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Electrochemical Impedance Analysis of Polyaniline Films on Electrodes

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ABSTRACT

The ac response of polyaniline films on Pt electrodes in 2.0M HCl was measured at different applied dc potentials, varied in the positive and negative directions. Experimental complex capacitance plots were reproduced using a computer simulation program based upon the equivalent circuit approach. With 150 nm films the complex capacitance plots at +0.55V (vs. SCE) comprise a single capacitive element, which develops at more negative potentials into a parallel combination of two discrete elements C_1 (a capacitor) and Z_D (a finite transmission line) in series with a polymer resistance R_p . C_1 and Z_D are interpreted as double-layer and faradaic (diffusion-controlled) components. The hysteresis observed in the voltammetric behavior of polyaniline is evident in the potential-dependence of R_p , C_1 , and Z_D , obtained under constant-potential conditions.

Certain organic polymers, particularly conjugated polymers, become electronically conducting when oxidized or reduced chemically or electrochemically (1). Such polymers are the focus of considerable current attention because of the fundamental interest in their chemistry and physics, as well as in their potential application in batteries (2), solar energy conversion (3), electrochromic devices (4), electrocatalysis (5), and electronics (6). The electrochemical behavior of these systems is of substantial importance since, (i) some of the most widely investigated conducting polymers are commonly synthesized electrochemically, e.g. polypyrrole (7), polythiophene (8), polyphenylene (9), and polyaniline (4); (ii) most of the applications mentioned above take advantage of electrochemical switching, which can effect the transition between a neutral insulating form and an oxidized (or reduced) electronically conducting form.

Most of the electrochemical information on conducting polymers has been obtained from dc experiments, notably cyclic voltammetry (other than charging/discharging experiments for battery applications). The polymers display a characteristic voltammetric behavior, which involves a marked apparently time-independent hysteresis of the switching process, remarkably similar for different polymers, e.g. polyaniline (4), polyphenylene (9), polypyrrole (7), and polyacetylene (10). A model which explains this peculiar and ubiquitous behavior has been developed, based upon N-shaped free energy curves (11). An excellent example of such behavior is polyaniline (4, 12). A typical voltammogram of polyaniline includes characteristic oxidation/reduction peaks, a region of very low currents below ≈ -0.2 V (vs. SCE) where the polymer is an insulator, and an apparently capacitive region above $\approx +0.4$ V, where the polymer is highly conducting. It has been suggested (13) that voltammetric switching curves reflect some combination of faradaic and capacitive charging processes. Cyclic voltammetry, however, has not provided much insight into the different processes occurring upon electrochemical switching of such polymers.

In the present publication we wish to report a study of the ac-impedance behavior of polyaniline films on electrodes. Glarum and Marshall (14) recently published data on the impedance behavior of polyaniline; they observed a major capacitive element in the complex admittance plot at different potentials, and concentrated on the deterioration of the properties at high positive overpotentials.¹ In the present work we analyze the various circuit

elements which are apparent in the complex capacitance plots of polyaniline at intermediate frequencies. The dc bias was restricted to the voltage range of the first oxidation peak, where the polymer is stable towards voltage cycling.

Experimental

Chemicals.—Aniline (Fluka, puriss.) was distilled at reduced pressure and kept refrigerated under argon. Hydrochloric acid (Frutarom, Analytical, 32%) was used as received. All solutions were prepared with triply-distilled water, and deaerated by passing argon.

Cell and electrodes.—We used the experimental setup described previously (15). The working electrode was a Pt disk sealed in soda glass (15), the geometric area of the Pt being 0.02 cm². The reference electrode was a KCl-saturated calomel electrode (SCE).

Instrumentation.—AC as well as dc measurements were performed using a Solartron Model 1286 potentiostat and a Solartron Model 1250 frequency response analyzer. The impedance was measured at seven discrete frequencies per decade, from 0.1 Hz to 65 kHz, at an amplitude of 5 mV (rms).

Results

Polyaniline films on Pt electrodes were deposited from a solution containing 1.0M aniline and 2.0M HCl (4). The deposition was performed by cycling the potential rather than using a constant current, since it was found that films deposited by cycling display lower background currents and, thus, better insulating properties at the negative end of the voltage span. Figure 1a shows a typical deposition at a scan rate of 0.1 V/s with occasional recording of the current-voltage trace; the polymer is gradually oxidatively deposited above ≈ 0.6 V during each cycle. The first two cycles were extended to +0.8V, then the positive potential limit was lowered to +0.7V, for the rest of the deposition. The process is notably similar to polyphenylene deposition in HF/benzene (9). The resultant voltammetric trace for the polymer is sustained when the coated electrode is transferred to background solution (2.0M HCl), as shown in Fig. 1b. Figure 1b is characteristic of the voltammetric behavior of a large number of conducting polymers, showing a significant voltage separation of the current peaks which is virtually independent of the scan rate, while the peak heights are proportional to the scan rate. This interesting and apparently general behavior is treated elsewhere (11). The thickness of the deposited film was estimated from the published relationship of 8×10^2 C $\cdot$ cm⁻³ for voltammetric switching of the polymer between 0.0-0.55V (16).

