LETTERS

Measurement of Lateral Charge Propagation in Polyaniline Layers with the Scanning Electrochemical Microscope

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The local injection and lateral propagation of charge in ultrathin polyaniline (PAN) layers have been studied with the scanning electrochemical microscope (SECM). Monolayers of PAN were deposited on a glass substrate using the LB method and were chemically reduced using sodium dithionite. A microelectrode held close to the PAN layer was used to generate a flux of an oxidant, i.e., $Fe(phen)_3^{3+}$ (phen = 1,10-phenanthroline) which diffused to the surface and locally oxidized the reduced PAN. By simulating the current−time transients, the kinetics of lateral charge propagation have been evaluated.

Electron and charge transfer across thin films has been the subject of numerous studies.[1] On the other hand, *lateral* charge transfer in either thin films or monolayers has received much less attention,[2−12] mostly due to the inadequacy of experimental methods to study this process. Yet, lateral charge propagation plays a major role in biological membranes and in the operation of some electronic devices based on conducting polymer films. In principle, charge can propagate laterally by two different mechanisms, hopping (based on electron transfer) and mass transfer (based on ion transfer). Distinguishing between these two processes is not trivial, particularly if the charge carriers are also free to diffuse laterally, as in Langmuir films. Only a few approaches have been developed over the years to study lateral charge transfer. Majda and co-workers[4,8,9,13−15] have used two-dimensional electrochemical measurements, carried out with line microelectrodes, as well as horizontal touch voltammetry at the air/water interface to study the kinetics of lateral electron transport in Langmuir monolayers. The rate of lateral charge transfer was estimated by probing the dependence of the

apparent charge transport diffusion coefficient on the degree of monolayer compression. Murray and co-workers utilized generation-collection measurements at microband electrode arrays to study lateral charge propagation in polymer films under both steady-state[16] and time dependent (time-of-flight)[12] conditions. More recently, Amatore's group developed a single microband electrode feedback method to investigate the electrochemically mediated carbonization of Teflon and the associated electronic conductivity.[17] Grätzel et al.[2,18] studied lateral electron hopping in monolayers adsorbed onto oxides, e.g., ZrO_2. Lateral diffusion in Langmuir monolayers at the air/water interface was recently investigated with the scanning electrochemical microscope (SECM).[3,19,20]

From scientific and technical points of view, there are a few prerequisites for studying lateral charge transport. The system should be homogeneous, preferably not thicker than a few monolayers and exhibit relatively fast charge transport. The perturbation to be applied should be localized, well-controlled and should not have an irreversible effect on the film structure. The scanning probe microscopy technique SECM,[21] which is capable of generating a well-controlled flux of electroactive species in close proximity to an interface, possesses exactly these features, making it an ideal tool for studying lateral charge transport. There is only one recent report of the use of SECM

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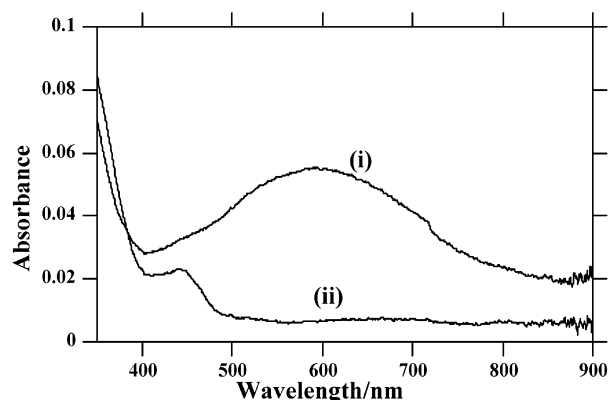
Figure 1. Absorption spectra of a five-layer PAN film deposited on glass, taken in 0.1 M KNO$_3$, before (i) and after treating (ii) with 10 mM of sodium dithionite for 10 s.

for such measurements, in which the insulator−conductor transition in an assembly of metal nanoparticles at the air/water interface, was demonstrated as a function of surface pressure.[22]

