Reinterpretation of Polypyrrole Electrochemistry. Consideration of Capacitive Currents in Redox Switching of Conducting Polymers

Stephen W. Feldberg

Contribution from the Department of Applied Science, Division of Chemical Sciences, Brookhaven National Laboratory, Upton, New York 11973. *Received June 29, 1983*

Abstract: A simple analysis of the capacitive currents associated with the electrochemical (cyclic voltammetric) switching of a polypyrrole film between its reduced (insulating) and oxidized (electronically conducting) states offers a reasonably precise description of the form of the voltammogram. The theory demonstrates that a unique value for the faradaic component of the switching current cannot be extracted from the cyclic voltammetric data. Thus the number of electrons per pyrrole, γ, required for switching cannot be uniquely determined. Reported results of gaseous oxidation of a pyrrole film (by O_2, $FeCl_3$, or I_2) which produces optical and conductance changes comparable to those observed during electrochemical switching also indicate a comparable degree of oxidation (determined by % weight uptake of the oxidant). Here too, irresolvable faradaic and capacitive electron-transfer components render γ indeterminate. The same analysis resolves the seemingly anomalous cyclic voltammetric behavior of polythiophene (another electrochemically switched polymer) and in principle is applicable to any polymer or film which can be electrochemically switched from an insulating to an electronically conducting state.

Switching polypyrrole from its reduced (insulating) state to its oxidized (electronically conducting) state simplistically involves the removal of electrons from a delocalized π-system, and Street and co-workers[1-3] have suggested that conductance is due to the movement of polarons and bipolarons (a polaron is a radical cation and the associated local modifications in the geometry of the polypyrrole chain). The formulation of any theory for the conduction mechanism requires information about the number of electrons required for the switching process (along with other physical-chemical properties). Myriad electrochemical[4-7] and chemical studies[1,8-10] suggest that complete switching is achieved when ~0.3 electron per pyrrole has been removed from the neutral polypyrrole. I shall demonstrate that the value of 0.3 may include significant capacitive charging and that the true value of γ (=electrons per pyrrole *required for switching*) cannot be deduced from simple electrochemical experiments (e.g., cyclic voltammetry)[4,5,7] or gaseous oxidations.[1,8-10] The difficulty derives from the inseparability of faradaic and capacitive current components.

A cyclic voltammogram of polypyrrole (Figure 1)[4] approximates behavior of a quasi-reversible couple with the distinguishing characteristic of large capacitive currents once oxidation is complete. Bull, Fan, and Bard[7] measured ac capacitance and resistance during cyclic voltammetric switching. Their data suggest that oxidized polypyrrole is effectively a porous metal[11] electrode with a high surface to volume ratio and a large double layer capacitance proportional to the amount of oxidized film on the surface of a substrate platinum electrode. Their data show that changes in differential capacitance do follow the switching and suggest further that the differential capacitance per unit area of oxidized polypyrrole is constant, even when the film is partially oxidized. The possibility that the potential region 0.2–0.4 V (Figure 1) is not exhibiting capacitive behavior but is the manifestation of an unusual redox process or combination of redox processes is countered by optical data[12] which indicate that the optical changes associated with switching occur primarily in the potential region −0.3 to +0.2 V.

In the present paper I develop a simple analysis of the capacitive and faradaic currents associated with the electrochemical (cyclic voltammetric) switching of a film between its insulating and electronically conducting states. The analysis will demonstrate that cyclic voltammetric data alone (or gaseous oxidation data alone) do not permit the separation of the faradaic and capacitive current components. The same analysis will be shown to resolve the seemingly anomalous cyclic voltammetric behavior of polythiophene[13] (another electrochemically switching polymer) and in principle is applicable to any other polymer (e.g., ref 14–20)

---

(1) Scott, J. C.; Pfluger, P.; Krounbi, M. T.; Street, G. B. *Phys. Rev. B.* **1983**, *28*, 2140.

(2) Scott, J. C.; Bredas, J. L.; Yakushi, K.; Pfluger, P.; Street, G. B. *Synth. Metals* **1984**, in press.

(3) Bredas, J. L.; Scott, J. C.; Yakushi, K.; Street, G. B. *Phys. Rev. Lett.* **1984**, in press.

(4) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115-132 and references therein.