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¹The work of Glarum and Marshall was brought to our attention through private communication during the preparation of this manuscript.

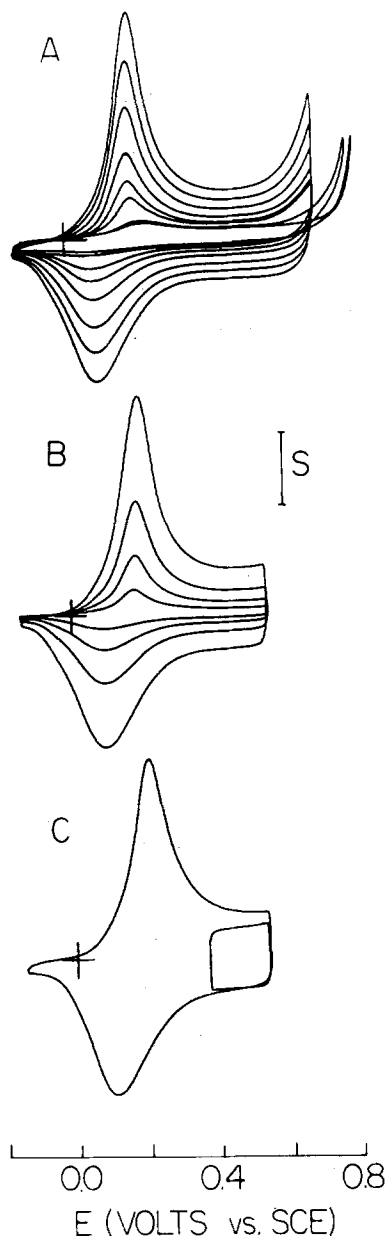


Fig. 1. Cyclic voltammograms for (a) deposition of polyaniline on Pt in 2.0M HCl + 1.0M aniline at 0.10 V/s. Typical deposition time ≈ 15 min, with occasional recording of voltammograms ($s = 40 \mu\text{A}$); (b) ≈ 150 nm polyaniline on Pt, cycled in 2.0M HCl at 0.02, 0.05, 0.10, 0.20 V/s ($s = 80 \mu\text{A}$); (c) same as (b), at 0.10 V/s ($s = 40 \mu\text{A}$).

The ac-impedance measurements were performed by the following procedure: The film was equilibrated in background solution at +0.55V for 10 min, and the ac response in the range 0.1 Hz–65 kHz was measured. The potential was then varied to a more negative value, the system maintained at the new potential for 10 min, and another impedance measurement performed. This procedure was repeated at a number of potentials down to -0.20V . The direction was then reversed, and the same procedure repeated, this time varying the bias potential incrementally in the positive direction, up to +0.55V. Note that in the results reported below, arrows above potential numbers indicate the direction in which the potential was varied to arrive at the specified potential.

Figure 2 presents characteristic complex capacitance plots of ≈ 150 nm polyaniline film on Pt electrode, at various bias potentials. The complex capacitance $\bar{C}$ is defined as $\bar{C} = 1/j\omega\bar{Z}$, where $\bar{Z}$ is the complex impedance and ω is the modulation frequency (17). C' and C'' are the real and imaginary components, respectively. Note that the ac response at +0.55V (the last measurement in a set of experiments) is similar to that initially obtained at the same potential, i.e., there is no irreversible effect ob-