In this letter we report the study of lateral charge transport in polyaniline (PAN) LB layers and demonstrate how quantitative information on this process can readily be obtained. Mono and multilayers of electronically conducting polymers, such as PAN, are foreseen as building blocks in molecular electronic devices and have thus been studied intensively.[23,24] Yet, the low processibility of most conducting polymers (due to their low solubility in organic solvents) requires either chemical derivatization or the employment of mixtures of organic solvents, as well as the addition of amphiphilic dopants.[25−28]

We have found that very homogeneous and reproducible PAN layers can be deposited using the LB method by cospreading PAN and the amphiphile dodecylbenzenesulfonic acid (DBSA).[29] Figure 1 shows the electronic absorption spectrum of a five-layer film deposited on a glass plate before and after treatment in 10 mM sodium dithionite (Na$_2$S$_2$O$_4$) solution (pH 7) for 10 s. The change in the absorption from blue to pale yellow, which could also be followed by eye, is due to the reduction of the emeraldine salt to the leucoemeraldine base.[30,31] The latter is a complete insulator and is slowly oxidized by air, vide infra.

Figure 2a shows typical SECM approach curves (microelectrode tip current versus distance from the film surface) recorded over both an oxidized and reduced film, upon approaching the same sample (five layers of PAN on glass) with a 25 μm diameter Pt disk microelectrode (E_{tip} = 1.0 V vs SCE) in a deaerated solution consisting of 0.1 mM Fe(phen)$_3^{2+}$ (phen = 1,10-phenanthroline) and 0.1 M KNO$_3$. As expected, the steady-state current at the microelectrode decreases as it approaches the oxidized PAN, since the latter can neither be further oxidized nor is it conducting, due to the neutral pH of the solution used. On the other hand, a clear increase of the steady-state current, the so-called positive feedback effect,[32] is observed upon approaching the tip to the sample with PAN in reduced form. Clearly, the tip-generated oxidized mediator, Fe(phen)$_3^{3+}$, is capable of oxidizing PAN$_{red}$, thereby regenerating Fe(phen)$_3^{2+}$ which diffuses back to the tip. Moreover, the fact that a pronounced positive feedback current is maintained, when employing low concentrations of the redox mediator in solution, suggests that the charge injected into the multilayer propagates laterally. A schematic of this process is shown in Figure 2b.

Figure 2c shows the cyclic voltammetry of a five-layer PAN film deposited on indium tin oxide. The fact that the oxidation wave is at ca. 0.35 V vs Ag/AgCl reference electrode suggests
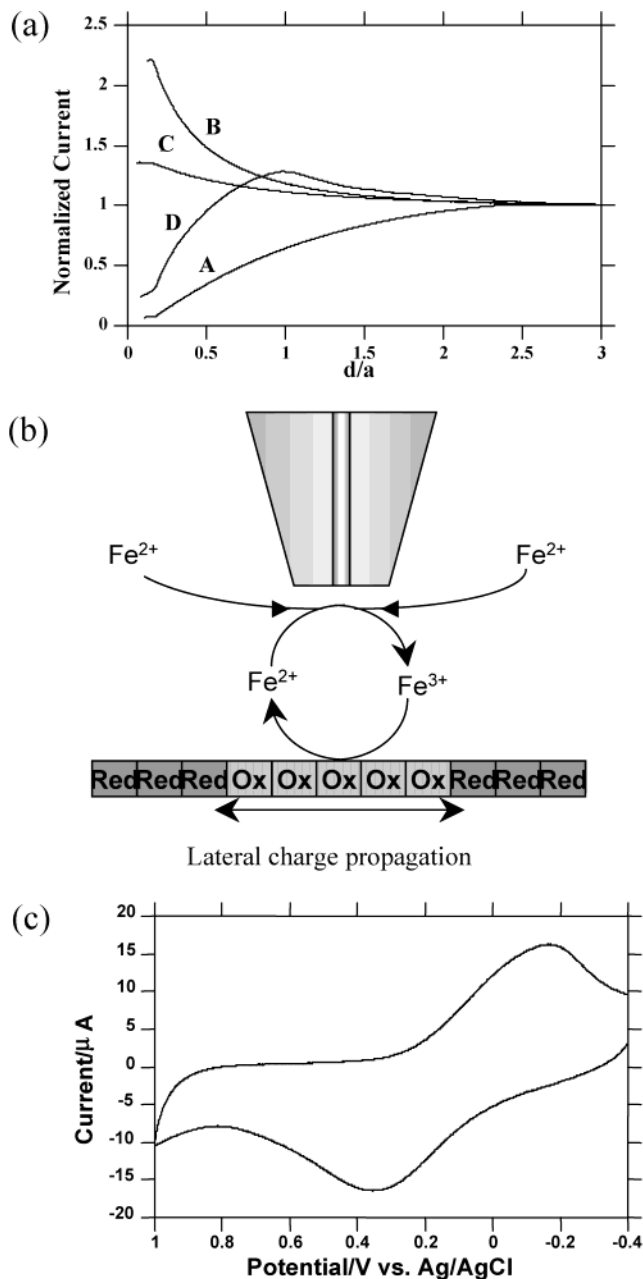