(5) Diaz, A. F.; Kanazawa, K. K. "Extended Linear Chain Compounds"; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, p 437.

(6) Genies, E. M.; Bidan, G.; Diaz, A. F.; *J. Electroanal. Chem.* **1983**, *149*, 101-113.

(7) Bull, R. A.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1982**, *129*, 1009-1015.

(8) Pfluger, P.; Krounbi, M.; Street, G. B.; Weiser, G. *J. Chem. Phys.* **1983**, *78*, 3212.

(9) Street, G. B.; Clarke, T. C.; Krounbi, M.; Kanazawa, K. K.; Lee, V.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253-264.

(10) Gaseous oxidation of dry, reduced polypyrrole, by O_2, $FeCl_3$, or I_2,[1,8,9] produces conductance and optical changes for a given level of oxidation (as measured by uptakes of oxidant) qualitatively comparable to those observed during electrochemical oxidation. The maximum uptake (of iodine) corresponds to the removal of about 0.3 electron per pyrrole unit.[9]

(11) It is probably not strictly correct to refer to the oxidized polypyrrole as a metal, and Scott et al.[1] have proposed a semiconductor band model for the oxidized polypyrrole. Nevertheless, the high conductivity ($>10^{-2}\ \Omega^{-1}\ cm^{-1}$) of the oxidized polypyrrole makes it reasonable to contend that it may be a degenerate semiconductor. A simple computation demonstrates that unless it is very much like a metal the observed capacitive currents would not be possible. The data of Diaz et al. (see Figure 1)[4] or Bull et al.[7] indicate that the differential capacitance per unit volume, C_v, of an oxidized polypyrrole film is ~100 farads/cm³. Assuming a conducting rod-shaped fibril or radius r the surface to volume ratio if $2/r$. If the fibril is behaving like a metal the differential capacitance, C_d, will be ~2 × 10⁻⁵ farads/cm². Then

$$r = 2C_d/C_v \sim 4 \times 10^{-7}\ \text{cm}$$

The greatly diminished value of C_d that might be associated with a semiconductor would require an unreasonably small value of r in order to effect the large capacitance that is observed.

(12) (a) Yakushi, K.; Lauchlan, T. J.; Clarke, T. C.; Street, G. B. *J. Chem. Phys.* **1984**, in press. (b) Street, G. B. private communication. (c) Skotheim, T., private communication.

(13) Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459-1463.

(14) Diaz, A. F.; Martinez, A.; Kanazawa, K. K. *J. Electroanal. Chem.* **1981**, *130*, 181-187.

(15) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *111*, 111-114.

(16) Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J. C. *J. Electroanal. Chem.* **1983**, *148*, 299-303.

(17) Diaz, A. F.; Clarke, T. C. *J. Electroanal. Chem.* **1980**, *111*, 115-117.

(18) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173-178.

(19) Diaz, A. F.; Castillo, J.; Kanazawa, K. K.; Logan, J. A. *J. Electroanal. Chem.* **1982**, *133*, 233-239.

0002-7863/84/1506-4671$01.50/0

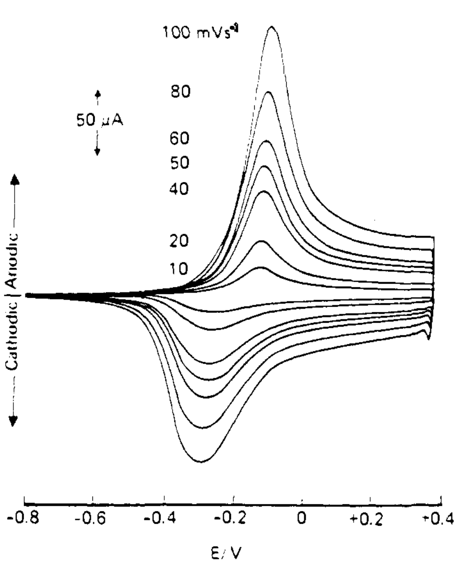

Figure 1. Cyclic voltammograms of [Pt]polypyrrole-BF_4 (20 nm thick) in 0.1 M Et_4NBF_4/CH_3CN solution. Electrode area = 0.5 cm^2. (Reprinted with permission from ref 4. Copyright 1981 Elsevier Publishing Co., Lausanne, Switzerland.)

or film which can be electrochemically switched from an insulating to an electronically conducting state.