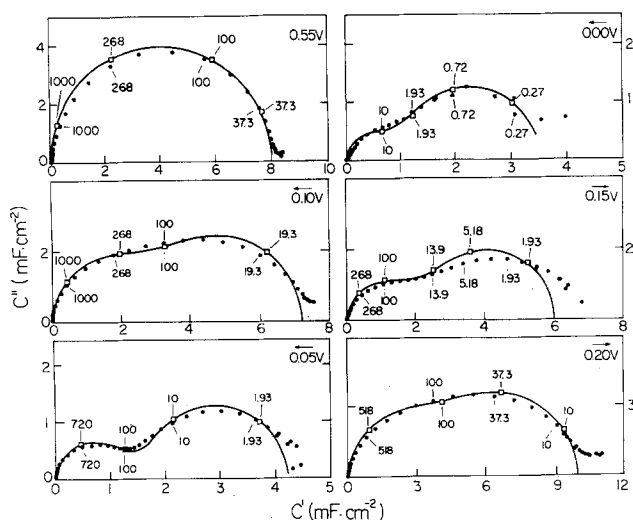


Fig. 2. Complex capacitance plots at indicated bias potentials for ≈ 150 nm polyaniline on Pt in 2.0M HCl. $\bullet\bullet\bullet$ Experimental points; solid lines are simulated curves (see text). Frequencies (in Hz) are indicated for selected experimental ($\bullet$) and simulated ($\square$) points.

served at the end of a complete set of experiments. (Thus, 0.55V in Fig. 2 represents measurements in both directions.)

The complex capacitance presentation was preferred in this case, since it is evident from the capacitance plots (Fig. 2) that the major processes observed in this system are of pronounced capacitive nature. It should be realized, though, that this kind of presentation, in which the measured response is divided by the frequency (see definition of $\bar{C}$), emphasizes intermediate and slow processes, rather than the very high frequency domain.

Although a complete set of experiments included bias potentials down to -0.20V , the ac response at potentials more negative than 0.0 V is not shown in Fig. 2. The reason is that negative of 0.0 V the clear features in the capacitance plots disappear, displaying instead very low currents and spread experimental points due to the dramatic increase in the series resistance following polymer reduction (18).

At positive potentials ($\approx 0.20\text{V}$ in the negative direction or $\approx 0.30\text{V}$ in the positive direction) the complex capacitance plots comprise a single, nearly perfect semicircle, indicative of a simple series combination of a capacitor C_1 of 8.0 to 10.0 $\text{mF} \cdot \text{cm}^{-2}$ and a resistor R_s of $0.12 \Omega \cdot \text{cm}^2$ (see Table I). C_1 is measured as the extrapolated intercept with the real axis at $\omega \rightarrow 0$; R_s is calculated from the frequency at the upper point of the semicircle ω_{max} , according to $\omega_{\text{max}} = 1/R_s C_1$. The same value for the series resistance is also obtained from the extrapolated intercept with the real axis of the complex impedance plot at high frequencies (Fig. 3). Note that the solution resistance calculated from Newman's equation for the access resistance to a disk electrode (19), using $\lambda = 263 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ for 2.0M HCl at 20°C (20), is $0.12 \Omega \cdot \text{cm}^2$. It is, thus, clear that the oxidized polymer behaves from an electrical point of view as a pure capacitor in series with the solution resistance. The polymer resistivity in this potential range is negligible in comparison, as is indeed known from independent measurements (18). The complex capacitance plots at more negative bias potentials develop into two well-defined charging processes, and, thus, a more elaborate equivalent circuit is required in order to quantitatively accommodate the experimental results in the entire potential range.

Figure 2 also presents simulated curves produced using an appropriate computer program (17). It was found that the shape of the experimental capacitance plots at different bias potentials is satisfactorily consistent with the equivalent circuit presented in Fig. 4. Z_D in Fig. 4 is a finite transmission line, the mathematical form of which can be found in, e.g. Ref. (15). This element comprises a repetitive combination of a capacitor C_L and

Table I. Values of the parameters of the equivalent circuit in Fig. 4 used to construct the simulated curves of the type presented in Fig. 2

E V	R_s $\Omega \text{ cm}^2$	R_p $\Omega \text{ cm}^2$	C_1 mF cm^{-2}	C_L mF cm^{-2}	C_i mF cm^{-2}	R_L $\Omega \text{ cm}^2$	l^2/D s	$\sim D$ $\text{cm}^2 \text{ s}^{-1}$
0.55	0.12	0.0			8.0			
0.40	0.12	0.0			8.0			
0.30	0.12	0.0			8.0			
0.20	0.12	0.0			10.0			
0.10	0.12	0.0	3.0	4.2	7.2	0.80	0.01	10^{-8}
0.05	0.12	0.10	1.2	3.0	4.2	11	0.10	10^{-9}
0.00	0.12	7.0	0.7	2.8	3.5	83	0.70	10^{-10}
0.15	0.12	0.5	1.8	4.2	6.0	8.0	0.10	10^{-9}
0.20	0.12	0.0	4.5	5.5	10.0	0.60	0.01	10^{-8}
0.30	0.12	0.0			9.0			
0.40	0.12	0.0			8.0			
0.55	0.12	0.0			8.0			

a resistor R_L , as shown schematically in Fig. 4. C_L is thus the total capacitance associated with the element, measurable at low frequencies, so that $\omega \ll D/l^2$ (where D is a diffusion coefficient and l is a characteristic length). The product $R_L C_L$ satisfies the expression $R_L C_L = l^2/3D$ (15) in the case where the finite transmission line represents a diffusional process. R_s and R_p , which formally comprise a single resistive element, were split in order to maintain a constant value for the solution resistance represented by R_s . Values for the various circuit elements of the equivalent circuit in Fig. 4 were chosen for the simulations, so as to fit both the shape and the frequencies of the different experimental results presented in Fig. 2.