Figure 2. (a) Normalized current-distance curves of a Pt microelectrode approaching a five-layer PAN film. The distance d between the tip and film has been normalized by the electrode radius a, while the tip current has been normalized by the steady-state value in bulk solution. (A) PAN$_{ox}$ and (B) PAN$_{red}$ under an inert N$_2$ atmosphere. (C) and (D) after exposing the reduced PAN to aerated solution and to air, respectively. (b) Schematic of the solution and film processes during the oxidation of Fe(phen)$_3^{2+}$ to Fe(phen)$_3^{3+}$ at a microelectrode positioned above a PAN film initially in its reduced form. The PAN film is oxidized locally by tip-generated Fe(phen)$_3^{3+}$ and the feedback process in solution can be fed by lateral redox process between oxidized and reduced PAN moieties in the film. (c) Cyclic voltammogram (scan rate 50 mV s^{-1}) of a five-layer PAN film deposited on an indium tin oxide electrode.

that the kinetics of PAN$_{red}$ oxidation by Fe(phen)$_3^{3+}$ is likely to be very facile on the SECM time scale. Figure 2a also shows approach curves recorded after exposing the reduced PAN film to air. Evidently, because the film is oxidized, the feedback current changes from positive to negative. It should be noted that all of the effects observed are entirely due to the chemistry of the PAN film, since there is absolutely no contribution to the feedback current from the underlying insulating glass support.
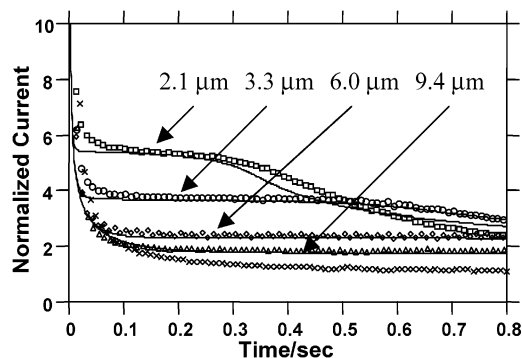
Figure 3. Current−time response of a Pt microelectrode held at different distances above a five-layer PAN film in the reduced state, deposited on glass. The microelectrode potential was stepped from 0.5 to 1.0 V vs SCE to promote the diffusion-limited one-electron oxidation of $Fe(phen)_3^{2+}$ to $Fe(phen)_3^{3+}$. The dotted lines are the experimental results while the continuous lines are the simulations using the model from ref 3. The tip−substrate separations indicated were 2.1 μm (□), 3.3 μm (○), 6.0 μm (◇), and 9.4 μm (△). The bottom curve (×) shows the response with the probe electrode positioned in bulk solution.