Theory and Discussion

Three basic assumptions are made. (1) The differential capacitance is proportional to the amount of oxidized polypyrrole. (2) The differential capacitance of the oxidized polypyrrole is independent of potential. (3) The differential capacitance of the platinum electrode is ignorably small. All these assumptions are supported by the observations of Bull et al.[7] (see previous discussion). Assumptions 1 and 2 are undoubtedly oversimplifications.

Consider a platinum electrode with a polypyrrole film. The capacitive charge density required to form the nascent electrical double layer will be

$$Q_{C,E} = a(E - E_{pzc})Q_{s,E} \tag{1}$$

where a is a constant (V^{-1}) assumed to be independent of potential, E is the electrode potential, E_{pzc} is the potential of the point of zero charge[21] (both potentials measured vs. an appropriate reference electrode), and $Q_{s,E}$ is the coulombs of oxidized polypyrrole per unit area. Equation 1 is a manifestation of the three basic assumptions, as is clearly shown by differentiation of eq 1 with respect to E (assuming for the moment only that $dQ_{s,E}/dE = 0$) to give the differential capacitance

$$C_d = dQ_{c,E}/dE = aQ_{s,E} \tag{2}$$

This equation will be valid if, for example, the faradaic process associated with switching does not follow an ac perturbation. The general analysis, however, requires not only consideration of the change in $Q_{s,E}$ but also the faradaic charge required to effect that change. The total charge density, $Q_{T,E}$, associated with both the faradaic and capacitive processes is

$$Q_{T,E} = Q_{C,E} + Q_{s,E} = Q_{s,E}[a(E - E_{pzc}) + 1] \tag{3}$$

For cyclic voltammetry, where $dE/dt = v$ (a constant), the total current density, $i_{T,E}$, is simply

$$i_{T,E} = dQ_{T,E}/dt = a[i_{s,E}(E - E_{pzc} + a^{-1}) + vQ_{s,E}] \tag{4}$$

where $i_{s,E}$, the faradaic current density required for switching, is

$$i_{s,E} = dQ_{s,E}/dt \tag{5}$$

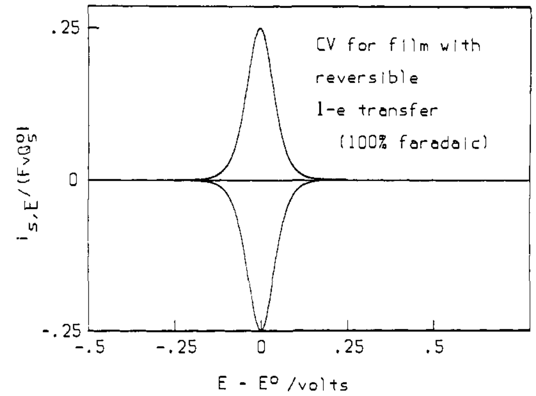

Figure 2. Theoretical cyclic voltammogram showing normalized faradaic current for a Nernstian, reversible, 1-e transfer computed from eq 14 and 15 (T v 25 °C).

An important property of eq 4 is immediately apparent and intuitively expected: at a sufficiently positive potential, E_a, when the maximal quantity of oxidized polymer, Q_s°, has been formed, and therefore $i_{s,E} = 0$ since $dQ_s^\circ/dt = 0$ (see eq 5), eq 4 becomes

$$i_{T,E_a} = avQ_s^\circ \tag{6}$$

$$i_{s,E_a} = 0$$

The current is then due entirely to capacitive charging (see Figure 1, for example; note the behavior at potential $> \sim 0.2$ V).

The term $E - E_{pzc} + a^{-1}$ (eq 4) can be rewritten

$$E - E_{pzc} + a^{-1} = E - E^\circ - (E_{pzc} - E^\circ - a^{-1}) \tag{7}$$

The variables E and E_{pzc} are thus referenced to the E° for the switching reaction and may be defined

$$\Delta E = E - E^\circ \tag{8}$$

and

$$\Delta E^* = E_{pzc} - E^\circ - a^{-1} \tag{9}$$

The charge density, Q_f°, required for formation of the oxidized pyrrole film from the pyrrole monomer is experimentally known and corresponds to $(2 + \gamma)$ electrons per pyrrole, where γ is the number of electrons per pyrrole required for switching. Thus

$$\gamma = 2/(Q_f^\circ/|Q_s^\circ| - 1) \underset{\gamma \to 0}{\simeq} 2|Q_s^\circ|/Q_f^\circ \tag{10}$$