The values used to generate the simulated curves in Fig. 2 at different potentials are summarized in Table I. C_i in Table I is the total low frequency capacitance given by $C_i = C_1 + C_L$; it corresponds to the extrapolated intercept of the simulated curves with the real axis at $\omega \rightarrow 0$. D is a formal diffusion coefficient calculated from l^2/D and taking $l = 150 \text{ nm}$ (the film thickness).

A graphic presentation of the data in Table I, i.e., the variation of R_p , C_1 , C_L , and l^2/D with applied potential, when starting with the conducting or the insulating forms, is given in Fig. 5. Notable features in Table I and Fig. 5 are the following. Both C_1 and C_L increase with a positive shift of the potential, and decrease with a negative shift. R_p is negligible at positive potentials, and becomes predominant when the potential is shifted to more negative values.

l^2/D decreases with increased positive potential. In terms of a diffusion process, D respectively increases; this is also manifested as a considerable respective increase in R_L .

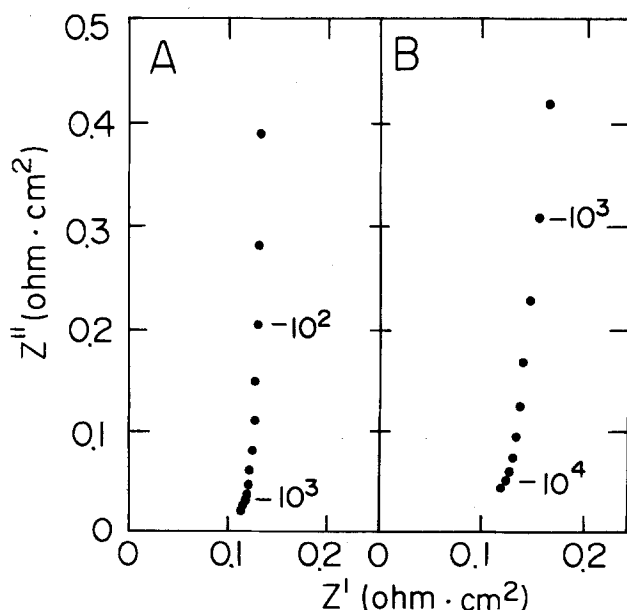


Fig. 3. Complex impedance plots at +0.55V for (a) $\approx 150 \text{ nm}$ and (b) $\approx 15 \text{ nm}$ polyaniline films on Pt in 2.0M HCl. Frequencies (in Hz) are indicated.

At positive enough potentials where the two charging processes converge into a single semicircle in the capacitance plot (and thus no values for C_1 and C_L are given in Table I), the two circuit elements cannot be resolved on the basis of the ac results alone. In other words, the kind of combination of the two processes which produces the observed total capacitance in the pure capacitive region remains an open question. It should be realized with respect to Z_D that for a small enough l^2/D (e.g., large D) the element may behave as a pure capacitor in the measured frequency range.

C_i goes through a maximum around 0.20V, where its magnitude is greater than the constant value of 8.0 mF cm^{-2} observed at more positive potentials. The maxima of C_i are observed in the vicinity of the voltammetric current maxima.

The steep variations in all the parameters coincide in both the positive and negative directions, with the oxidation and reduction of the polymer, respectively. Thus, the hysteresis observed in the voltammetric behavior of polyaniline (i.e., the apparently scan-rate independent peak separation) is clearly observed under constant-potential conditions, as well.

It is of interest to compare at this point the capacitance value of 8.0 mF cm^{-2} obtained from the ac response at positive potentials (the "capacitive" region, above $\approx 0.4\text{V}$) to the capacitance in the same potential range calculated from cyclic voltammetry (Fig. 1), assuming that the nearly flat voltammetric response represents pure capacitive currents. A straightforward calculation using the relationship $i_c = C_i v$ (where v is the scan rate) yields 10 mF cm^{-2} for the apparent voltammetric capacitance. To resolve the discrepancy between the two numbers, we recorded a "capacitance box" in the range 0.4-0.55V, as shown in Fig. 1c. The value obtained from the voltammetric box is indeed 8.0 mF cm^{-2} , in agreement with the ac results. It is thus evident that in the "capacitive region" the anodic voltammetric current includes a non-capacitive contribution amounting to about 20% of the measured current.