To measure lateral charge propagation inside PAN layers, potential step chronoamperometric studies were undertaken in which the tip was first positioned close to the substrate and the potential then stepped from a value of 0.5 V vs SCE, where there were no faradaic processes to 1.0 V to oxidize $Fe(phen)_3^{2+}$ at a diffusion-limited rate. Figure 3 shows the current−time transients acquired at different distances above five layers of PAN_{red}. The exact distance of the microelectrode from the surface was determined from the initial plateau current attained in each transient and comparing it with the theoretical positive feedback current.[31] This was permissible since the reaction between $Fe(phen)_3^{3+}$ and PAN_{red} was rapid. Each transient was carried out at a different location, which was 50 μm away from the previous spot. After a short decay due partly to charging current, the faradaic current in each case drops to a quasi-steady value. However, the current subsequently decreases further after a short time, with a strong distance effect; the closer the distance, the earlier the subsequent drop in the current. This can be explained simply in the following way: $Fe(phen)_3^{3+}$ generated initially at the microelectrode diffuses and reacts with PAN_{red} until the whole area opposing the microelectrode is oxidized. The closer the tip/substrate distance, the quicker this process will be complete. From this point, the regeneration of the mediator is governed by lateral charge propagation inside the PAN. If the flux of the oxidized mediator from the microelectrode is greater than charge propagation in the film, the current will drop. The flux of oxidant from the tip increases (due to feedback) as the distance between the microelectrode and film decreases, which explains the significant distance effect.

Drawing on a recent numerical model for SECM studies of lateral diffusion,[3] the current−time response can be calculated by adjusting six parameters; the distance of the microelectrode from the surface, the bulk concentration of the mediator, its diffusion coefficient, the concentration (mol cm^{-2}) of oxidizable PAN_{red} units on the surface, the rate constant between the mediator and PAN_{red} and the ratio between surface to solution diffusion coefficients. The model takes full account of diffusion of the $Fe(phen)_3^{2+/3+}$ couple in solution and electron hopping inside the PAN film. This is an important point, because Amatore has shown that lateral charge propagation in a related system involves these two processes in a competitive dual-pathway.[17] Our transient experiment and model allows the relative effects of these processes to be readily identified, so that the true rate of lateral charge propagation is measured. The
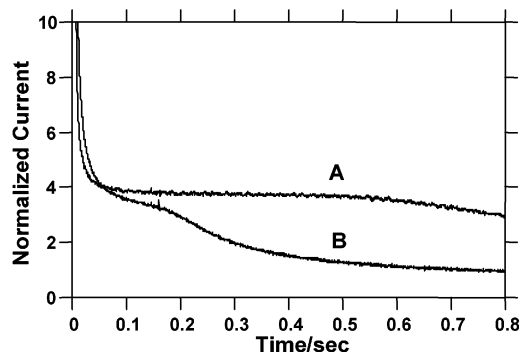

Figure 4. Current−time response of a Pt microelectrode held 3.3 μm above five (A) and three (B) PAN layers deposited on glass. All other parameters are the same as those in Figure 3.

first five parameters mentioned are known or can be derived from other measurements. The diffusion coefficient of $Fe(phen)_3^{3+}$ was estimated ca. 4.3×10^{-6} cm^2 s^{-1} [32] from the steady-state current in bulk solution. The surface concentration of PAN_{red} was calculated from cyclic voltammetry (Figure 2b), by integrating the charge under the oxidation or reduction waves (9.4×10^{-10} mol cm^{-2}). Finally, the rate constant is considered to be fairly large, which limited our simulations to varying the ratio between the surface to solution diffusion coefficients. Figure 3 shows the simulated curves, alongside the experimental data, obtained for all transients by applying identical parameters (except the distance). The best fit was obtained for diffusion-limited ET between $Fe(phen)_3^{3+}$ and PAN_{red}, which corresponded to a rate constant of 0.8 cm s^{-1} or higher and a surface to bulk diffusion coefficient ratio of 1.0. It is worth mentioning that the simulation is very sensitive to the latter parameter, which results in accuracy of approximately ±15% in this measurement.