The behavior of eq 4 is best demonstrated by assuming that the redox process is a simple reversible one-electron transfer.[22] To simplify the data presentation eq 4 is rearranged into dimensionless groupings:

$$\frac{i_{T,E}}{avQ_s^\circ} = \frac{i_{s,E}(\Delta E - \Delta E^*)}{vQ_s^\circ} + \frac{Q_{s,E}}{Q_s^\circ} \tag{11}$$

For a reversible one-electron transfer[23,24]

$$i_{s,E} = \frac{FvQ_s^\circ \exp[F\Delta E/RT]}{RT(1 + \exp[F\Delta E/RT])^2} \tag{12}$$

and

$$Q_{s,E} = \frac{Q_s^\circ \exp[F\Delta E/RT]}{1 + \exp[F\Delta E/RT]} \tag{13}$$

For reference, a reversible cyclic voltammogram for a simple

---

[20] Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelmann, H.; Kaplan, S.; Harbour, J.; Yang, X.-Q.; Tanner, D. B.; Pochan, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4417–4431.

[21] Delahay, P. "Double Layer and Electrode Kinetics"; Interscience: New York, 1965; p 23 ff, p 126 ff.

[22] Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248–4253.

[23] Bard, A. J.; Faulkner, L. R. "Electrochemical Methods: Fundamentals and Applications"; Wiley: New York, 1981; pp 521–525.

[24] To be consistent with most experimental presentations anodic currents are defined as positive and cathodic currents as negative, contrary to traditional electroanalytical practice.

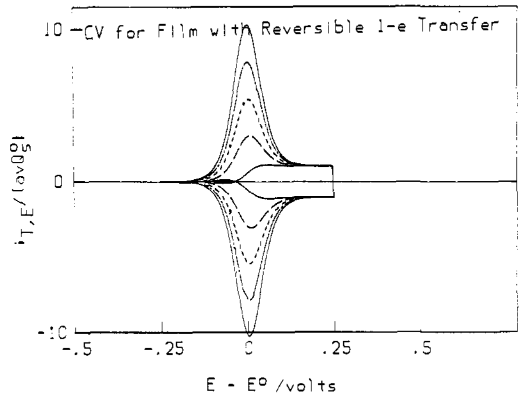

Figure 3. Theoretical cyclic voltammograms showing the mixed (normalized) faradaic, capacitive currents for a Nernstian, reversible electron transfer computed from eq 15–17 (T = 25 °C) with ΔE^* (see eq 9) = −1.0 V (—), −0.75 V (— - — -), −0.5 V (———), −0.25 V (— — —), and 0.0 V (···).

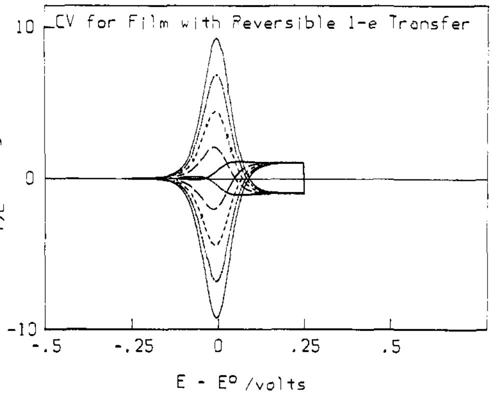

Figure 4. Everything the same as for Figure 3 but corresponding values of ΔE^* are positive.

reversible redox film (i.e., no capacitive current) is computed from a dimensionless form of eq 12 (Figure 2):

$$\frac{RTi_{s,E}}{FvQ_s°} = \frac{e^{\Delta u}}{(1 + e^{\Delta u})^2} \tag{14}$$

where

$$\Delta u = F\Delta E/RT \tag{15}$$

The general equation (including capacitance effects) is obtained by combining eq 11–15 to give

$$\frac{i_{T,E}}{avQ_s°} = \frac{(\Delta u - \Delta u^*)e^{\Delta u}}{(1 + e^{\Delta u})^2} + \frac{e^{\Delta u}}{1 + e^{\Delta u}} \tag{16}$$

where

$$\Delta u^* = F\Delta E^*/RT \tag{17}$$

Voltammograms are computed from eq 16 for several *negative* values of ΔE^* (Figure 3) and for several *positive* values of ΔE^* (Figure 4). Note that when $\Delta E^* > 0$ the currents are inverted, exhibiting cathodic current peaks during the positive potential sweep and anodic current peaks during the negative potential sweep. Note also that in all examples (Figures 3 and 4) once $E - E° >$ ~0.2 V the expected constant capacitive current is observed (eq 6).