We also performed experiments similar to those described above, with thinner polyaniline films of $\approx 15 \text{ nm}$.

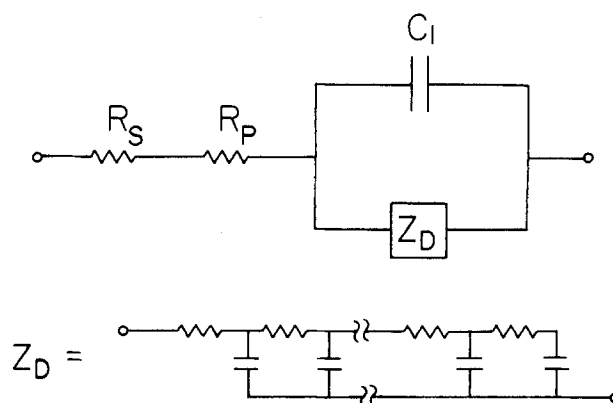


Fig. 4. The equivalent circuit used to obtain the simulated curves in Fig. 2.

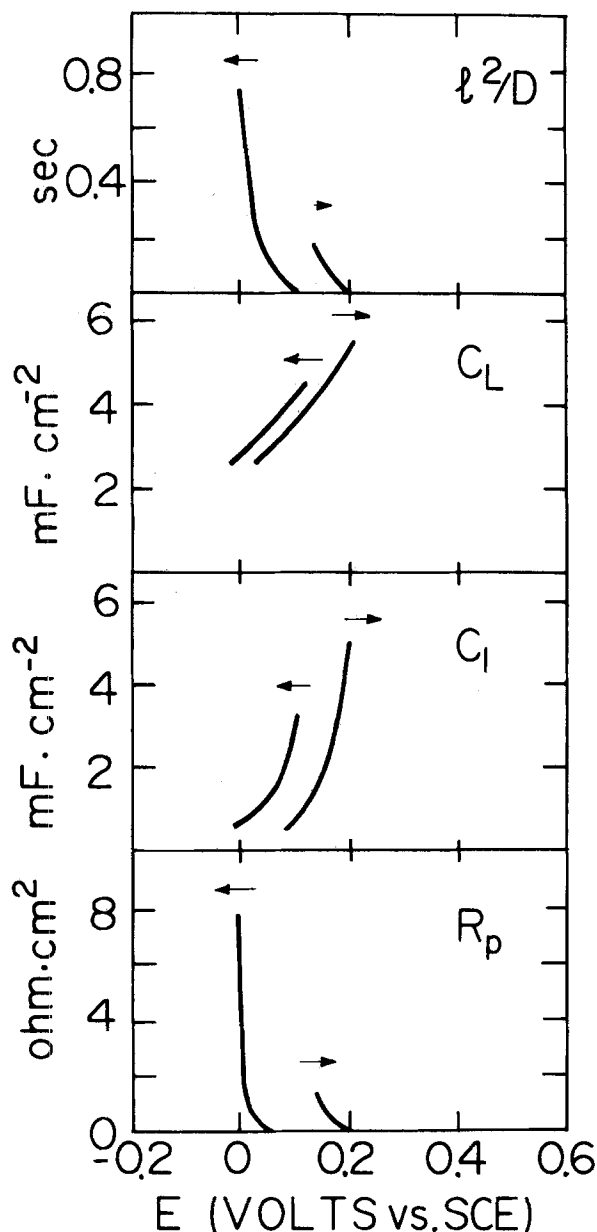


Fig. 5. Simulation results for the potential dependence of R_p , C_1 (see Fig. 4), C_L , and l^2/D (associated with Z_D in Fig. 4, see text) for the electrode in Fig. 2 (the values are given in Table I).