Obviously, the film thickness, i.e., the number of layers of PAN, has a significant impact on the transients, as it affects the surface concentration of PAN_{red}. This can clearly be seen in Figure 4 where transients, obtained with samples of three and five monolayers of PAN_{red}, are compared. The current−time response of a three-layer PAN film is similar to that obtained with a thicker film; however, the decrease of the steady-state current commences earlier, as would be expected based on the analysis above.

In conclusion, we have shown that the SECM can be used to study lateral charge transfer inside molecular films. It is important to emphasize that the investigation of ultrathin films on a relatively small length scale means that the measured lateral charge propagation is unlikely to be limited by the ingress of ions during the doping process. Moreover, the fact that the PAN units cannot diffuse indicates that the lateral charge transport measurement is entirely due to electron hopping. Under these conditions, the lateral electron diffusion coefficient D_e can be related to the electron self-exchange rate constant k_{ex} in the PAN film:[34]

$$D_e = \theta k_{ex} \delta^2 c \qquad (1)$$

where c is the concentration of charge carriers (1.9×10^{-10} mol cm^{-2} layer^{-1}; 1 layer = 3 nm thick), δ is the donor−acceptor separation in the PAN system (ca. 1 nm based on the measured concentration of charge carriers), and θ depends on the dimensionality of the system (0.25 for the two-dimensional case here). With the measured value of $D_e = 4.3 \times 10^{-6}$ cm^2 s^{-1}, a value of $k_{ex} = 3 \times 10^{12}$ mol^{-1} cm^3 s^{-1} is obtained, which is at the diffusion limit.

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References and Notes

(1) Lyons, M. E. G. *Electroactive Polymer Electrochemistry*; Plenum Press: New York, 1994.

(2) Papageorgiou, N.; Grätzel, M.; Enger, O.; Bonifazi, D.; Diederich, F. *J. Phys. Chem. B* **2002**, *106*, 3813.

(3) Zhang, J.; Slevin, C. J.; Morton, C.; Scott, P.; Walton, D. J.; Unwin, P. R. *J. Phys. Chem. B* **2001**, *105*, 11120.

(4) Forster, R. J.; Keyes, T. E.; Majda, R. *J. Phys. Chem. B* **2000**, *104*, 4425.

(5) Lalchev, Z. I.; Wilde, P. J.; Clark, D. C. *J. Colloid Interface Sci.* **1994**, *167*, 80.

(6) Mohwald, H.; Bliznyuk, V.; Kirstein, S. *Synth. Met.* **1993**, *61*, 91.

(7) Prats, M.; Gabriel, B.; Teissie, J. *J. Am. Chem. Soc.* **1993**, *115*, 10153.

(8) Miller, C. J.; Widrig, C. A.; Charych, D. H.; Majda, M. *J. Phys. Chem.* **1988**, *92*, 1928.

(9) Wittek, M.; Moller, G.; Johnson, M. J.; Majda, M. *Anal. Chem.* **2001**, *73*, 870.

(10) Johnson, A. T.; Bergeron, D. J.; Grason, G.; Chen, X.; Pilloud, D. L.; Smith, W. F.; Dutton, P. L. *Biophys. J.* **2000**, *78*, 1711.

(11) Hicks, J. F.; Zamborini, F. P.; Osisek, A.; Murray, R. W. *J. Am. Chem. Soc.* **2001**, *123*, 7048.

(12) Feldman, B. J.; Feldberg, S. W.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 6558.

(13) Charych, D. H.; Majda, M. *Thin Solid Films* **1992**, *210*, 348.

(14) Goss, C. A.; Majda, M. *J. Electroanal. Chem.* **1991**, *300*, 377.