The value of ΔE^* may be estimated from a cyclic voltammogram without knowing the functional dependence of $i_{s,E}$. Assume that a cyclic voltammogram can be scanned to a potential, E_a, which is sufficiently positive of the anodic peak so that eq 6 obtains. Then, at potential E_a, eq 3 becomes

$$Q_{T,E_a} = aQ_s°(E_a - E_{pzc} + a^{-1}) = aQ_s°\lambda \tag{18}$$

where

$$\lambda = E_a - E_{pzc} + a^{-1} = Q_{T,E_a}/aQ_s° \tag{19}$$

With eq 6 one then obtains

$$\lambda = vQ_{T,E_a}/(i_{T,E_a}) \tag{20}$$

Q_{T,E_a} is obtained by integration of the anodic or cathodic portion of an experimental cyclic voltammogram. Thus, $Q_s°$ and therefore γ (eq 10) can be determined only if a or E_{pzc} can be determined. Determination of the E_{pzc} of a solid electrode is difficult.[25] Problems such as specific ion adsorption[26] can lead to an incorrect evaluation of E_{pzc} and may be responsible for some of the observed anomalies induced by different electrolytes.[4] It is possible that $Q_s°$ might be estimated directly from some other physical measurements, e.g., EPR, but the interpretation of the EPR data for polypyrrole has proved difficult.[1-3] The very low intensity of the signals is explained by the existence of bipolarons, but a contributing factor may be that $Q_s°$ is very small (i.e., $\gamma \ll 0.3$). It is worth noting that in principle the value of $Q_s°$ or γ can be infinitesimal, corresponding to $a^{-1} \rightarrow 0$ (see eq 18). Interestingly, if such a condition obtains the value of E_{pzc} is directly calculable from eq 19.[27]

Interpretation of Existing Data for Polypyrrole and Polythiophene

Cyclic voltammetric data for a polypyrrole film lead to an evaluation of λ (eq 20) and therefore of $E_{pzc} - a^{-1}$ since E_a is an experimental known. The data for a cyclic voltammogram (Figure 1, for v = 0.1 V/s) are as follows: E_a = 0.37 V (vs. SCE), $Q_{T,E_a} = -1.04 \times 10^{-3}$ C/cm^2 (for the cathodic scan),[28] $i_{T,E_a} = -7.4 \times 10^{-5}$ A/cm^2,[29] and $Q_f° = 8.0 \times 10^{-3}$ C/cm^2.[3] This leads directly to λ = 1.41 V. With eq 19 one obtains $E_{pzc} - a^{-1} = E_a - \lambda = -1.04$ V. If $a^{-1} = 0$ then $E_{pzc} = -1.04$ V, a minimum value. There is in principle no maximum value for E_{pzc}. It is interesting to note, however, that if one were to assume that $\gamma \sim 0.25$ (the presently accepted, but not necessarily correct, value; see, for example, ref 4) one deduces from eq 10 and 6 that $a \sim 0.46$ and from eq 20 that $E_{pzc} \sim -0.58$ V.

As pointed out in ref 10, electrochemical and gaseous oxidations of polypyrrole seem to produce qualitatively similar conductances and optical changes for comparable degrees of oxidation. There is certainly less ambiguity at maximal oxidation where both methods indicate the removal of ~0.3 electron per pyrrole. This still does not mean that $\gamma \sim 0.3$ since the concept of capacitive charging described for the electrochemical system should also apply to gaseous oxidation. The dielectric constant of vacuum (the "solvent" for I_2 oxidation) will certainly be lower than the dielectric constant of acetonitrile or whatever solvent is used with electrochemical switching, thereby diminishing the differential capacitance of a compact layer of adsorbed counterions. However, the value of E_{pzc} may also be different and that can modify the uptake of gaseous oxidant. At high levels of doping obtained with I_2 the absorbed I_3^- may participate in the conductive mechanism. Direct comparison is further complicated by the ambiguity of the

---

[25] Frumkin, A. N.; Petrii, O. A.; Damaskin, B. B. "Comprehensive Treatise of Electrochemistry"; Bockris, J. O'M., Conway, B. E., Yeager, E., Eds.; Plenum Press: New York, 1980; Vol. 1, pp 221–290.