Typical results showing the ac response of a thin film at two bias potentials are presented in Fig. 6. The complex capacitance plots comprise a clear capacitive element at higher frequencies, and a poorly defined slow process at low frequencies. While the high-frequency capacitive element is highly reproducible in repeated experiments with different films, the shape of the low-frequency element may vary between experiments; furthermore, it cannot be simulated with the equivalent circuit of Fig. 4. This may suggest that the low-frequency domain comprises, in addition to the transmission line, a contribution from a poorly reproducible low-frequency background process, becoming more pronounced with the lower currents associated with the thin film. We, therefore, did not attempt to simulate the results for the thin film, and Table II presents data for R_s , R_p , and C_1 , calculated in a straightforward manner from the extrapolated intercept and $\omega_{\max}$ of the high-frequency semicircle at different potentials. Evidently, the variations in these parameters with applied bias potential are qualitatively similar to the thicker films, and R_s is the same in both cases, within experimental error, as would be expected, if R_s indeed represents the solution resistance. The extrapolated high-frequency region of the impedance plots

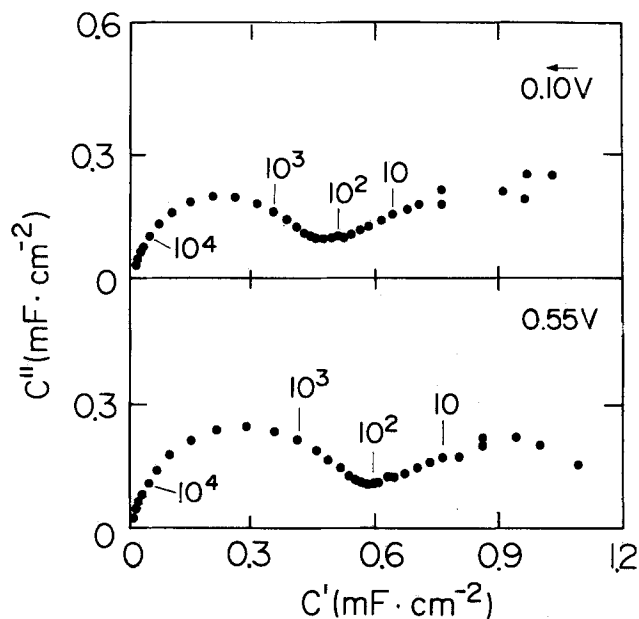


Fig. 6. Complex capacitance plots at two bias potentials for ≈ 15 nm polyaniline on Pt in 2.0M HCl. Frequencies (in Hz) are indicated.

(Fig. 3) also illustrates the similarity of R_s for different thicknesses.

Discussion

The analysis of the experimental complex capacitance plots with thicker polyaniline films produces very good agreement with the equivalent circuit of Fig. 4. We shall use these results and previous data on the polyaniline system to suggest a possible interpretation of various circuit elements in terms of physical processes.

The resistive elements appear to comprise a potential-independent solution resistance R_s , and a potential-dependent polymer series resistance R_p , which increases as the polymer is reduced and gradually becomes insulating (18). This is supported by the fact that the measured value of R_s is the same (within experimental error) for the thick and thin films, and that R_s is consistent with the calculated solution resistance (19).

A basic question is "what are the two potential-dependent processes represented by C_1 and Z_D ?" The following is a discussion of two possible models:

The two-phase model.—Here one attributes the two parallel components to two different phases within the polymer, i.e., "more conducting" segments displaying one type of behavior, and "more insulating" segments displaying a different type of behavior. Keeping in mind that the switching of the polymer occurs gradually over a certain potential span, and that the switching may involve a sequential phase transition of polymer segments, the co-existence of two phases may be expected. According to this model, C_1 , which is a faster process, is related to the more conducting phase, while the slower Z_D represents the more insulating phase. The exact nature of each process under these assumptions is otherwise un-

Table II. Values calculated from capacitance plots of the type presented in Fig. 6 (see text)

E V	C_1 mF cm ⁻²	R_s Ω cm ²	R_p Ω cm ²
0.55	0.55	0.13	0.00
0.30	0.55	0.13	0.00
0.15	0.46	0.13	0.00
0.10	0.44	0.13	0.00
0.05	0.23	0.13	0.04
0.00	0.15	0.13	1.87
0.15	0.32	0.13	0.13
0.20	0.65	0.13	0.03
0.30	0.57	0.13	0.00
0.55	0.55	0.13	0.00

clear. A two-phase picture is consistent with the suggested model for the peculiar voltammetric behavior of conducting polymers (11).

A problem in adopting this model is the fact that both C_1 and C_2 vary in magnitude in the same direction. If the experimental results reflect switching of polymer segments, one would expect the two components to grow at the expense of each other, and not together. We therefore emphasize, in more detail, the second model below, which appears to be more consistent with the experimental results.

The double-layer/faradaic model.—Here one assumes that, from an electrical point of view, the polymer behaves as a single homogeneous phase; C_1 and Z_D represent some combination of double-layer capacitance and faradaic reaction (13), both being potential dependent and related to the polymer switching. According to this model, if indeed switching of the polymer involves a phase transition of polymer segments, it is not directly reflected in the electrical behavior.