(15) Lee, W. Y.; Majda, M.; Brezesinski, G.; Wittek, M.; Mobius, D. *J. Phys. Chem. B* **1999**, *103*, 6950.

(16) Feldman, B. J.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 2844.

(17) Amatore, C.; Combellas, C.; Kanoufi, F.; Sella, C.; Thiébault, A.; Thouin, L. *Chem. Eur. J.* **2000**, *6*, 820.

(18) Bonhote, P.; Gogniat, E.; Tingry, S.; Barbe, C.; Vlachopoulos, N.; Lenzmann, F.; Comte, P.; Grätzel, M. *J. Phys. Chem. B* **1998**, *102*, 1498.

(19) Slevin, C. J.; Unwin, P. R. *J. Am. Chem. Soc.* **2000**, *122*, 2597.

(20) Zhang, J.; Unwin, P. R. *J. Am. Chem. Soc.* **2002**, *124*, 2379.

(21) Bard, A. J., Mirkin, M. V., Eds. *Scanning Electrochemical Microscopy*; Marcel Dekker: New York, 2001.

(22) Quinn, B. M.; Prieto, I.; Haram, S. K.; Bard, A. J. *J. Phys. Chem. B* **2001**, *105*, 7474.

(23) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.

(24) Angelopoulos, M. *IBM J. Res. Dev.* **2001**, *45*, 57.

(25) Dhanabalan, A.; Malmonge, J. A.; Riul, A.; Faria, R. M.; Oliveria, O. N. *Thin Solid Films* **1998**, *329*, 808.

(26) Stubb, H.; Punkka, E.; Paloheimo, J. *Mater. Sci. Eng. R—Rep.* **1993**, *10*, 85.

(27) Cheung, J. H.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 990.

(28) Reitzel, N.; Greve, D. R.; Kjaer, K.; Hows, P. B.; Jayaraman, M.; Savoy, S.; Mccullough, R. D.; Mcdevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788.

(29) 0.2 mg mL^{-1} of PAN was mixed with 0.38 mg mL^{-1} of DBSA in a mixture of 90% chloroform and 10% *m*-cresol v/v. Between 150 and 200 μL was spread over a 1 mM HCl aqueous subphase. The Langmuir trough (500 cm^2 maximum surface area) (Nima, UK) was left for 30 min before the monolayer was compressed at a speed of 25 cm^2 min^{-1} until a surface pressure of 20 mN m^{-1} was reached. Films were deposited on clean glass as Y-type (upward deposition) under constant pressure of 20 mN.m^{-1}, with a dipping speed of 5 mm min^{-1}. The time interval between the first and the second monolayer was 10 min while the interval between the following monolayers was always 1 min.

(30) Moon, D. K.; Ezuka, M.; Maruyama, T.; Osakada, K.; Yamamoto, T. *Makromol. Chem.—Macromol. Chem. Phys.* **1993**, *194*, 3149.

(31) Moon, D. K.; Ezuka, M.; Maruyama, T.; Osakada, K.; Yamamoto, T. *Macromolecules* **1993**, *26*, 364.

(32) Kwak, J.; Bard, A. J. *Anal. Chem.* **1989**, *61*, 1221.

(33) Tominaga, T.; Matsumoto, S.; Koshiba, T.; Yamamoto, Y. *J. Chem. Soc., Faraday Trans. I* **1988**, *84*, 4261.

(34) Dahms, H. J. *J. Phys. Chem.* **1968**, *72*, 362. Ruff, I.; Friedrich, V. J. *J. Phys. Chem.* **1971**, *75*, 3297. Ruff, I.; Friedrich, V. J.; Demeter, K.; Csillag, K. *J. Phys. Chem. B* **1971**, *75*, 3303. Murray, R. W. *Philos. Trans. R. Soc. London* **1981**, *A302*, 253. Andrieux, C. P.; Savéant, J.-M. *J. Electroanal. Chem.* **1980**, *111*, 377.