[26] (a) Delahay, P. "Double Layer and Electrode Kinetics"; Interscience: New York, 1965; p 53 ff. (b) Habib, M. A.; Bockris, J. O'M. In ref 25; pp 135–220.

[27] For the reader who may be bothered that one can educe the value of the E_{pzc} for a solid electrode from cyclic voltammetric data I point out the unique aspect of the electrochemically switched film: as it is oxidized it is a growing (electrochemically generated) capacitance. The system is thus analagous to the classical dropping mercury electrode (DME) where the E_{pzc} (in the absence of redox processes) is easily determined by noting the potential where there is no residual current associated with the drop growth. See, for example: Kolthoff, I. M.; Lingane, J. J. "Polarography", 2nd ed.; Interscience: New York, 1952; Vol. I, p 144 ff.

[28] Note that the total current is integrated; thus $Q_{T,E}$ will be larger than the value reported by Diaz.[4] $Q_{T,E_a} = 1.18 \times 10^{-3}$ C/cm^2 for the anodic scan (compared to -1.04×10^{-3} C/cm^2 for the cathodic scan). This inequality of the numerical values of Q_{T,E_a} probably indicates some background oxidation occurring in the region of E_a. I shall assume that the cathodic value is the more accurate.

[29] The value for i_{T,E_a}, assumed to be a purely capacitive current, is estimated by halving the difference between the anodic and cathodic currents at E_a.

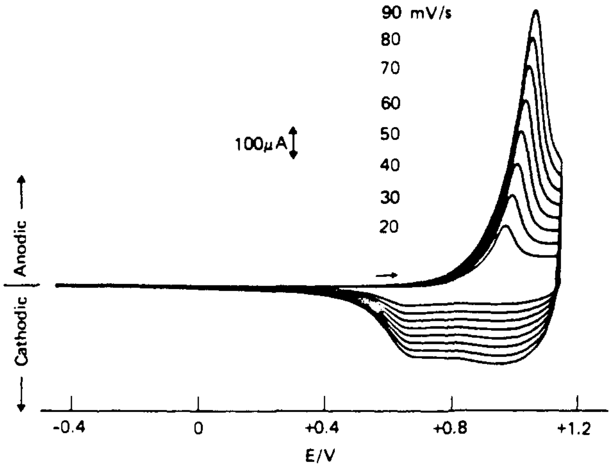

Figure 5. Cyclic voltammograms of [Pt]polythiophene-BF_4 film (60 nm thick) in 0.1 M Et_4NBF_4/CH_3CN solution. (Reprinted with permission from ref 13. Copyright 1983 American Chemical Society.)

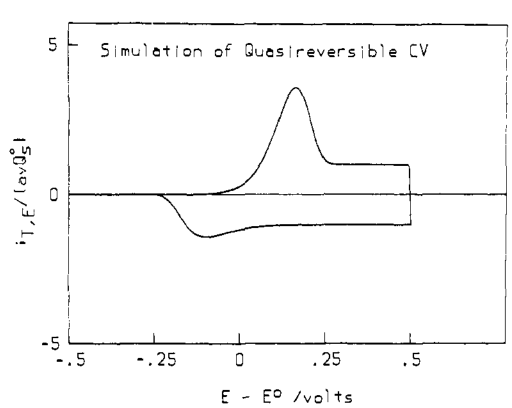

Figure 6. Theoretical cyclic voltammogram for quasi-reversible electron transfer from eq 11 and 24 with $k^* = k°/(vF/RT) = 0.005$, $\alpha = 0.5$, $\Delta E^* = -0.25$ V, and $T = 25$ °C.

potential (corresponding to an $E°$) of the gaseous oxidant. Nevertheless it may be possible to obtain informative differences (between electrochemical and gaseous oxidations) if enough experimental detail were available.