The next step in evaluating this model is the assignment of the two electrical components. Here two possibilities appear reasonable.

1. C_1 is the double-layer capacitance, which, as suggested by Feldberg (13), increases gradually upon switching of the polymer due to the increasing effective electrode area. Z_D will then represent a diffusion-controlled faradaic process, responsible for the oxidation/reduction of the polymer. Under diffusion-control conditions (within the polymer) the process will be electrically analogous to a finite transmission line (15). The decrease of l^2/D towards positive potentials can be reasonably assumed to reflect an increase in D for reacting species or counterions. At the positive end l^2/D (the time-constant of the diffusion process) drops to a value low enough so that the element becomes purely capacitive within the measured frequency range. Thus, depending on the value of C_1 in that region (which is not known), it may contribute to the overall capacitance at the positive end.

2. C_1 is a faradaic pseudo-capacitance, associated with a fast electron-transfer process confined to the film. In terms of a finite transmission line, the switching reaction has a low enough l^2/D so that it behaves as a pure capacitor throughout the measured potential range. Z_D then represents the double-layer capacitance, which appears as a transmission line due to the porous nature of the electrode. Depending on the values of C_1 , R_L , and the frequency domain, the double-layer capacitance of a porous electrode may behave as a transmission line (21). In this case of a rather low electrode conductivity, R_L will represent the resistance on the electrode side, rather than the solution side which is the usual case (21). At positive potentials where R_L becomes very small, this element will behave as a pure capacitor in the measured frequency range.

For both cases, the potential dependence of the various elements in Table I is consistent with the physical picture. Thus, a precise assignment of C_1 and Z_D , i.e., the choice between cases 1 and 2 above, is not possible on the basis of the present results. In addition, in both cases the single capacitive process observed at the positive end may reflect either of the two elements, or a combination.

The results obtained with thin films (Fig. 6) may shed some light on this last question. The fact that the capacitance plots for the thin film at +0.55V clearly show the contribution of two circuit elements to the total capacitance suggests that the single capacitive process observed with thick films at positive potentials analogously includes contributions of the two parallel elements. It can be reasonably argued that as the film thickness l is tenfold increased, the time constant l^2/D corresponding to Z_D becomes large enough so that its characteristic capacitive response is shifted to a lower frequency domain, where it becomes indistinguishable from C_1 .

Summary

AC-impedance measurements in a wide frequency range were performed with polyaniline films on Pt elec-

trode in 2.0M HCl solution. Measurements were performed under steady-state conditions at various bias potentials, with the dc potential being varied in the negative and positive directions. The results were presented primarily as complex capacitance plots, with the series resistance being also extracted from impedance plots at high frequencies. The capacitance plots for ≈ 150 nm polyaniline films indicate a single series RC behavior at positive potentials (the voltammetric "capacitive" region), which develops into two well-defined processes at lower potentials. The ac capacitance at +0.55V is identical to the one obtained from voltammetric curves in the "capacitive" region.

The complex capacitance plots in the entire voltage range can be satisfactorily simulated (both the shape of the curves and the values of individual frequencies) using an equivalent circuit comprising a constant resistance R_s , in series with a potential-dependent resistance R_p , both in series with a parallel combination of a capacitor C_1 and a finite transmission line Z_D .

The thickness independence of R_s and the agreement with the calculated solution resistance indicate that R_s represents the solution series resistance. Thus, at positive potentials polyaniline behaves as a pure capacitor in series with a solution resistance. R_p is interpreted as polymer series resistance, becoming pronounced upon reduction of the polymer.

It is argued that C_1 and Z_D represent a double-layer capacitance component and a faradaic component, both of which may behave under different conditions, either as a pure capacitor or as a transmission line. It appears that at positive potentials the two combine into an apparent single capacitive element for ≈ 150 nm films, while they remain separated for ≈ 15 nm films due to the difference in the time-constant l^2/D . The values of R_p , C_1 , and Z_D , obtained under steady-state conditions, undergo sharp variations upon oxidation or reduction of the polymer, displaying the same type of hysteresis evident in voltammetric experiments.

Acknowledgment

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Aqueous Redox Transition Metal Complexes for Electrochemical Applications as a Function of pH

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ABSTRACT

The electrochemistry of a large number of transition metal complexes of iron, cobalt, chromium, and ruthenium have been examined regarding their anodic and cathode peak potential, peak separation, and reversibility as a function of a broad pH range. Criteria for reversibility are considered. In addition, absorption and/or color characteristics have been described at a fixed pH. The stability of stored samples in terms of cyclic voltammetry and absorption spectra has been examined for a given period of time. A significant number of redox couples have properties which should make them useful in photoelectrochemistry, and other electrochemical applications, catalysis, redox flow cells, and the like.

