitor associated with the sample. The effect is subtle though, since the sample is not directly connected to the measurement circuit, except through the solution. The sample can be considered as a capacitive transmission line,²⁵ short-circuited on one arm through the substrate but with a significant resistance in the other arm due to the low-concentration electrolyte solution. The characteristics of this transmission line also depend upon the (time-varying) state of oxidation of the polymer, since this determines the electronic resistance of the polymer film. If the transmission line is not uniformly charged, that is, if the polymer is spatially nonuniform in its state of oxidation, then there will be a current circulating through the solution that will also pass through the pipet. Spatial nonuniformity of oxidation state can arise because of nonuniform current distribution in the electrochemical cell, which would be caused by the cell geometry (a ring electrode around the CP electrode, with a low-conductivity electrolyte) and the local screening effect of the pipet tip. The capacitive discharge of the sample through the solution during the open-circuit part of the measurement cycle can be inferred from a relatively slow relaxation of the pipet current after the circuit is opened, not characteristic of the amplifier (see Figure S6). This slow relaxation is the cause of the permanent offset seen in Figure 3. It depends on whether the CP is being oxidized or reduced, upon the time after the potential step, and upon the number of cycles previously imposed, all of these being effects that alter the electrical resistance and charge-storage capacity of the polymer.

The effect of the sign of the pipet bias on the apparent form of the transients can be understood because the current density through the gap between pipet and substrate was rather large for these proof-of-principle experiments: 1500 pA corresponds to $\sim 25 \text{ mA cm}^{-2}$. Since the mobility of Cl^- is greater than that of Na^+ , a negative current through the pipet tip will increase the local salt concentration, whereas a positive current will decrease it. These local concentration gradients would affect the development of the spatial variation of the oxidation state of the polymer. The consequence appears to be that the discrimination of the different phases of ion movement into and out of the polymer is altered.

In conclusion, we have introduced a novel type of SICM setup designed to measure CP ion flux. Its technological advance is that it is the first SICM that uses an electrochemical cell, and its strategic significance is that it combines ion flux detection capability with localized measurements. For our PEDOT system, we deduced a complex time-dependent mixed-ion actuation process with different time scales, which was dependent on the cycling history of the film. This new technique should complement existing tools such as AFM, EQCM, and ECMD for CP actuation studies. Using it, ion flux imaging is feasible, but artifacts need to be controlled. Measurement of the ion flux characteristics of individual nanostructures such as CP nanotubes may be possible.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details, characterization, and additional acknowledgments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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