The unusual form of the cyclic voltammograms of polythiophene (Figure 5)[13] is easily explained when the capacitive currents are properly considered. The virtually flat cathodic wave suggests that the electrochemical switching (from the oxidized, conducting state to the reduced, insulating state) occurs in the vicinity where $\Delta E^* = 0$ (see Figure 3 or 4). The faradaic current, $i_{s,E}$, can be redefined according to the general equation for a quasi-reversible electron transfer[23,24]

$$i_{s,E} = k°((Q_s° - Q_{s,E}) \exp[(1-\alpha)F(E - E°)/RT] - Q_{s,E} \exp[-\alpha F(E - E°)/RT]) \quad (21)$$

where $k°$ is the rate constant for electron transfer (note units are s^{-1}) and α is the transfer coefficient. When eq 11 and 17 (the value of $Q_{s,E}$ must be obtained by numerical integration) are combined a theoretical cyclic voltammogram was computed for $k^* = k°/(vF/RT) = 0.005$, $\alpha = 0.5$, and $\Delta E^* = -0.25$ V (Figure 6). Its form is remarkably similar to the experimental cyclic voltammogram for polythiophene ($v = 0.02$ V/s, Figure 5). Exact fitting was not attempted since the experimental voltammograms include significant background current when $E > 0.8$ V. As with polypyrrole the values of a, γ, or E_{pzc} cannot be deduced without additional physical-chemical data.

The analagous simulation does not work well for polypyrrole since both the anodic and cathodic peaks (Figure 1) are too broad to be explained by the simple equation for quasi-reversible electron transfer (eq 24).[23,30]

Conclusions

The primary objective of this paper has been to demonstrate some subtleties in the interpretation of the electrochemistry of an electrochemically switched polymer film. Under certain conditions, when the capacitance of a conducting film is very small, the faradaic current may be assumed to dominate, and the faradaic stoichiometry can be established. In the case of cyclic voltammetry of polypyrrole, however, the faradaic and capacitive current components cannot be separated without additional physical-chemical information (e.g., EPR[1-3] or a determination of E_{pzc}). Thus the value of γ (electrons per pyrrole *required for switching* the film from the insulating to the conducting state) remains unknown.

I did not attempt to extract electrokinetic data, although the computation of cyclic voltammogram of polythiophene looked reasonable. The broad peaks of the polypyrrole remain enigmatic. It has been suggested that counterions diffuse into and out of the film.[6] This could cause the broadening. Interestingly, the differential capacitance data and conductance data of Bull et al.[7] (their Figure 3) obtained during a slow (0.005 V/s) cyclic voltammetric scan seem to exhibit much less hysteresis than is exhibited in Figure 1 and could be evidence against diffusion. It is also possible that there may be an array of redox domains with each domain associated with its own $E°$. In spite of the freedom such a model affords, with variables $E_j°$, α_j, $k_j°$, and $Q_{s,j}°$ for j domains, there is some (but not much) constraint in that the same set of equations must generate the proper shape for both the anodic and cathodic voltammograms.

The present theory invokes a number of simplifications such as the presumption that the differential capacitance is constant. Perhaps ac impedance measurements[7,31] (under fortuitous conditions, e.g., electron transfer that is too slow to follow the ac perturbation, and adequately small iR drop within the film or in the electrolyte) can more precisely characterize differential capacitance as a function of potential. Such details could be built into the theory.

Acknowledgment. S.W.F. thanks T. Skotheim, A. F. Diaz, K. Kanazawa, and G. B. Street for valuable stimulating discussions and A. F. Diaz and G. B. Street for preprints prior to publication. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, under Contract No. DE-AC02-CH00016.

Registry No. Polypyrrole (homopolymer), 30604-81-0; polythiophene (homopolymer), 25233-34-5.

---

(30) For an irreversible cyclic voltammograms (without capacitive current) the width of half height, $\Delta E_{p/2}$, is $0.0625/(1-\alpha)$ V for the anodic peak and $0.0625/\alpha$ V for the cathodic peak. The value of $\Delta E_{p/2}$ for a reversible cyclic voltammogram (without capacitive current) is 0.0906 V. A one-electron transfer is assumed in both cases.[22]

(31) Reference 23, pp 316–369.