Soluble redox systems are suitable for a number of electrochemical applications, including: photoelectrochemical cells (PEC) (1-3), redox flow cells (1, 2), electroluminescence (4), photosensitizers for PEC (3, 5), photocatalysis at semiconductor electrodes (6), homogeneous catalysis (7), selective etching of semiconductors (4), corrosion suppression (8), etc. Unfortunately, the instability of the radicals involved in some redox processes and the low solubilities of a large number of couples are responsible for the limited usefulness of aqueous systems (9). Although a much larger number of redox couples are available for use in nonaqueous systems (10), these require more specialized handling and storing techniques than their aqueous counterparts. Furthermore, it is often difficult to obtain both halves of the couple co-existing in these systems.

In the above examples where semiconductor electrodes are used, the interface between a solution and the electrode is obviously different than that between a solution and a metal electrode. Part of this work entails the determination of the heterogeneous standard electron transfer rate constant, from which the quality of reversibility of the couples is determined, using platinum electrodes (see Results and Discussion section). We do not intend to infer that the charge transfer kinetics between a metal electrode and solution are the same as between a semiconductor electrode and solution. The principal goal is to evaluate the quality of reversibility of couples that can be used in PEC since this is an important aspect for a useful PEC cell.

We were mainly interested in those redox couples that are stable in appropriate pH ranges and have appropriate redox potentials. For example, those couples to be used with n-type semiconductors (SC) often need to have positive redox potential, whereas the ones often most useful for p-type SC are those with negative potentials. In the beginning, those metal complexes with reasonably high equilibrium constants [screened from Ref. (11-18)] were selected for testing. It was also desired that they showed solubilities at least in the 10⁻³ millimolar (mM) range, and that their optical densities were as low as possible in the visible and near infrared spectral regions.

Several transition metal redox couples have been tested and reported in the literature, although not always over broad pH ranges (nor for extended time periods); these were not included in the present investigation. Some of them are: [Fe(II/III)(CN)₆]^{4-/3-} (19), Eu(II/III) (20), Ti(III/IV) (19, 21), Fe(II/III) (19, 21), Ce(III/IV) (19, 21), Co(II/III) (8), cobalt sepulchrate (3), and the chromium complex of ferrocene carboxylic acid (9).

Our literature screening revealed several complexes which appeared to have reasonable equilibrium constants. After preliminary tests, we discarded those not fulfilling the requirements of solubility and reversibility. We then focused on the study of Fe(EDTA, DTPA, HEEDTA, PHEN, BIPY, EN, DIEN, TEA, and SALEN), ferrocene dicarboxylic acid, Co(EN, BIPY, and ammonia), Cr(EDTA), and Ru(BIPY) complexes; regarding their redox potential properties as a function of the pH of the solution, their absorption spectra, and the time stability of both the absorption spectra and redox potentials. To our knowledge, a comprehensive study like the present one has not been reported before.

The pH of solutions of redox transition metal complexes is of paramount importance with regard to their stabilities, and often times with regard to their redox properties and absorption characteristics. Such pH dependence is not only important for the stability and reversibility characteristics of the complex, but also for the performance of cells involving the hydrogen or the water redox reaction (22), for oxide or hydroxide layer formation, and for surface states (that are frequently pH-sensitive (23)) involved in charge-transfer processes and semiconductor energetics at the SC-electrolyte.

Experimental

A PAR Model 174A polarographic analyzer and a PAR Model 173 potentiostat with appropriate current and/or charge-to-voltage converters (PAR Model 179 plug-in modules) were employed for the electrochemical experiments. The current-potential curves were recorded either on a Houston Instrument Model HR-97 X-Y recorder with the PAR Model 174A, or on a Houston Instrument Model 2000 X-Y recorder with the PAR Model 173. An EG & G PAR Model 175 universal programmer was employed for the potential programming. A Cary 15 was used for the measurements of absorption spectra of the solutions.

For cyclovoltammetric (CV) investigations at room temperature, a single compartment cell with a capacity of 30 ml was employed. All solutions were purged with prepurified argon (minimum 99.998%) or nitrogen (minimum 99.998%) prior to experimentation. A platinum electrode (area = 0.00196 cm²), a carbon disk electrode (area = 0.283 cm²), or a hanging mercury drop electrode was used as a working electrode; a platinum wire electrode was used as a counterelectrode; and a commercial aqueous saturated calomel electrode (SCE) was used as a reference electrode. All the potentials were measured with respect to the SCE reference electrode.